THE EFFECT OF THE SECONDARY COORDINATION SPHERE ON THE STABILITIES

OF CERIUM(III) AND CERIUM(IV) COORDINATION COMPLEXES

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Marie Curie said:

"You cannot hope to build a better world without improving the individuals. To that end each of us must work for his own improvement, and at the same time share a general responsibility for all humanity, our particular duty being to aid those to whom we think we can be most useful."

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ABSTRACT

THE EFFECT OF THE SECONDARY COORDINATION SPHERE ON THE STABILITIES OF CERIUM(III) AND CERIUM(IV) COORDINATION COMPLEXES

Jessica R. Levin

Eric J. Schelter

The lanthanides, the elements from La–Lu, have intrinsic properties that make them desirable components in many technological applications as well as useful catalysts. However, lanthanides can form unpredictable solid state and solution structures due to their ionic, non-directional, and kinetically labile bonds with ligands, which hampers the development of structure-function relationships. To enhance the stability of the lanthanide bonds, the use of the secondary coordination sphere about lanthanide complexes, including alkali metal cations lithium, sodium, and potassium, as well as hydrogen bonding guanidinium cations, as a framework to guide lanthanide-ligand bonding interactions was studied. This work can be applied to lanthanide coordination and redox chemistries.

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CHAPTER 1

Introduction and Outline of the Dissertation

1.1 Why Study the Lanthanides?

While traditional chemistry courses typically do not cover the chemistry of the lanthanide series, these elements from La–Lu are integral to technologies that we use and see every day. Several key "clean energy technologies" including wind power, batteries in electric vehicles, fuel cells, and energy-efficient lighting/displays as well as defense technologies such as SONAR, radar, communication systems, night vision, satellites, and guided munitions rely on rare earth (RE) elements (which include Sc, Y, and the lanthanide series) to function and show optimal performance.^[1, 2]

Additionally, the redox chemistry of the lanthanides is an important attribute in a number of organic reactions and industrial processes.^[3-8] Catalytic hydrocarbon cracking and catalytic converter catalysts utilize redox-active cerium to remove unwanted organic components or harmful pollutants such as CO.^[8]

To improve catalytic processes and discover new uses for the lanthanides, the focus of this research is to better understand solid state and solution structures of lanthanide complexes to establish structure-function relationships and to explore new areas of molecular cerium redox chemistry.

Since the lanthanide elements are not typically included in chemistry courses, a brief introduction to their properties and coordination chemistry is provided below. The introduction will not be extensive. For more information, a number of textbooks^[9-13] and reviews^[4, 5, 14-19] written on the lanthanides have been provided here for reference. An outline of the dissertation also is included.

1.2 Introduction. Properties of the Lanthanides.

The word "lanthanide" describing the 15 elements in the lanthanide series from La–Lu comes from the Greek "lanthaneien" meaning to lie hidden.^[14] While the lanthanides are relatively abundant in the Earth's crust (Figure 1.2.1), they, unlike Ni or Cu which have a similar crustal abundance, are typically dilute in their natural ore deposits, "lying hidden" in the earth.^[11, 12] Neighboring lanthanides are also chemically similar, leading to difficulties in separating their mixtures into constituent elements.^[9, 11, 20] These challenges slowed the elements' discovery and continue to impede the opening of new, economically viable mines.^[2, 20] It took over 100 years to identify all of the elements in the lanthanide series, from 1803 (Ce) to 1907 (Lu) for the natural lanthanides; the artificial and radioactive Pm was discovered in 1947.^[16]



Figure 1.2.1. Abundance of the elements in the Earth's crust (Haxel, Gordon B.;
Hedrick, James B.; Orris, Greta J. U. S. Geological Survey, 2002, Fact Sheet 087-02).
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The lanthanides make up part of the f-block in the periodic table, distinguishing them from the transition metal series located in the d-block. The lanthanides predominantly form complexes in the 3+ oxidation state where their valence orbitals can be described by $[Xe]4f^n$, n = 0-14.^[9, 11] The valence 4f orbitals lend the lanthanides their unique properties. The 4f orbitals are well-shielded by the 5s² and 5p⁶ orbitals and barely extend radially beyond the [Xe] core, making them very contracted compared to the 5d, 6s, and 6p orbitals (Figure 1.2.2).^[9, 11, 21, 22] Because the 4f orbitals are isolated, their magnetic and electronic behaviors are similar to that of free ions.^[9, 11] The unperturbed 4f orbitals result in sharp spectral bands and high color purity for luminescent materials, phosphors, sensors, and imaging probes. Large number of unpaired 4f electrons can be taken advantage for magnetic materials, NMR shift reagents, and MRI contrast agents.^[9, 11, 14-16, 23]



Figure 1.2.2. Radial extent of the 4d, 5d, 6s, and 6p orbitals for a Sm^{3+} cation. The solid lines show non-relativistic radial extent, and the dashed lines represent the radial extent including relativistic effects. Adapted from (Ref. 22) with permission of The Royal Society of Chemistry © 2004.

From La–Lu, the size of the cations decreases ("the Lanthanide Contraction").^{[9,} ^{11]} The contraction is attributed to the poor shielding of the 4f electrons as the series is traversed, increasing the effective nuclear charge of the later lanthanides.^[9, 11] The greater charge density of the later lanthanides results in the greater Lewis acidity of these cations. The lanthanides are hard Lewis acids that 'prefer' coordination by hard, anionic Lewis bases.^[9, 11] Because the contracted 4f orbitals preclude metal-ligand orbital overlap, the nature of bonding with the lanthanides is largely ionic and non-directional, and the ligand field splitting energy is small compared to the d-block transition metals.^[9, 11, 21] Thus, the arrangement of ligands about lanthanide metal centers is largely dictated by ligand sterics.^[9, 11] When bound to ligands with small steric profiles, the lanthanides have high coordination numbers and tend to form oligomeric complexes.^[16] For example, Ln³⁺ cations coordinate 8–9 water molecules, depending on their ionic radius, whereas transition metals typically form directional octahedral hexaaqua species (Figure 1.2.3).^[11, 24]



Figure 1.2.3. Thermal ellipsoid plots of (a) $[Tb(H_2O)_9]^{3+}$ and (b) $[Mn(H_2O)_6]^{2+}$ complexes, outer sphere trifluoromethanesulfonate anions removed for clarity.^[25]

The lanthanides form strong bonds with water, where the hydration enthalpy trends with the size of the Ln^{3+} cation (Figure 1.2.4).^[11] The greater charge density with the heavier, smaller lanthanides leads to larger (more negative), exothermic hydration enthalpies. Aqueous coordination chemistry of the lanthanides requires large enthalpic and/or entropic gains by the ligands upon coordination to out-compete water in the primary coordination sphere.^[19] Despite the thermodynamically strong water binding, the water, and ligands in general, form kinetically labile bonds with the lanthanides (Figure 1.2.5).^[11, 24] For example, $[Eu(H_2O)_7]^{2+}$ exchanges water every 2.9×10^{-11} s, as compared to more kinetically inert metal-ligand bonds such as those in $[Ir(H_2O)_6]^{3+}$, where water exchanges on the order of once every 50 years.^[24] The kinetic lability of ligands is important for catalysis and probes such as MRI contrast agents. But such lability can be challenging to design lanthanide complexes with well-defined coordination spheres and to develop structure-function relationships.



Figure 1.2.4. Plot of the ionic radius for 9-coordinate lanthanoids^[26] (blue squares) and the $-\Delta H_{hydration}$ for the lanthanide series.^[11]



Figure 1.2.5. Water exchange rate constants, k_{H2O} , for water molecules in the primary coordination sphere. Solid lines indicate values of k_{H2O} determined directly, whereas dashed lines indicate values of k_{H2O} estimated by ligand exchange. Reprinted from S. F. Lincoln, *Helv. Chim. Acta* **2005**, *88*, 523-545 (Ref. 24) with permission of WILEY-VCH Verlag Helvetica Chimica Acta AG, Zurich Switzerland, © 2005.

In addition to use of chelating ligands, sterically bulky anionic ligands are used to stabilize the lanthanide coordination sphere, lower the coordination number, and reduce the likelihood of forming oligomeric species.^[27] For example, with 2,6-disubstituted phenols, only the bulkiest ligands form monomeric species.^[27, 28] Homoleptic lanthanide complexes with 2,6-dimethylphenoxide as the supporting ligand form trimers or dimers;

2,6-di-*iso*-propylphenoxide (DIPP) form dimers.^[27, 28] Methyl or *tert*-butyl substituents in the meta- or para- positions also result in trimeric or dimeric species.^[27] However, homoleptic lanthanide complexes coordinated to 2,6-di-*tert*-butyl-phenoxide (TBP) only form monomeric species, Ln(TBP)₃.^[27] Another important sterically bulky supporting ligand imparting low-coordinate, well-defined lanthanide complexes is N(SiMe₃)₂⁻, which generates Ln[N(SiMe₃)₂]₃.^[29] The high basicity of the amide ligand, the volatility of HN(SiMe₃)₂ and the well-defined complex structure makes the Ln[N(SiMe₃)₂]₃ a useful protonolysis starting material.^[27]

Neutral Lewis bases also can be added to help break up higher order polymers of lanthanide complexes.^[27] Addition of THF to the dimeric lanthanide 2,6-di-*iso*-propylphenoxide yields $Ln(DIPP)_3(THF)_x$, where x = 2 or 3.^[27] Similarly, addition of pyridine or THF to $Ce^{IV}_2(O'Bu)_8$ forms monomeric $Ce^{IV}(O'Bu)_4(sol)_2$ where sol = py or THF.^[30, 31] However, the *tert*-butoxide supporting ligand tends to oligomerize with the larger lanthanides, including Ce^{III} , regardless of solvent conditions.^[28, 30] For example, there are 22 different Ce(III), Ce(IV), and mixed valent Ce(III)/Ce(IV) homoleptic cerium *tert*-butoxide structures submitted to the Cambridge Structural Database. The many different lanthanide *tert*-butoxide complex structures show how difficult it is to predict the solid state and solution speciation of homoleptic lanthanide complexes in different solvents, reaction conditions, and with different stoichiometries and starting materials.

While the Ln^{3+} formal oxidation state is most prevalent in lanthanide coordination chemistry, several lanthanides have accessible Ln^{2+} (Ln = Sm, Eu, and Yb) and Ln^{4+} (Ln = Ce, in solid state chemistry also Pr and Tb) oxidation states (see Table 1.2.1).^[10] Increased stability of the Ln^{4+} or Ln^{2+} oxidation states occurs when, upon Ln^{3+} oxidation to form the Ln^{4+} oxidation state or Ln^{3+} reduction to form the Ln^{2+} oxidation state, the lanthanide metal center achieves empty $(4f^0)$, half full $(4f^7)$, or full $(4f^{14})$ valence electronic configurations.^[10, 32] The Ln²⁺ formal oxidation state has proven useful in a variety of applications, including in phosphors and as reductants in organic transformations.^[3, 5, 33] The Evans' group expanded the Ln^{2+} oxidation state to all lanthanides except for Pm, synthesizing powerful reductants that can achieve difficult reduction reactions, such as the activation of N₂ (see Table 1.2.1).^[34, 35] High valent Ce⁴⁺ compounds are oxidants in both stoichiometric and catalytic reactions (examples given in section 1.1).^[4, 7, 8, 36] While Tb⁴⁺ and Pr⁴⁺ have been isolated in the solid state as oxides and fluorides, no molecular examples of Tb^{4+} or Pr^{4+} have been isolated and fully characterized (see Table 1.2.1).^[37, 38]

Ln	$E^{o}_{\text{IV-III}}$ (V)	<i>E°</i> ₁₁₁₋₁₁ (V)
La		-3.1
Ce	1.74	-3.2
Pr	3.2	-2.7
Nd	4.4	-2.6
Pm	4.7	-2.6
Sm	5.1	-1.55
Eu	6.3	-0.35
Gd	7.9	-3.9
Tb	3.1	-3.7
Dy	4.9	-2.6
Но	6.0	-2.7
Er	6.1	-3.1
Tm	6.1	-2.3
Yb	7.3	-1.15
Lu	9.1	

Table 1.2.1. Standard reduction potentials of Ln^{IV/III} and Ln^{III/II} versus NHE.^[32, 40]

Reaction conditions and choice of supporting ligand affect the outcomes of oxidation and reduction reactions with the lanthanides (Figure 1.2.6).^[18, 41] Upon oxidation of Ln^{3+} to Ln^{4+} , or reduction from Ln^{3+} to Ln^{2+} , the ionic radius of the

lanthanide changes ~0.1 Å, significantly altering the steric demands of the lanthanide metal center.^[26] As a result, ligand redistribution can occur, as in the case of the O₂ oxidation of Ce[N(Cy)₂]₃ (Cy = cyclohexyl) that resulted in the isolation of Ce[N(Cy)₂]₄.^[42] Ligand electrostatics also greatly affect the redox chemistry of the lanthanides.^[18] Focusing on Ce⁴⁺, the electron donating ligand 2-(^{*t*}BuNO)Py stabilizes the Ce⁴⁺ oxidation state over 2 V more than the electron withdrawing nitrate ligand (Figure 1.2.6).^[18]



Figure 1.2.6. Ce(III/IV) oxidation potentials for cerium complexes in non-aqueous and aqueous conditions. Reprinted from Coordin. Chem. Rev.; **2014** Vol. 260; Nicholas A. Piro, Jerome R. Robinson, Patrick J. Walsh, Eric J. Schelter; The electrochemical behavior of cerium(III/IV) complexes: Thermodynamics, kinetics, and applications in synthesis; pages 21–36 (Ref. 18); Copyright 2014; with permission from Elsevier.

1.3 Outline of the Dissertation

In this work, the ability of the secondary coordination sphere to rationally construct well-defined lanthanide complexes for applications in coordination chemistry and redox chemistry was evaluated. Lithium, sodium, potassium, and tetramethylguanidinium cations were used as scaffolds in the secondary coordination sphere to organize ligands with small steric profiles, 2-naphtholate, and 1,2-diarylhydrazido, about lanthanide complexes. Stability, reactivity, and mechanistic studies were undertaken to better understand the nature of these complexes in solution, the results of which have implications in their respective application areas.

In **Chapter 2**, the syntheses and characterization of a series of cerium naphtholate complexes with lithium, sodium, potassium and tetramethylguanidinium cations in the secondary coordination sphere was described. Smaller, more Lewis acidic cations in the secondary coordination sphere led to complex solution behavior and greater ligand lability, whereas larger cations formed better-defined solution structures. Alkali metal cerium naphtholate complexes showed solvent-dependent solution and solid state structures, whereas the tetramethylguanidinium cerium naphtholate complex structure remained intact regardless of the solvent, showing that the large, hydrogen bonding cation tetramethylguanidinium could be a good method to stabilize lanthanide complexes.

To study whether there was a preference to form the tetramethylguanidinium cerium naphtholate structure, alkali metal salts were added to the tetramethylguanidinium cerium naphtholate complex in **Chapter 3**. As seen in Chapter 2, the addition of lithium cations to cerium naphtholate complexes led to complex solution behavior. However, the tetramethylguanidinium cerium naphtholate solution structure dominated when sodium or potassium cations were in solution. Despite the maintenance of the tetramethylguanidinium cerium naphtholate structure, Ce₂Onaph₉, in solution, these

complexes were still labile, and the exchange rates and activation enthalpies were measured for complexes with the Ln₂Onaph₉ core structure. Intermolecular naphtholate exchange was observed in the solution, which indicated that despite the lability of the ligands, there was a barrier to convert the Ln₂Onaph₉ motif into a different structure. Based on this data, the tetramethylguanidinium cation organized the cerium naphtholate complex into its preferred solution structure regardless of the solvent, making the large hydrogen bonding cation a good template to rationally form new lanthanide complexes.

In **Chapter 4**, our goal was to use the secondary coordination sphere about cerium 1,2-diphenylhydrazido complexes to influence the oxidation state of the cerium metal center. Cerium 1,2-diphenylhydrazido complexes with lithium, sodium, or potassium cations in the secondary coordination sphere were synthesized. When the secondary coordination sphere contained lithium or sodium cations, spontaneous oxidation to cerium(IV) occurred with concomitant reduction of the 1,2-diphenylhydrazine ligand, while when the alkali metal in the secondary coordination sphere was potassium, no oxidation of cerium(III) occurred. The Lewis acidity of the alkali metals in the secondary coordination. These complexes were the first examples of the lanthanide oxidation state controlled by the secondary coordination sphere.

To further understand the alkali metal-promoted reduction of 1,2-diphenylhydrazine by cerium cations, a series of substitutions were made on the phenyl rings of 1,2diphenylhydrazine in **Chapter 5**. The reduction of electron-rich 1,2-diarylhydrazine

would be more difficult, but would form more electron rich Ce(IV) complexes, whereas electron poor 1,2-diarylhydrazine ligands would be easier to reduce but would form less stable, electron poor Ce(IV) complexes. Electron poor lithium cerium 1,2-diarylhydrazido complexes were synthesized, isolated, and characterized, but electron rich analogues could not be made. Alkali metal-promoted reduction of redox active ligands could be a good method to isolate very electron-poor cerium(IV) complexes.

In Chapter 6, two DFT methods were explored to correlate experimental and calculated redox potentials of 4-coordinate cerium complexes in dichloromethane with the goal of using the correlation to predict the redox properties of new complexes. The ligands coordinated to cerium greatly influence the cerium reduction potential. Thus, ligand design is paramount to fine-tune cerium redox chemistry. DFT could be a powerful tool in designing a ligand to achieve a certain cerium reduction potential. The first method to correlate and predict cerium redox chemistry was previously used in the group, where the free energies G of Ce(IV) and Ce(III) complexes were calculated in a solvent continuum. The ΔG of reduction, obtained by subtracting the G of Ce(IV) from the G of Ce(III), was then converted to $E_{1/2}$ by the Nernst equation, and was subsequently referenced to ferrocene. The calculated $E_{1/2}$ was then compared to the experimentally obtained $E_{1/2}$. The other, less time-consuming method was described by Gillmore and coworkers (see Chapter 6 for references). Here, the energy of the LUMO of the compound to be reduced, Ce(IV), was correlated with the experimental reduction potential of the compound. The more accurate way to correlate and predict cerium redox

potentials was by calculating the $E_{1/2}$ of cerium complexes. This was important groundwork to developing calculations methods for cerium complex design.

1.4 BIBLIOGRAPHY

- D. Bauer, D. Diamond, J. Li, D. Sandalow, P. Telleen, B. Wanner, U.S. Dept. of Energy Dec. 2010, U.S. Dept. of Energy Critical Materials Strategy, 6-110; B. M.
 Martin, U.S. Government Accountability Office April 1, 2010, Rare Earth Materials in the Defense Supply Chain.
- [2] M. Humphries, *Congressional Research Service* Sept. 6, 2011, *Rare Earth Elements: The Global Supply Chain.*
- [3] G. A. Molander, C. R. Harris, *Chem. Rev.* **1996**, *96*, 307-338.
- [4] G. A. Molander, *Chem. Rev.* **1992**, *92*, 29-68.
- [5] H. B. Kagan, *Tetrahedron* 2003, *59*, 10351-10372; H. B. Kagan, J. L. Namy, *Tetrahedron* 1986, *42*, 6573-6614.
- [6] A. K. Das, *Coord. Chem. Rev.* 2001, 213, 307-325; K. Eguchi, T. Setoguchi, T. Inoue, H. Arai, *Solid State Ionics* 1992, 52, 165-172; T. Bunluesin, R. J. Gorte, G. W. Graham, *Appl. Catal. B* 1998, 15, 107-114; S. Park, J. M. Vohs, R. J. Gorte, *Nature* 2000, 404, 265-267; G. A. Deluga, J. R. Salge, L. D. Schmidt, X. E. Verykios, *Science* 2004, 303, 993-997; E. P. Murray, T. Tsai, S. A. Barnett, *Nature* 1999, 400, 649-651; S. B. Adler, *Chem. Rev.* 2004, 104, 4791-4844; Y. Zhai, D. Pierre, R. Si, W. Deng, P. Ferrin, A. U. Nilekar, G. Peng, J. A. Herron,

D. C. Bell, H. Saltsburg, M. Mavrikakis, M. Flytzani-Stephanopoulos, *Science* **2010**, *329*, 1633-1636; J. A. Rodriguez, S. Ma, P. Liu, J. Hrbek, J. Evans, M.
Perez, *Science* **2007**, *318*, 1757-1760; L. Vivier, D. Duprez, *ChemSusChem* **2010**, *3*, 654-678; L. Xu, J. Wang, *Environ. Sci. Technol.* **2012**, *46*, 10145-10153; A.
Kawashima, K. Matsubara, K. Honda, *Bioresource Technol.* **2008**, *99*, 3439-3443.

- [7] V. Nair, L. Balagopal, R. Rajan, J. Matthew, *Acc. Chem. Res.* 2004, *37*, 21-30; V. Nair, A. Deepthi, *Chem. Rev.* 2007, *107*, 1862-1891; Y. Li, Q. Fu, M. Flytzani-Stephanopoulos, *Appl. Catal. B* 2000, *27*, 179-191; Q. Fu, H. Saltsburg, M. Flytzani-Stephanopoulos, *Science* 2003, *301*, 935-938.
- [8] J. Kaspar, P. Fornasiero, N. Hickey, *Catal. Today* 2003, 77, 419-449; J. Kaspar,
 P. Fornasiero, *J. Solid State Chem.* 2003, 171, 19-29; M. Dejhosseini, T. Aida, M.
 Watanabe, S. Takami, D. Hojo, N. Aoki, T. Arita, A. Kishita, T. Adschiri, *Energy Fuels* 2013, 27, 4624-4631.
- [9] H. C. Aspinall, *Chemistry of the f block Elements*, Gordon and Breach Science Publishers, Singapore, 2001.
- [10] A. W. G. Platt, *The Rare Earth Elements: Fundamentals and Applications*, John Wiley & Sons Ltd., Chichester, United Kingdom, **2012**.
- [11] S. Cotton, *Lanthanide and Actinide Chemistry*, John Wiley and Sons Inc., Hoboken, NJ, **2006**.

- V. S. Sastri, J.-C. Bunzli, V. Ramachandra Rao, G. V. S. Rayudu, J. R.
 Perumareddi, *Modern Aspects of Rare Earths and their Complexes*, Elsevier B.
 V., Netherlands, 2003.
- [13] N. Kaltsoyannis, P. Scott, *The f elements*, Oxford University Press, New York, 1999.
- [14] J.-C. G. Bunzli, C. Piguet, Chem. Soc. Rev. 2005, 34, 1048-1077.
- [15] C. Piguet, J.-C. G. Bunzli, *Chem. Soc. Rev.* 1999, 28, 347-358; J.-C. G. Bunzli, C. Piguet, *Chem. Rev.* 2002, *102*, 1897-1928; S. V. Eliseeva, J.-C. G. Bunzli, *Chem. Soc. Rev.* 2010, *39*, 189-227; A. F. Cockerill, G. L. O. Davies, R. C. Harden, D. M. Rackham, *Chem. Rev.* 1973, *73*, 553-588; C. Benelli, D. Gatteschi, *Chem. Rev.* 2002, *102*, 2369-2388; L. Sorace, C. Benelli, D. Gatteschi, *Chem. Soc. Rev.* 2011, *40*, 3092-3104.
- [16] J.-C. G. Bunzli, Acc. Chem. Res. 2006, 39, 53-61.
- [17] L. Armelao, S. Quici, F. Barigelletti, G. Accorsi, G. Bottaro, M. Cavazzini, E. Tondello, *Coordin. Chem. Rev.* 2010, 254, 487-505; J. Garcia, M. J. Allen, *Eur. J. Inorg. Chem.* 2012, 4550-4563; K. Binnemans, *Chem. Rev.* 2009, 109, 4283-4374; J. Kido, Y. Okamoto, *Chem. Rev.* 2002, 102, 2357-2368; G. F. de Sa, O. L. Malta, C. de Mello Donega, A. M. Simas, R. L. Longo, P. A. Santa-Cruz, E. F. da Silva Jr., *Coordin. Chem. Rev.* 2000, 196, 165-195; D. Parker, R. S. Dickins, H. Puschmann, C. Crossland, J. A. K. Howard, *Chem. Rev.* 2002, 102, 102, 1977-2010; P. Di Bernardo, A. Melchior, M. Tolazzi, P. L. Zanonato, *Coordin. Chem. Rev.*

2012, 256, 328-351; S. Aime, M. Fasano, E. Terreno, *Chem. Soc. Rev.* 1998, 27, 19-29; R. Sessoli, A. K. Powell, *Coordin. Chem. Rev.* 2009, 253, 2328-2341; D.
N. Woodruff, R. E. P. Winpenny, R. A. Layfield, *Chem. Rev.* 2013, *113*, 5110-5148; J. D. Rinehart, J. R. Long, *Chem. Sci.* 2011, 2, 2078-2085; L. Ma, C.
Abney, W. Lin, *Chem. Soc. Rev.* 2009, *38*, 1248-1256; D. J. Tranchemontagne, J.
L. Mendoza-Cortes, M. O'Keeffe, O. M. Yaghi, *Chem. Soc. Rev.* 2009, *38*, 1257-1283; H. C. Aspinall, *Chem. Rev.* 2002, *102*, 1807-1850; K. A. Gschneidner Jr., V. K. Pecharsky, A. O. Tsokol, *Rep. Prog. Phys.* 2005, *68*, 1479-1539.

- [18] N. A. Piro, J. R. Robinson, P. J. Walsh, E. J. Schelter, *Coord. Chem. Rev.* 2014, 260, 21-36.
- [19] S. J. Butler, D. Parker, Chem. Soc. Rev. 2013, 42, 1652-1666.
- [20] H. H. Dam, D. N. Reinhoudt, W. Verboom, *Chem. Soc. Rev.* 2007, *36*, 367-377;
 A. Jordens, Y. P. Cheng, K. E. Waters, *Miner. Eng.* 2013, *41*, 97-114.
- [21] J. Friedman, H. G., G. R. Choppin, D. G. Feuerbacher, J. Chem. Educ. 1964, 41, 354-358.
- [22] G. R. Giesbrecht, J. C. Gordon, *Dalton Trans.* 2004, 2387-2393.
- [23] A. Grichine, A. Haefele, S. Pascal, A. Duperray, R. Michel, C. Andraud, O. Maury, *Chem. Sci.* 2014, *5*, 3475-3485.
- [24] S. F. Lincoln, *Helv. Chim. Acta* **2005**, *88*, 523-545.

- [25] A. Abbasi, P. Lindqvist-Reis, L. Eriksson, D. Sandstrom, S. Lidin, I. Persson, M. Sandstrom, *Chem. Eur. J.* 2005, *11*, 4065-4077; P. J. Riedel, N. Arulsamy, M. P. Mehn, *Inorg. Chem. Commun.* 2011, *14*, 734-737.
- [26] R. D. Shannon, Acta Cryst. 1976, A32, 751-767.
- [27] T. J. Boyle, L. A. M. Ottley, Chem. Rev. 2008, 108, 1896-1917.
- [28] T. J. Boyle, L. J. Tribby, S. D. Bunge, *Eur. J. Inorg. Chem.* **2006**, 4553-4563.
- [29] D. C. Bradley, J. S. Ghotra, F. A. Hart, J. Chem. Soc., Dalton Trans. 1973, 1021-1023.
- [30] ; J. Schlafer, S. Stucky, W. Tyrra, S. Mathur, *Inorg. Chem.* **2013**, *52*, 4002-4010.
- U. J. Williams, D. Schneider, W. L. Dorfner, C. Maichle-Mossmer, P. J. Carroll,
 R. Anwander, E. J. Schelter, *Dalton Trans*. 2014, 43, 16197-16206.
- [32] L. R. Morss, Chem. Rev. 1976, 76, 827-841.
- [33] G. Blasse, *Philips Res. Rep.* 1969, 24, 131-144; G. Blasse, *J. Solid State Chem.*1986, 62, 207-211; J. S. Kim, P. E. Jeon, J. C. Choi, H. L. Park, S. I. Mho, G. C. Kim, *Appl. Phys. Lett.* 2004, 84, 2931-2933; J. W. H. van Krevel, J. W. T. van Rutten, H. Mandal, H. T. Hintzen, R. Metselaar, *J. Solid State Chem.* 2002, 165, 19-24.
- [34] W. J. Evans, D. J. Drummond, L. R. Chamberlain, R. J. Doedens, S. G. Bott, H. Zhang, J. L. Atwood, *J. Am. Chem. Soc.* **1988**, *110*, 4983-4994; M. E. Fieser, M. R. MacDonald, B. T. Krull, J. E. Bates, J. W. Ziller, F. Furche, W. J. Evans, *J. Am. Chem. Soc.* **2015**, *137*, 369-382; W. J. Evans, *J. Organomet. Chem.* **2002**,

652, 61-68; C. M. Kotyk, M. R. MacDonald, J. W. Ziller, W. J. Evans,
Organometallics 2015, 34, 2287-2295; W. J. Evans, Coordin. Chem. Rev. 2000,
206-207, 263-283; W. J. Evans, J. Organomet. Chem. 2002, 647, 2-11; W. J.
Evans, D. S. Lee, Can. J. Chem. 2005, 83, 375-384; M. E. Fieser, J. E. Bates, J.
W. Ziller, F. Furche, W. J. Evans, J. Am. Chem. Soc. 2013, 135, 3804-3807; M. R.
MacDonald, J. E. Bates, J. W. Ziller, F. Furche, W. J. Evans, J. Am. Chem. Soc.
2013, 135, 9857-9868; W. J. Evans, B. L. Davis, Chem. Rev. 2002, 102, 21192136; W. J. Evans, J. Alloy Cmpd. 2009, 488, 493-510.

- [35] J. H. Farnaby, M. Fang, J. W. Ziller, W. J. Evans, *Inorg. Chem.* 2012, *51*, 11168-11176.
- [36] T. Imamoto, Y. Koide, S. Hiyama, Chem. Lett. 1990, 19, 1445-1446.
- [37] J. K. Marsh, J. Chem. Soc. 1946, 15-17; D. E. Hobart, K. Samhoun, J. P. Young,
 V. E. Norvell, G. Mamantov, J. R. Peterson, *Inorg. Nucl. Chem. Lett.* 1980, 16, 321-328.
- [38] A. L. Hector, W. Levason, *Eur. J. Inorg. Chem.* **2005**, 3365-3370.
- [39] D. E. Hobart, K. Samhoun, J. P. Young, V. E. Norvell, G. Mamantov, J. R. Peterson, *Inorg. Nucl. Chem. Lett.* 1980, *16*, 321-328.
- [40] L. J. Nugent, R. D. Baybarz, J. L. Burnett, J. L. Ryan, J. Inorg. Nucl. Chem. 1971, 33, 2503-2530.
- [41] I. J. Casely, S. T. Liddle, A. J. Blake, C. Wilson, P. L. Arnold, *Chem. Commun.* **2007**, 5037-5039; C. Morton, N. W. Alcock, M. R. Lees, I. J. Munslow, C. J.

Sanders, P. Scott, J. Am. Chem. Soc. 1999, 121, 11255-11256; P. Drose, A. R.
Crozier, S. Lashkari, J. Gottfriedsen, S. Blaurock, C. G. Hrib, C. MaichleMossmer, C. Schadle, R. Anwander, F. T. Edelmann, J. Am. Chem. Soc. 2010, 132, 14046-14047; P. B. Hitchcock, A. G. Hulkes, M. F. Lappert, Inorg. Chem.
2004, 43, 1031-1038; N.-D. H. Gamage, Y. Mei, J. Garcia, M. J. Allen, Angew.
Chem. Int. Ed. 2010, 49, 8923-8925; R. A. Flowers, II, Synlett 2008, 1427-1439;
E. Prasad, B. W. Knettle, R. A. Flowers II, J. Am. Chem. Soc. 2002, 124, 14663-14667.

[42] P. B. Hitchcock, M. F. Lappert, A. V. Protchenko, *Chem. Commun.* 2006, 3546-3548.

CHAPTER 2

Stabilization of lanthanide naphtholate complexes through interligand non-covalent interactions

Abstract:

A series of alkali metal lanthanide naphtholate complexes, $M_x(sol)_y[Ln_z(Onaph)_a]$, M = Li, Na, and K; x = 3 (Li, Na, and K sol = py), 4 (Li and Na, sol = DME) or 6 (K, sol = DME); y = 4 (Li, Na, and K sol = DME) or 6 (Li, Na, and K sol = py); sol = py and DME; Ln = La and Ce; z = 1 (Li and Na, sol = py) or 2 (Li, Na, and K, sol = DME, K, sol = py); a = 6 (Li and Na, sol = py), 9 (K, sol = py), 10 (Li and Na, sol = DME), and 12 (K, sol = DME), were synthesized to probe how the secondary coordination sphere impacted the primary coordination environment and resulting properties of a cerium cation. The solid state and solution structures of the heterobimetallic cerium naphtholate complexes were found to be strongly dependent on the identity of the solvent. However, when the hydrogen bonding cation tetramethylguanidinium (HTMG)⁺ interacted with the naphtholate ligands in the secondary coordination sphere, the cerium naphtholate complex maintained the same coordination regardless of solvent. To observe the structural changes that occurred upon changing solvation, X-ray crystallography, NMR spectroscopy, and DOSY ¹H NMR studies were performed on the complexes. Finally, cyclic voltammetry was performed to measure the effect of the structural changes on the electronics at the cerium metal center.

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2.1 Introduction

Lanthanide aryloxide complexes prepared in non-aqueous conditions are a structurally diverse class of compounds used as precursors for oxide materials,^[1] and as homogeneous Lewis acid catalysts.^[2] The diversity of the lanthanide aryloxides is a result of the size and Lewis acidity of the metal ion, steric demand and denticity of the ligand, and the presence and identity of donor solvent molecules and secondary cations.^[3] Although lanthanide-aryloxide Ln–O bonds are thermodynamically strong, they are kinetically labile towards substitution due to their ionicity.^[4] As a result, solid state species isolated by crystallization may not represent the complete population of solution structures. The disparity between the solution- and solid state structures of lanthanide aryloxide complexes is an important problem because it impedes the development of structure-function relationships for materials synthesis and catalysis. It is of interest to develop new methods for rendering the coordination spheres of Ln-aryloxide complexes inert.

We recently initiated studies of f-block complexes possessing non-covalent interactions between ligands.^[5] By creating collective secondary structures we postulated that the complexes we obtained would be both thermodynamically stable and kinetically inert.^[6] To accomplish these goals in the current work we have used the hydrogen bond donor 1,1,3,3-tetramethylguanidinium, (HTMG⁺), as a secondary cation for lanthanide 2-naphthoxide complexes.

Runde and Goff,^[7] and others,^[8] have used guanidinium cations, $[C(NH_2)_3]^+$, to isolate the discrete lanthanide carbonate complexes, $[C(NH_2)_3]_5[Ln(CO_3)_4(H_2O)_n]$, Ln = Nd, Dy n = 1; Er, Ce n = 0.^[7] Bunge and co-workers have also used tetramethylguanidine as a co-ligand with aryloxides to synthesize the precatalyst

 $[Nd(TMG)_2(4MeDBP)_2(OEt)]$, 4MeDBP = 2,6-di-*tert*-butyl-4-methyl-phenolate, for the intramolecular hydroalkoxylation of 4-pentyn-1-ol.^[9] Our group has also observed that the $(HTMG)^+$ cation rendered the rare earth BINOLate catalysts,

 $[M_3(THF)_n][RE(BINOLate)_3]$ where RE = Sc, Y, La–Lu, M = Li, Na, and K, and BINOLate = 1,1'-bi-2-naphtholate, inert to air and water, whereas the alkali metal rare earth BINOLate complexes readily decompose on the benchtop.^[10] In the work presented here, we disclose that alkali metal/Ln, Ln = La, Ce; heterobimetallic complexes of 2naphthoxide show variable solution and solid state structures depending on solvent conditions. However, the use of (HTMG)⁺ in the lanthanide 2-naphthoxide mixtures biases the complex towards a structure that is both relatively stable and inert.

2.2 Results

2.2.1. Syntheses and structural characterization of $Li_3(py)_6[Ce(Onaph)_6]$ and $Li_4(DME)_4[Ce_2(Onaph)_{10}]$.

Reaction of anhydrous $Ce(OTf)_3$ with 6 equiv lithium 2-naphtholate (LiOnaph) in THF followed by crystallization from pyridine afforded monomeric $Li_3(py)_6[Ce(Onaph)_6]$ (2.1) (Scheme 2.2.1). By avoiding the formation of the side-product LiOTf, the yield of 2.1 was subsequently improved using 1 equiv $Ce[N(SiMe_3)_2]_3$ with 6 equiv 2-naphthol and 3 equiv $Li[N(SiMe_3)_2]$ (see section 2.4 for details). The Ce(III) cation in complex 2.1 in the solid state was monomeric and coordinated by 6 naphtholate ligands in a pseudo-
octahedral geometry (Figure 2.2.1). The Ce–O distances ranged from 2.3556(13)– 2.3959(13) Å and were comparable to other reported Li/Ce heterobimetallic alkoxide and aryloxide complexes.^[11]



Scheme 2.2.1. Synthesis of Li₃(py)₆[Ce(Onaph)₆] (2.1) (left) and

Li₄(DME)₄[Ce₂(Onaph)₁₀] (2.2) (right). 2-naphthyl groups were omitted for clarity.

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Figure 2.2.1. 30 % thermal ellipsoid plot of Li₃(py)₆[Ce(Onaph)₆] (2.1). Hydrogen atoms were omitted for clarity. Selected bond distances (Å): Ce(1)–O(1) 2.3959(13), Ce(1)–O(2) 2.3556(13), Li(1)–N(1) 2.075(4), Li(1)–N(2) 2.073(4). Reproduced by permission of The Royal Society of Chemistry.

The ¹H NMR spectrum of **2.1** in CDCl₃ showed five broad, paramagnetically shifted signals between 4.00–9.14 ppm. ⁷Li NMR spectra were particularly informative for monitoring solutions of the Li/Ce/Onaph system because the paramagnetism of the cerium(III) ion sensitized the ⁷Li NMR signal. Complex **2.1** displayed a single, paramagnetically shifted ⁷Li NMR signal in the parent solvent pyridine at 4.00 ppm (Table 2.2.1). However, NMR spectra in other solvents made it apparent that the solution structure of the lithium cerium naphtholate complex was solvent-dependent. Complex **2.1**

showed two ⁷Li signals in CDCl₃, five signals in THF, and two signals in DME, indicating multiple species present in each solution. The solution structural changes were reversible.

To verify that the lithium cerium naphtholate complex solid state structure as well as solution structure was dependent on solvent, we then set out to crystallize a lithium cerium naphtholate complex in a solvent other than pyridine. The analogous reaction of Ce(OTf)₃ with 6 equiv LiOnaph following workup and crystallization from DME yielded the dimeric complex Li₄(DME)₄[Ce₂(Onaph)₁₀] (**2.2**) (Scheme 2.2.1, Figure 2.2.2). The yield of complex **2.2** was similarly improved using 1 equiv Ce[N(SiMe₃)₂]₃ with 5 equiv 2-naphthol and 2 equiv Li[N(SiMe₃)₂]. Complex **2.2** also contained six coordinate cerium(III) ions in pseudooctahedral environments. However, in **2.2**, two of the naphtholate ligands were bridging between the two cerium(III) ions. Those Onaph⁻ ligands that bridged the cerium(III) ions had longer Ce–O bonds, from 2.4256(13)– 2.4374(12) Å. The ⁷Li NMR of **2.2** in DME showed a single resonance at 17.11 ppm, indicating that the ⁷Li NMR resonance of **2.1** dissolved in DME was likely a dimeric species with the formation of LiOnaph (Table 2.2.1, Scheme 2.2.2).



Figure 2.2.2. 30 % thermal ellipsoid plot of Li₄(DME)₄[Ce₂(Onaph)₁₀] (2.2). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) for 2.2: Ce(1)–O(1) 2.3492(13), Ce(1)–O(2) 2.4256(13), Li(1)–O(7) 1.994(4). Reproduced by permission of The Royal Society of Chemistry.

 Table 2.2.1. Summary of the ⁷Li NMR data^{a, b} for complexes 2.1 and 2.2. Reproduced by

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Solvent	Li ₃ (py) ₆ [Ce(Onaph) ₆] (2.1)	Li ₄ (DME) ₄ [Ce ₂ (Onaph) ₁₀] (2.2)
Pyridine	4.00	23.68 (0.09), 7.58 (1)
DME	16.80 (1), 1.50 (0.14)	17.11
THF	24.64 (0.1), 20.49 (0.1), 17.54	17.81 (0.47), 14.64 (1), 1.32
	(0.05), 14.86 (1), 1.79 (0.26)	(0.16)
CDCl ₃	18.87 (0.57), 2.03 (1)	17.17

^{*a*}Reported as chemical shift (δ) in ppm. ^{*b*}Referenced against an external standard of LiCl in H₂O at 0.00 ppm. ^{*c*}Values in parenthesis represent relative ratios of the signal obtained from integration of the peaks.



Scheme 2.2.2. Proposed degradation of complex 2.1 in DME. Naphthyl groups were omitted for clarity.

2.2.2. Synthesis and structural characterization of (HTMG)₃[Ce₂(Onaph)₉] (2.3).

Outside of their parent solvents, dissolution of crystals of **2.1** and **2.2** almost invariably produced multiple solution species as observed in their ⁷Li NMR spectra (Table 2.2.1 and section 2.4). It was evident that more than the two complexes isolated by crystallization contributed to the solution populations of complexes for the Li/Ce/Onaph system. The equilibria responsible for the solution species were complex and strongly dependent on the starting materials and the identities of coordinating solvents. In order to stabilize the solution structures of the Ce/Onaph system, we next considered the hydrogen bonding donor cation tetramethylguanidinium (HTMG)⁺.

Arrays of cooperative hydrogen bonds are known to provide kinetic stabilization in synthetic and biological systems.^[12] We postulated that 1,1,3,3tetramethylguanidinium cations, (HTMG)⁺, could similarly confer stability to the Ce/Onaph⁻ system. The complex (HTMG)₃[Ce₂(Onaph)₉] (**2.3**) was prepared by stirring 9 equiv 2-naphthol with 3 equiv 1,1,3,3-tetramethylguanidine in THF followed by addition of 2 equiv Ce[N(SiMe₃)₂]₃ (Scheme 2.2.3). Complex **2.3** was severely crystallographically disordered about the 2-naphthyl groups but an acceptable refinement was achieved. Importantly, unlike complexes **2.1** and **2.2**, crystals of **2.3** were obtained regardless of crystallizing solvent– DME, pyridine, CH₂Cl₂, or THF– verified by the unit cell parameters of the complex.



Scheme 2.2.3. Synthesis of complex **2.3**. The same complex could be synthesized in different coordinating solvents, like THF, DME, or pyridine. Naphthyl groups were omitted for clarity. Reproduced by permission of The Royal Society of Chemistry.

Complex **2.3** was determined to be a dimer in the solid state, where three of the Onaph⁻ ligands bridged the two metal centers and three Onaph⁻ ligands were terminally bound to each cerium(III) ion (Figure 2.2.3). The three (HTMG)⁺ cations showed hydrogen bonding interactions with Onaph⁻ ligands in the solid state; two (HTMG)⁺ cations with close contacts between terminal Onaph⁻ ligands at each metal ion with N– $H\cdots O$ contacts of ~2.3–2.4 Å. The third (HTMG)⁺ cation showed one short contact with a terminal Onaph⁻ ligand at ~2.2 Å.



Figure 2.2.3. 30 % thermal ellipsoid plot for [HTMG]₃[Ce₂(Onaph)₉] (**2.3**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) for **2.3**: Ce(1)–O(1) 2.278(4), Ce(1)–O(8) 2.473(4), O(6)–H(7A) 2.33, O(3)–H(7B) 2.26. Reproduced by permission of The Royal Society of Chemistry.

Based on the success of the tetramethylguanidinium hydrogen bond donor, we attempted to use several other basic amines to form new cerium naphtholate hydrogen bonded complexes. Primary and secondary amines piperidine, diisopropylamine, and ^tBuNH₂ were used to deprotonate 2-naphthol. Then $Ln[N(SiMe_3)_2]_3$ (Ln = La, Ce) was added to the deprotonated 2-naphtholate solution either in THF or toluene. When the reaction was performed in THF, the amines were too weakly hydrogen bonded to the 2naphtholates and were removed under reduced pressure. When the reaction took place in toluene, the acidic amines evidently remained part of the structure (Figure 2.4.43). The most promising of the amines was piperidine, where the ¹H NMR spectrum of the piperidinium cerium naphtholate complex showed a significantly shifted downfield resonance for the hydrogen bonded amine NH_2^+ , which was similar to the (HTMG)₃[Ce₂(Onaph)₉] complex ¹H NMR spectrum (Figure 2.4.44). The shifted NH₂⁺ resonance was absent from the diisopropylaminium cerium naphtholate ¹H NMR spectrum (Figure 2.4.45). However, because the piperidinium was easily displaced in the presence of coordinating solvents, the piperidinium cerium naphtholate complex was challenging to crystallize, and crystals were never isolated from this complex. Other organic superbases, 1,8-diazabicycloundec-7-ene (DBU) and 1,3-diphenylguanidine were also used to deprotonate 2-naphthol to form other lanthanide naphtholate hydrogen bonded complexes. Deprotonation of 2-naphthol with DBU and subsequent reaction with $Ln[N(SiMe_3)_2]_3$ (Ln = La, Ce) in THF showed a promising ¹H NMR spectrum where the DBU-H⁺ had a resonance that was significantly shifted downfield (Figure 2.4.46). Unlike the amines, the DBU hydrogen bonding reactions remained intact in donor solvents. Despite the strong hydrogen bonds, this complex could not be isolated. Reactions with

1,3-diphenylguanidine showed extremely broad ¹H NMR spectra (Figure 2.4.47). This was likely due to the multiple hydrogen bonding sites in 1,3-diphenylguanidine which contributed to the fluxionality of the lanthanide naphtholate complex.

2.2.3. Solution characterization of complexes $Li_3(py)_6[Ln(Onaph)_6] Ln = La$ (2.4), Ln = Ce (2.1); $Li_4(DME)_4[Ln_2(Onaph)_{10}] Ln = La$ (2.5), Ln = Ce (2.2); and [HTMG]_3[Ln_2(Onaph)_9] Ln = La (2.6), Ln = Ce (2.3)

Encouraged by the consistent structure of complex 2.3 in the solid state, we set out to compare the solution structure of 2.3 with those of complexes 2.1 and 2.2. The ¹H NMR spectrum for 2.3 collected in CDCl₃ showed two broadened aryl resonances at 7.65 and 7.10 ppm (Figure 2.2.4). These resonances were much sharper for 2.3 than the aryl proton resonances observed for 2.1 and 2.2. The relative sharpness of the resonances for complex 2.3 provided supporting evidence for the relative kinetic inertness through attenuated fluxionality of that complex.



Figure 2.2.4. ¹H NMR spectra of complexes **2.1–2.3** recorded in CDCl₃. Peaks indicated with an asterisk are due to exogenous proteo-solvent impurities. Reproduced by permission of The Royal Society of Chemistry.

Diffusion-Ordered ¹H NMR SpectroscopY (DOSY) experiments then were performed on the complexes 2.1–2.3 in order to determine their hydrodynamic radii for comparison of the solid state and average solution structures. DOSY NMR has been used previously to differentiate monomeric and dimeric cerium complexes in solution.^[13] Initial work showed that ¹H DOSY NMR experiments performed on complexes 2.1 and 2.2 exhibited fast relaxation such that the diffusion coefficients for those compounds could not be reliably established. The combined fluxionality and paramagnetism of 2.1 and 2.2 in solution contributed to their fast relaxation. Complex 2.3, however, was wellresolved by DOSY ¹H NMR and produced a consistent hydrodynamic radius of 13 + 1.5Å. This result agreed reasonably well with the approximate radius of the compound, determined by measurement between a centroid, defined by all non-hydrogen atoms in the crystal structure of 2.3, to the outermost carbon atom of the 2-naphthoxide groups, ~ 10.1 Å. In order to measure approximate hydrodynamic radii for 2.1 and 2.2, diamagnetic analogues of those complexes were prepared using 4f⁰ lanthanum(III) starting materials.

The complexes Li₃(py)₆[La(Onaph)₆] (**2.4**), Li₄(DME)₄[La₂(Onaph)₁₀] (**2.5**) and [HTMG]₃[La₂(Onaph)₉] (**2.6**) were isolated in good yields following identical procedures for the syntheses of **2.1–2.3** (see section 2.4). As expected, complex **2.6** provided a comparable hydrodynamic radius to complex **2.3** as determined in the DOSY experiment (Table 2.2.2). Surprisingly, the hydrodynamic radii of complexes **2.4** and **2.5** were *both* comparable to those determined for **2.3** and **2.6**, indicating that all four species had average solution structures that were dimeric in CDCl₃ (Table 2.2.2). This result highlighted the complexity of the Li/Ce/Onaph system; complex **2.1** and its diamagnetic analogue **2.4** were monomeric in the solid state but evidenced multiple species in their solution ⁷Li NMR spectra with an average hydrodynamic radius for **2.4** that corresponded to a dimeric complex. Only in the cases of complexes **2.3** and **2.6**, with their hydrogen-bonded secondary structures, were well-defined solution species observed that could be directly correlated to their solid state structures.

Table 2.2.2. Results of DOSY ¹H NMR experiments performed in CDCl₃ including diffusion coefficients (D_o) and approximate hydrodynamic radii (r) for complexes 2.3–
2.6. Reproduced by permission of The Royal Society of Chemistry.

Complex	D_o	r (Å)	Benzene D _o ^b
	$(\times 10^{-10} \text{ m}^2/\text{s})^a$		$(\times 10^{-9} \text{ m}^2/\text{s})$
$Li_{3}(py)_{6}[La(Onaph)_{6}]$ (2.4)	$5.2(0.9)^{c}$	10(1)	2.3(0.07)
$Li_4(DME)_4[La_2(Onaph)_{10}]$ (2.5)	5.3(0.7)	11(1)	2.2(0.2)
(HTMG) ₃ [Ce ₂ (Onaph) ₉] (2.3)	4.6(0.4)	13(0.5)	2.3(0.1)
(HTMG) ₃ [La ₂ (Onaph) ₉] (2.6)	$4.4(0.4)^d$	12	2.3

^{*a*} The radius of benzene was set at 2.54 Å for the calculation of *r*.^[14] ^{*b*}Benzene was used as an internal standard in each case. ^{*c*}Values in parenthesis are standard deviations. ^{*d*}Compared to benzene in a single measurement. All other measurements are correlated by the co-crystallizing solvent, either THF or DME

2.2.4. Syntheses and structural characterization of complexes $Na_3(py)_6[Ce(Onaph)_6]$ (2.7), $Na_4(DME)_4[Ce_2(Onaph)_{10}]$ (2.8), $K_3(py)_6[Ce_2(Onaph)_9(py)_2]$ (2.9), and $K_6(DME)_4[Ce_2Onaph)_{12}]$ (2.10).

We had shown that the Li/Ln/Onaph system presents variable solid state

structures depending on the solvent used to crystallize the complexes. However, it was

not clear if the lanthanide naphthoxide complexes were stabilized by the larger size of the

(HTMG)⁺ cation compared to the Li⁺ cation or if the stabilization could be attributed to

the directional nature of the hydrogen bonds. Thus cerium naphthoxide complexes supported by sodium or potassium cations were synthesized in both DME and pyridine.



Scheme 2.2.4. Syntheses of complexes 2.7–2.10. Naphthyl groups were omitted for clarity.

 $Na_3(py)_6[Ce(Onaph)_6]$ (complex 2.7) was isolated by first deprotonating 6 equiv 2-naphthol with 3 equiv $NaN(SiMe_3)_2$ and then stirring in one equiv $Ce[N(SiMe_3)_2]_3$ in pyridine (Scheme 2.2.4). The complex formed a microcrystalline powder in a mixture of toluene and pyridine layered with hexanes in 77% yield. In DME, however, a different complex was isolated. $Na_4(DME)_4[Ce_2(Onaph)_{10}]$ (complex **2.8**) was synthesized by first deprotonating 10 equiv 2-naphthol with 4 equiv $NaN(SiMe_3)_2$ in a mixture of DME and toluene (Scheme 2.2.4). 2 equiv $Ce[N(SiMe_3)_2]_3$ were dissolved in hexanes and layered over the DME and toluene mixture, resulting in yellow crystals in 69% yield.

Complexes of the even larger K^+ cation also demonstrated solvent dependent behavior. $K_3(py)_6[Ce_2(Onaph)_9(py)_2]$ (complex **2.9**) was similarly synthesized by first deprotonating 9 equiv 2-naphthol with 3 equiv KN(SiMe_3)_2 in pyridine (Scheme 2.2.4). 2 equiv Ce[N(SiMe_3)_2]_3 were dissolved in hexanes and layered over the pyridine mixture, resulting in yellow crystals in 83% yield. { $K_6(DME)_4[Ce_2(Onaph)_{12}]$ }_n (complex **2.10**) also was synthesized by first deprotonating 12 equiv 2-naphthol with 6 equiv KN(SiMe_3)_2 in DME (Scheme 2.2.4). 2 equiv Ce[N(SiMe_3)_2]_3 were dissolved in hexanes and layered over the DME mixture, resulting in yellow crystals in 69% yield.

Similar to complexes **2.1**, **2.2**, and **2.3**, complexes **2.7**, **2.8**, **2.9**, and **2.10** all contained 6-coordinate pseudo-octahedral geometries at the cerium(III) center (Figures 2.2.5–2.2.8, only connectivity for complex **2.8** could be established). Ce–O bond lengths were typical for a Ce(III) center, where the terminal Ce–O bonds ranged from 2.280(3)–2.398(6) Å. The main structural differences of these complexes were the number and position of the alkali metal and (HTMG)⁺ cations in the secondary coordination sphere, which varied because of the size and coordination preference of each cation in the secondary coordination sphere. Li⁺ and Na⁺ showed similar coordination preferences, as complexes **2.1** and **2.7**, and **2.2** and **2.8** had the same cerium naphtholate stoichiometry and connectivity within the same solvent. In pyridine, complex

2.9 and the hydrogen bonded complex **2.3** had the same Ce_2Onaph_9 core with the cations in the secondary coordination sphere bridging between the two cerium centers. While the Na⁺ and K⁺ cations displayed solvent-dependent solid state and solution behavior, the ¹H NMR resonances of the naphtholates in the series of alkali metal cerium naphtholate complexes became sharper with cation size (Figure 2.2.9). Thus larger alkali metal cation size did somewhat stabilize the cerium naphtholate complexes.



Figure 2.2.5. 30 % thermal ellipsoid plot of Na₃(py)₆[Ce(Onaph)₆] (**2.7**). Hydrogen atoms are omitted for clarity. Due to the poor quality of the data, this structure can only be used for connectivity.



Figure 2.2.6. 30 % thermal ellipsoid plot of Na₄(DME)₄[Ce₂(Onaph)₁₀] (**2.8**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) for **2.8**: Ce(1)–O(1) 2.363(4), Ce(1)–O(2) 2.346(4), Ce(1)–O(3) 2.280(3), Ce(1)–O(4) 2.361(4), Ce(1)–O(5) 2.486(3), Ce(1)–O(6) 2.480(4).



Figure 2.2.7. 30 % thermal ellipsoid plot of K₃(py)₆[Ce₂(Onaph)₉(py)₂] (**2.9**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) for **2.9**: Ce(1)–O(1) 2.398(6), Ce(1)–O(2) 2.342(6), Ce(1)–O(3) 2.394(6), Ce(1)–O(4) 2.350(6), Ce(1)–O(5) 2.350(6), Ce(1)–O(6) 2.384(6).



Figure 2.2.8. 30 % thermal ellipsoid plot of $\{K_6(DME)_4[Ce_2(Onaph)_{12}]\}_n$ (2.10). The top thermal ellipsoid plot shows the structure of the monomeric unit, and the bottom thermal ellipsoid plot shows just the metal core structure. Hydrogen atoms are omitted for clarity

in both thermal ellipsoid plots, carbon atoms are omitted for clarity in the thermal ellipsoid plot shown at the bottom. Selected bond distances (Å) for **2.10**: Ce(1)–O(1) 2.3028(14), Ce(1)–O(2) 2.3826(14), Ce(1)–O(3) 2.3896(13), Ce(1)–O(4) 2.4445(13), Ce(1)–O(5) 2.4036(13), Ce(1)–O(6) 2.3432(13).



Figure 2.2.9. Stacked ¹H NMR spectra of complexes **2.1**, **2.2**, **2.7**, **2.8**, **2.9**, and **2.10** in CDCl₃.

2.2.5. Cyclic voltammetry of complexes 2.1–2.10.

Toward quantifying the effects of the Lewis acidity of the cation in the secondary coordination sphere on the Ce(III) center, cyclic voltammetry was performed in methylene chloride (Table 2.2.3 and Figures 2.4.1–2.4.17 in section 2.4). Decreasing the Lewis acidity of the cation in the secondary coordination sphere resulted in a more electron-rich Ce(III) metal center, favoring the formation of Ce(IV) by \sim 200 mV.

Table 2.2.3. A summary of cyclic voltammetry (CV) data of complexes **2.1–2.10** collected in ~0.1 M [n Pr₄N][B(3,5-(CF₃)₂-C₆H₃)₄] in methylene chloride (DCM). The scan rate was 100 mV/s unless otherwise indicated. ${}^{a} E_{1/2}$ was measured by DPV instead of CV. b Since the waves were ill-defined in the CV, the E_{pa} and the ΔE could not be ascertained. c The E_{pa} and E_{pc} were still poorly defined by DPV. $E_{1/2}$ was estimated using second derivative plots.

Complex	E_{pa}	E_{pc}	ΔE	$E_{1/2}$
	(V vs. Fc)	(V vs. Fc)	(V vs. Fc)	(V vs. Fc)
Li ₄ (DME) ₄ [Ce ₂ (Onaph) ₁₀] (2.2)	-0.24	-0.83	0.59	-0.53
$Na_4(DME)_4[Ce_2(Onaph)_{10}]$ (2.8)	-0.33	-0.90	0.58	-0.61
$K_6(DME)_4[Ce_2(Onaph)_{12}]$ (2.10)	-0.65	-0.81	0.16	-0.73
Li ₃ (py) ₆ [Ce(Onaph) ₆] (2.1)	n/a ^b	-0.80	n/a ^b	-0.35 ^c
Na ₃ (py) ₆ [Ce(Onaph) ₆] (2.7)	n/a ^b	-0.65	n/a ^b	-0.54^{a}
$K_3(py)_6[Ce_2(Onaph)_9(py)_2]$ (2.9)	-0.29	-0.76	0.47	-0.52/ -0.34^{a}
(HTMG) ₃ [Ce ₂ (Onaph) ₉] (2.3)	-0.52	-0.92	0.40	-0.72
	-0.52	-1.21	0.70	-0.86

The reduction potentials of complexes **2.1–2.3** showed that the cerium naphtholate complexes should be easy to oxidize. 1–2 equiv the oxidants I_2 , Ph₃CCl, NaNO₂, FcPF₆, and FcBAr^F₄ were added to **2.1** or **2.3** in THF, toluene, pyridine, and

DME in an attempt to oxidize either of these complexes. However, none of these reactions were successful (a few examples of reaction results monitored by ¹H NMR spectroscopy were shown in Figures 2.4.48–2.4.50), yielding unidentifiable mixtures of products. In the case of $FcBAr_{4}^{F}$ reacting with complex **2.3**, the only product evident in the ¹H NMR spectrum was the formation of HTMG BAr₄^F (Figure 2.4.50).

Ligand oxidations were also apparent in the electrochemistry of the cerium naphtholate complexes (Figures 2.4.1–2.4.17). Unlike phenoxides, alkoxides are more difficult to oxidize, which make them attractive supporting ligands for Ln^{III} oxidation reactions. Comparatively sterically bulky alkoxides, L-menthol and 'BuOH were also used in an effort to isolate new cerium complexes with (HTMG)⁺ in the secondary coordination sphere (Figures 2.4.51–2.4.54 for examples of NMR spectra). However, rational products from the reaction mixtures were not isolated. One reason for the failure was that the TMG base was not strong enough to deprotonate the alkoxides. Thus, a strongly basic, neutral TMG was present in these reactions, and the TMG, instead of remaining in the secondary coordination sphere, likely coordinated directly to cerium. Addition of TMG to cerium mentholate or cerium ¹butoxide formed *in situ* by reacting menthol or 'BuOH with Ce[N(SiMe₃)₂]₃, also resulted in coordination of TMG to the cerium center. No apparent hydrogen bonding interactions in the secondary coordination sphere formed in these reactions.

2.3 Discussion and Conclusions

To develop methods to stabilize labile species in solution, a series of cerium naphtholate complexes were synthesized. Particularly because the naphtholate ligand, a monodentate,

sterically unhindered ligand, was paired with a cerium(III) cation, a hard, ionic metal center that forms labile bonds, we observed a wide variety of cerium naphtholate coordination motifs both in the solid state and in solution. All of the alkali metal cerium naphtholate complexes synthesized had solution and solid state structures that were strongly dependent on solvent. The lithium cerium naphtholate complexes were the most labile, where the Li⁺ cation was likely too small to saturate the coordination sphere about the cerium metal center. Furthermore, Li⁺ cations themselves are highly ionic species which added to the lability of the products. Thus, multiple ⁷Li NMR signals were observed, as well as unexpected hydrodynamic radii were observed. Na⁺ or K⁺ cerium naphtholates had sharper ¹H NMR resonances, indicating less kinetically labile complexes in solution. The alkali metal cation size likely had a role to play in stabilizing these complexes in solution relative to Li⁺.

The alkali metal cationic interaction with the naphtholates and solvent could be considered as a non-directional point charge which did not orient the cerium coordination sphere in space. When hydrogen bonding instead of alkali metal cations was used to complete the cerium naphtholate coordination sphere, the hydrogen bonding interactions were directional. Even though the nature of the hydrogen bonding interactions is still ionic, the (HTMG)⁺ hydrogen bonding motif served to pre-organize the cerium naphtholate complex in space and orient the naphtholate ligands to maximize the hydrogen bonding. Furthermore, the (HTMG)⁺ cation was relatively large compared to lithium, which helped saturate the coordination sphere about the cerium cation. Because of the large, pre-organizing, directional hydrogen bonds, the (HTMG)⁺ cerium naphtholate complex solution and solid state structures did not depend on the solvent and

appeared to be relatively kinetically inert compared to the alkali metal cerium naphtholate complexes, as observed by NMR spectroscopy. Thus, hydrogen bonding cations could be used as a strategy to stabilize cerium complex structures in the solid state and in solution.

2.4 Experimental Section

General Methods. Unless otherwise indicated all reactions and manipulations were performed under an inert atmosphere (N₂) using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. Nexus II drybox equipped with a molecular sieves 13X / Q5 Cu-0226S catalyst purifier system. Glassware was oven-dried overnight at 150 °C prior to use. ¹H, ¹³C, and ⁷Li NMR spectra were obtained on a Bruker DMX-300, on a Bruker DMX-360, on a Bruker UNI-400, or on a Bruker BioDRX-500 Fourier transform NMR spectrometer at 300, 360, 400, and 500 MHz respectively. Chemical shifts were recorded in units of parts per million downfield from residual proteo solvent peaks (¹H), or characteristic solvent peaks (¹³C). The ⁷Li spectra were referenced to external solution standards of LiCl in H₂O. Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility using a Perkin-Elmer Series II 2400 CHNS analyzer and also at Complete Analysis Laboratories Inc. in Parsippany, NJ using a Carlo Erba EA 1108 analyzer.

Materials. Tetrahydrofuran, dimethoxyethane, toluene, fluorobenzene, hexane, and pentane were purchased from Fisher Scientific. The solvents were sparged for 20 min with dry N_2 and dried using a commercial two-column solvent purification system comprising columns packed with Q5 reactant and neutral alumina respectively (for hexane and pentane), or two columns of neutral alumina (for THF and toluene). Pyridine,

also purchased from Fisher Scientific, was freeze-pump-thawed for 4 cycles and stored over 4 Å molecular sieves for three days before use. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. Pyridine-*d*₅ was stored over 4 Å molecular sieves for three days before use, and benzene-*d*₆ was dried and stored over potassium for 2 days before use. CDCl₃ was freeze-pump-thawed for 4 cycles and stored over 4 Å molecular sieves for three days before use or was stirred over calcium hydride for 3 days, distilled, and then freeze-pump-thawed for 4 cycles. Ln[N(SiMe₃)₂]₃^[15] (Ln = La, Ce) was prepared following published procedures. Ce(OTf)₃ was dried under vacuum at 150 °C for 12 hours. Li[N(SiMe₃)₂] (Acros) was recrystallized from hot pentane prior to use. Lithium *tert*-butoxide (Acros), K[N(SiMe₃)₂] (Sigma Aldrich) and Na[N(SiMe₃)₂] (Acros) were used as purchased. 2-naphthol (Acros, Sigma Aldrich) was sublimed under reduced pressure prior to use. 1,1,3,3-tetramethylguanidine (Acros, Sigma Aldrich) was freeze-pump-thawed for 4 cycles and stored over 4 Å molecular sieves for three days before use.

Electrochemistry. Voltammetry experiments (CV and DPV) were performed using a CH Instruments 620D Electrochemical Analyzer/Workstation and the data were processed using CHI software v 9.24. All experiments were performed in an N₂ atmosphere drybox using electrochemical cells that consisted of a 4 mL vial, glassy carbon (3 mm diameter) working electrode, a platinum wire counter electrode, and a silver wire plated with AgCl as a quasi-reference electrode. The working electrode surfaces were polished prior to each set of experiments, and were periodically replaced to prevent the buildup of oxidized product on the electrode surfaces. Potentials were reported versus ferrocene (Fc). Solutions employed during CV studies were ~3 mM in analyte. For

electrochemistry collected in dichloromethane, the solution was 100 mM in $[nPr_4N][B(3,5-(CF_3)_2-C_6H_3)_4]$ ($[nPr_4N][BAr^F_4]$). All data were collected in a positive-feedback IR compensation mode. Scan rate dependences of 25–1000 mV/s were performed to determine electrochemical reversibility. Differential pulse voltammetry (DPV) experiments were also performed, particularly to help identify poorly defined waves observed in CV studies.

$Li_3(py)_6[Ce(Onaph)_6]$



Figure 2.4.1. Cyclic voltammetry of $Li_3(py)_6[Ce(Onaph)_6]$ (**2.1**) in methylene chloride and 0.1 M ([ⁿPr₄N][BAr^F₄]). Scan rate was 500 mV/s.



Figure 2.4.2. Scan rate dependence of the $Ce^{III/IV}$ redox wave of $Li_3(py)_6[Ce(Onaph)_6]$ (2.1) in methylene chloride and 0.1 M ([${}^{n}Pr_4N$][BAr ${}^{F}_4$]). Scan rates ranged from 50–1000 mV/s.



Figure 2.4.3. Differential pulse voltammogram of $Li_3(py)_6[Ce(Onaph)_6]$ (**2.1**) in methylene chloride and 0.1 M ([ⁿPr₄N][BAr^F₄]).

 $Li_4(DME)_4[Ce_2(Onaph)_{10}]$



Figure 2.4.4. Cyclic voltammetry of $Li_4(DME)_4[Ce_2(Onaph)_{10}]$ (**2.2**) in methylene chloride and 0.1 M ([ⁿPr₄N][BAr^F₄]). Scan rate was 500 mV/s.



Figure 2.4.5. Scan rate dependence of the Ce^{III/IV} redox wave of

 $Li_4(DME)_4[Ce_2(Onaph)_{10}]$ (2.2) in methylene chloride and 0.1 M ([ⁿPr₄N][BAr^F₄]). Scan rates ranged from 50–1000 mV/s.



Figure 2.4.6. Cyclic voltammetry of $(HTMG)_3[Ce_2(Onaph)_9]$ (2.3) in methylene chloride and 0.1 M ([ⁿPr₄N][BAr^F₄]). Scan rate was 100 mV/s.



Figure 2.4.7. Scan rate dependence of the Ce^{III/IV} redox wave of $(HTMG)_3[Ce_2(Onaph)_9]$ (2.3) in methylene chloride and 0.1 M ([ⁿPr₄N][BAr^F₄]). Scan rates ranged from 25–1000 mV/s.

 $Na_3(py)_6[Ce(Onaph)_6]$



Figure 2.4.8. Cyclic voltammetry of $Na_3(py)_6[Ce(Onaph)_6]$ (2.7) in methylene chloride and 0.1 M ([ⁿPr₄N][BAr^F₄]). Scan rate was 100 mV/s.



Figure 2.4.9. Cyclic voltammetry of $Na_3(py)_6[Ce(Onaph)_6]$ (2.7) in methylene chloride and 0.1 M ([ⁿPr₄N][BAr^F₄]). Scan rate was 100 mV/s.



Figure 2.4.10. Scan rate dependence of the $Ce^{III/IV}$ redox wave of $Na_3(py)_6[Ce(Onaph)_6]$ (2.7) in methylene chloride and 0.1 M ([${}^{n}Pr_4N$][BAr ${}^{F}_4$]). Scan rates ranged from 25–1000 mV/s.



Figure 2.4.11. Differential pulse voltammogram of $Na_3(py)_6[Ce(Onaph)_6]$ (2.7) in methylene chloride and 0.1 M ([ⁿPr₄N][BAr^F₄]).



Figure 2.4.12. Cyclic voltammetry of $Na_4(DME)_4[Ce_2(Onaph)_{10}]$ (**2.8**) in methylene chloride and 0.1 M ([ⁿPr₄N][BAr^F₄]). Scan rate was 100 mV/s.



Figure 2.4.13. Scan rate dependence of the Ce^{III/IV} redox wave of

 $Na_4(DME)_4[Ce_2(Onaph)_{10}]$ (2.8) in methylene chloride and 0.1 M ([ⁿPr₄N][BAr^F₄]). Scan rates ranged from 25–1000 mV/s.



Figure 2.4.14. Cyclic voltammetry of $K_3(py)_6[Ce_2(Onaph)_6(py)_2]$ (2.9) in methylene

chloride and 0.1 M ([ⁿPr₄N][BAr^F₄]). Scan rate was 100 mV/s.



Figure 2.4.15. Scan rate dependence of the Ce^{III/IV} redox wave of

 $K_3(py)_6[Ce_2(Onaph)_9(py)_2]$ (2.9) in methylene chloride and 0.1 M ([ⁿPr₄N][BAr^F₄]). Scan rates ranged from 25–1000 mV/s.



Figure 2.4.16. Cyclic voltammetry of $K_6(DME)_4[Ce_2(Onaph)_{12}]$ (**2.10**) in methylene chloride and 0.1 M ([ⁿPr₄N][BAr^F₄]). Scan rate was 100 mV/s.



Figure 2.4.17. Scan rate dependence of the Ce^{III/IV} redox wave of

 $K_6(DME)_4[Ce_2(Onaph)_{12}]$ (2.10) in methylene chloride and 0.1 M ([ⁿPr₄N][BAr^F₄]). Scan rates ranged from 25–1000 mV/s.

X-ray Crystallography. X-ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at a temperature of 143(1) K. In all cases, rotation frames were integrated using SAINT,^[16] producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the SHELXTL^[17] program package for further processing and structure solution on a Dell Pentium 4 computer. The intensity data were corrected for Lorentz and polarization effects and for absorption using TWINABS^[18] or SADABS.^[19] The structures were solved by direct methods (SHELXS-97).^[20] Refinement was by full-matrix least squares based on F² using SHELXL-97.^[20] All reflections were used during refinements. The weighting scheme used was $w=1/[\sigma^2(F_o^2) + (0.0907P)^2 + 0.3133P]$ where $P = (F_o^2 + C_o^2)^2 + (0.0907P)^2 + 0.3133P$ $2F_c^2$)/3. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. The weighting scheme used was $w=1/[\sigma^2(F_0^2)+(0.0907P)^2]$ + 0.3133P] where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Complex 2.1 ($C_{90}H_{72}CeLi_3N_6O_6$) M = 1494.48) lies on a crystallographic 3-fold axis (at 1/3, 2/3, z); the asymmetric unit is 1/3 of a molecule. The naphthyl group C(11)–C(20) is disordered by a rotation of 180° , where each naphthyl group had an occupancy of 0.50. In complex 2.3 ($C_{105}H_{105}Ce_2N_9O_9$, M = 1917.22), the naphthyl rings exhibited varying degrees of disorder; naphthyls C(21)– C(30) and C(61)-C(70) were modeled with two contributing orientations. All naphthyl groups were refined as rigid units. The weighting scheme used for 2.3 was $w=1/[s^2(F_o^2)]$)+ $(0.0943P)^2$ + 92.6350P] where P = $(F_o^2 + 2F_c^2)/3$.

	2.1 (Penn4098)	2.2 (Penn4119)
Empirical formula	C ₉₀ H ₇₂ N ₆ O ₆ Li ₃ Ce	$C_{116}H_{110}O_{18}Li_4Ce_2$
Formula weight	1494.48	2100.04
Temperature (K)	143(1)	143(1)
Wavelength (Å)	0.71073	0.71073
Crystal system	Rhombohedral	Triclinic
Space group	R3	PT
Cell constants		
a (Å)	20.7351(11)	11.7345(7)
b (Å)	20.7351(11)	15.1830(9)
c (Å)	30.1140(18)	16.6050(9)
α (°)	90.00	82.260(3)
β (°)	90.00	74.755(3)
γ (°)	120.00	87.099(3)
$V(Å^3)$	11212.7(11)	2828.0(3)
Z	6	1
ρ_{calc} (mg/cm ³)	1.328	1.233
μ (Mo K α) (mm ⁻¹)	0.669	0.856
F(000)	4614	1078
Crystal size (mm ³)	0.35 x 0.05 x 0.05	0.50 x 0.08 x 0.03
Theta range for data collection	1.76 to 27.51°	1.74 to 27.72°
Index ranges	$-26 \le h \le 26, -26 \le k \le 26, -39 \le 1 \le 38$	$-15 \le h \le 15, -19 \le k \le 19,$ $-21 \le 1 \le 21$
Reflections collected	114733	80553
Independent collections	5743 [R(int) = 0.0270]	13008 [R(int) = 0.0272]
Completeness to theta = 27.40°	99.9%	97.9%
21.47	Somi ampirical from	Somi ampirical from
Absorption correction	equivalents	equivalents
Max and min. transmission	0.7456 and 0.6741	0.7456 and 0.6649
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints /	5743 / 86 / 362	13008 / 0 / 636
$Goodness-of-fit on F^2$	1 055	1 075
Final R indices	$R_1 = 0.0277 \text{ w}R_2 =$	R1 = 0.0267 wR2 =
[I > 2 sigma(I)]	0.0657	0.0673
	R1 = 0.0324, wR2 =	$R_1 = 0.0324$, wR2 =
K indices (all data)	0.0698	0.0694

 Table 2.4.1. Crystallographic parameters for compounds 2.1 and 2.2.

	2.3 (Penn4211)	
Empirical formula	$C_{105}H_{105}N_9O_9Ce_2$	
Formula weight	1917.22	
Temperature (K)	143(1)	
Wavelength (Å)	0.71073	
Crystal system	Monoclinic	
Space group	C2/c	
Cell constants		
a (Å)	36.8108(18)	
b (Å)	20.6080(10)	
c (Å)	27.9312(13)	
α (°)	90.00	
β (°)	108.529(2)	
γ (°)	90.00	
V (Å ³)	20090.2(17)	
Z	8	
$\rho_{calc} (mg/cm^3)$	1.268	
μ (Mo K α) (mm ⁻¹)	0.953	
F(000)	7888	
Crystal size (mm ³)	0.25 x 0.18 x 0.18	
Theta range for data collection	1.54 to 27.56°	
Index ranges	$-47 \le h \le 47, -26 \le k \le 26, -36 \le l \le$	
index ranges	36	
Reflections collected	378757	
Independent collections	23161 [R(int) = 0.0382]	
Completeness to theta = 27.61°	99.7%	
Absorption correction	Semi-empirical from equivalents	
Max and min. transmission	0.7456 and 0.6872	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	23161 / 1313 / 1043	
Goodness–of–fit on F^2	1.105	
Final R indices [I>2sigma(I)]	R1 = 0.0739, WR2 = 0.1951	
R indices (all data)	R1 = 0.1007, wR2 = 0.2112	
Largest diff. peak and hole $(e.Å^{-3})$	2.850 and -1.694	

Table 2.4.2. Crystallographic parameters for compound 2.3.

	<u>2.7 (Penn4727)</u>	2.8 (Penn4545)
Empirical formula	$C_{90}H_{72}N_6O_6Na_3Ce$	$C_{116}H_{110}O_{18}Na_4Ce_2$
Formula weight	1542.63	2164.24
l'emperature (K)	100(1)	100(1)
Wavelength (A)	0./10/3	0./10/3
Crystal system	Iriclinic	Iriclinic
Space group	PT	PT
Cell constants		
a (Å)	15.238(2)	16.5363(10)
b (Å)	15.724(2)	17.6841(11)
c (Å)	16.029(2)	20.0695(12)
α (°)	87.667(7)	102.622(3)
β (°)	85.013(7)	102.236(3)
γ (°)	83.291(7)	108.718(3)
$V(A^3)$	3798.0(8)	5165.4(5)
Z	2	2
$\rho_{calc} (mg/cm^3)$	1.349	1.391
μ (Mo K α) (mm ⁻¹)	0.676	0.954
F(000)	1586	2220
Crystal size (mm ³)	0.50 x 0.28 x 0.10	0.52 x 0.20 x 0.15
Theta range for data collection	1.28 to 27.66°	1.82 to 27.55°
Index ranges	$-19 \le h \le 19, -20 \le k \le 20,$	$-21 \le h \le 21, -22 \le k \le 22,$
index ranges	$0 \le l \le 20$	$-26 \le l \le 26$
Reflections collected	224342	140863
Independent collections	17585 [R(int) = 0.1114]	23407 [R(int) = 0.0232]
Completeness to theta = 27.66° and 27.55°	99.2%	98.2%
Absorption correction	Semi-empirical from	Semi-empirical from
Max and min. transmission	equivalents 0.7456 and 0.4488	equivalents 0.7456 and 0.6344
Refinement method	Full-matrix least-squares Γ^2	Full-matrix least-squares Γ^2
Data / machine /	on F	on F ⁻
Data / restraints / parameters	17585 / 0 / 969	23407 / 378 / 1321
Goodness–of–fit on F ²	2.308	1.239
Final R indices	R1 = 0.1595, wR2 =	R1 = 0.0691, $wR2 =$
[I>2sigma(I)]	0.4598	0.1312
R indices (all data)	R1 = 0.1857, wR2 = 0.4930	R1 = 0.0909, wR2 = 0.1466

 Table 2.4.3. Crystallographic parameters for compounds 2.7 and 2.8.
	2.9 (Penn4696)	2.10 (Penn4513)
Empirical formula	$C_{265}H_{211}N_{17}O_{18}K_6Ce_4$	$C_{136}H_{124}O_{20}K_6Ce_2$
Formula weight	4716.59	2593.19
Temperature (K)	100(1)	100(1)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	РТ
Cell constants		
a (Å)	26.6516(13)	12.7467(7)
b (Å)	18.4761(9)	15.9250(8)
c (Å)	23.6043(12)	32.0779(17)
α (°)	90.00	99.029(2)
β (°)	106.731(2)	98.357(3)
γ (°)	90.00	106.862(2)
$V(A^3)$	11131.1(10)	6027.6(6)
Z	2	2
$\rho_{calc} (mg/cm^3)$	1.407	1.429
μ (Mo K α) (mm ⁻¹)	0.985	1.022
F(000)	4820	2660
Crystal size (mm ³)	0.35 x 0.30 x 0.24	0.30 x 0.18 x 0.06
collection	1.36 to 27.55°	1.64 to 27.52°
Index ranges	$-34 \le h \le 34, -24 \le k \le 24,$ $-30 \le l \le 30$	$-16 \le h \le 16, -19 \le k \le 20,$ $-41 \le 1 \le 41$
Reflections collected	546055	196756
Independent collections	25646 [R(int) = 0.0262]	27608 [R(int) = 0.0248]
Completeness to theta = 27.55° and 27.52°	99.9%	99.4%
Absorption correction	Semi-empirical from	Semi-empirical from
Max and min. transmission	0.7456 and 0.6825	0.7456 and 0.6632
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F ²
Data / restraints / parameters	25646 / 0 / 1439	27608 / 844 / 1619

Table 2.4.4. Crystallographic parameters for compounds 2.9 and 2.10.

Goodness-of-fit on F ²	1.223	1.078
Final R indices	R1 = 0.0346, $wR2 =$	R1 = 0.0262, wR2 =
[I>2sigma(I)]	0.0682	0.0551
R indices (all data)	R1 = 0.0452, wR2 = 0.0775	R1 = 0.0349, wR2 = 0.0592
Largest diff. peak and hole $(e.Å^{-3})$	1.366 and -0.788	0.819 and -0.651

Synthetic Details and Characterization

Synthesis of [Li(THF)][Onaph]. 2-naphthol (2.46 g, 17.1 mmol) was dissolved in 15 mL of THF in a 20 mL scintillation vial and the solution was chilled to -35 °C. Lithium *tert*-butoxide (1.37 g, 17.1 mmol, 1 equiv) was added to the cold mixture, which was stirred for 2 h resulting in a clear yellow solution. The THF solution was concentrated under reduced pressure and layered with 10 mL of hexanes. Colorless crystals of the product were collected by filtration, washed with hexanes and dried under reduced pressure. Yield 2.88 g, 13.0 mmol, 76 %. ¹H NMR (400 MHz, CDCl₃) δ : 7.64 (doublet, *J* = 8.0 Hz, 1H), 7.58 (doublet, *J* = 8.8 Hz, 1H), 7.47 (doublet, *J* = 8.2 Hz, 1H), 7.25 (triplet, *J* = 7.0 Hz, 1H), 7.07 (multiplet, 1H), 7.03 (doublet of doublets, *J*₁ = 8.8 Hz, *J*₂ = 2.4 Hz, 1H), 6.94 (singlet, 1H). ⁷Li NMR (400 MHz, CDCl₃) δ : 1.04 (s).

Synthesis of $Li_3(py)_6[Ce(Onaph)_6]$ (2.1). In a 20 mL scintillation vial, 2-naphthol (0.21 g, 1.45 mmol, 6 equiv) was dissolved in 5 mL of pyridine. Once dissolved, $Li[N(SiMe_3)_2]$ (0.12 g, 0.73 mmol, 3 equiv) was added to the vial and the clear yellow solution was stirred for half an hour. After stirring, the pyridine was removed under reduced pressure, and the resulting gel-like pale yellow solid was re-dissolved in 2 mL of pyridine. Ce[N(SiMe_3)_2]_3 (0.15 g, 0.24 mmol, 1 equiv) was dissolved in 12 mL of hexanes and the bright yellow solution was layered over the clear, pale yellow pyridine solution. After

two days, yellow crystals formed. The yellow crystals of the product were collected by filtration, washed with hexanes and dried under reduced pressure. Yield 0.21 g, 0.14 mmol, 57 %. ¹H NMR (360 MHz, CDCl₃) δ : 9.14 (broad singlet, 12H), 7.67 (broad singlet, 6H), 7.24 (broad singlet, 18H), 6.85 (broad singlet, 12H); ¹³C NMR (75 MHz, CDCl₃) δ : 150.34, 136.63, 126.78, 124.30, 120.96; ⁷Li NMR (194 MHz, CDCl₃) δ : 1.99 (s). CHN analyses for compound **2.1** were consistently within ±0.5 % for the H and N values but the carbon value was consistently low on four attempts. We attribute the problem with the carbon value to incomplete combustion for this complex. The same result was obtained for complex **2.4**, the lanthanum analog of complex **2.1**.



Figure 2.4.18. ¹H NMR spectrum of Li₃(py)₆[Ce(Onaph)₆] (**2.1**) collected in CDCl₃. The asterisks indicate exogenous solvent peaks. Reproduced by permission of The Royal Society of Chemistry.



Li₃(py)₆[Ce(Onaph)₆] (**2.1**) collected in CDCl₃. Reproduced by permission of The Royal Society of Chemistry.

Synthesis of Li₄(DME)₄[Ce₂(Onaph)₁₀] (2.2). In a 20 mL scintillation vial, 2-naphthol (0.17 g, 1.21 mmol, 10 equiv) was dissolved in 5 mL of DME to form a clear, colorless solution. Once dissolved, Li[N(SiMe₃)₂] (0.081 g, 0.48 mmol, 4 equiv) was added to the vial and stirred over a period of 0.5 hour. After stirring, the DME was removed under reduced pressure, and the white gel-like solid was re-dissolved in 2 mL of DME. A bright yellow solution of Ce[N(SiMe₃)₂]₃ (0.15 g, 0.24 mmol, 2 equiv) was prepared from in 12 mL hexanes and then layered over the clear, colorless DME solution. After two days, off-white needle-like crystals formed. The off-white crystals of the product were collected by filtration, washed with hexanes and dried under reduced pressure. Yield 0.19 g, 0.091 mmol, 75%. ¹H NMR (360 MHz, CDCl₃) δ : 7.0–6.2 (broad singlet, 6H), 5.76 (broad 65

singlet, 2H), 4.65 (broad singlet, 4H), 4.06 (broad singlet, 6H); ¹³C NMR (360 MHz, CDCl₃) δ: 133.68, 126.62, 125.30, 124.01, 120.68, 73.05, 60.82; ⁷Li NMR (194 MHz, CDCl₃) δ: 17.18 (singlet). Analysis calculated for C₁₁₆H₁₁₀O₁₈Ce₂Li₄: C, 66.34; H, 5.28. Found: C, 66.09; H, 5.59.



Figure 2.4.20. ¹H NMR spectrum of Li₄(DME)₄[Ce₂(Onaph)₁₀] (**2.2**) collected in CDCl₃.

Asterisks indicate exogenous solvent species. Reproduced by permission of The Royal Society of Chemistry.



Figure 2.4.21. ⁷Li NMR (left) and ¹³C NMR (right) spectra of Li₄(DME)₄[Ce₂(Onaph)₁₀] (2.2) collected in CDCl₃. Asterisks indicate exogenous solvent species. Reproduced by permission of The Royal Society of Chemistry.

Synthesis of [HTMG]₃[Ce₂(Onaph)₉]·(THF)₂ (2.3). In a 20 mL scintillation vial, 2naphthol (0.21 g, 1.45 mmol, 9 equiv) was dissolved in 4 mL of THF. Once dissolved, 1,1,3,3-tetramethylguanidine (92 μ L, 0.73 mmol, 3 equiv) was added by syringe and the clear, colorless solution was stirred over a period of 1 h. Then, Ce[N(SiMe₃)₂]₃ (0.209 g, 0.32 mmol, 2 equiv) was added to the clear, colorless solution. The clear yellow THF solution was concentrated to 2 mL after stirring for 2 h, and then layered with 20 mL hexanes. After 2 days, yellow crystals formed. The crystals were collected by filtration, washed with hexanes, and dried under reduced pressure. Yield: 0.23 g, 0.11 mmol, 68%. ¹H NMR (360 MHz, CDCl₃) δ : 11.80 (broad singlet, 3H), 7.65 (broad singlet, 20H), 7.30 (broad singlet, 17H), 7.10 (broad singlet, 14H), 2.84(broad singlet, 36H) ¹H NMR (360 MHz, THF-*d*₈) δ : 10.65 (broad singlet, 3H), 8.85 (broad singlet, 6H), 7.97 (singlet, 6H), 7.69 (singlet, 16H), 7.29 (singlet, 9H), 7.07 (singlet, 12H), 2.88 (singlet, 36H); ¹H NMR (360 MHz,-pyridine- d_5) δ : 9.87 (broad singlet, 3H), 8.83 (singlet, 4H), 8.39 (singlet, 6H), 8.01 (singlet, 9H), 7.88 (singlet, 9H), 7.48 (singlet, 9H), 7.23 (singlet, 9H), 2.35 (singlet, 36H); ¹³C NMR (360 MHz, CDCl₃) δ : 162.37, 136.02, 128.40, 127.16, 126.77, 126.13, 125.02, 120.84, 113.98, 39.35, 31.69. Analysis calculated for C₁₁₃H₁₂₁O₁₁N₉Ce₂: C, 65.84; H, 5.92; N, 6.12. Found: C, 65.81; H, 5.70; N, 6.40. The product can also be crystallized from DME or pyridine by following the same procedure with those solvents.



Figure 2.4.22. ¹H NMR spectrum of [HTMG]₃[Ce₂(Onaph)₉] (2.3) crystallized from THF

collected in CDCl₃. Reproduced by permission of The Royal Society of Chemistry.



Figure 2.4.23. ¹H NMR spectrum of [HTMG]₃[Ce₂(Onaph)₉] (**2.3**) crystallized from DME (top) and pyridine (bottom) collected in CDCl₃. Asterisks indicate exogenous solvent peaks. Reproduced by permission of The Royal Society of Chemistry.



Figure 2.4.24. ¹H NMR spectrum of [HTMG]₃[Ce₂(Onaph)₉] (**2.3**) crystallized from DME collected in THF– d_8 (top) and pyridine– d_5 (bottom). Asterisks indicate the exogenous solvent species present. Reproduced by permission of The Royal Society of Chemistry.



Figure 2.4.25. ¹³C NMR spectrum of [HTMG]₃[Ce₂(Onaph)₉] (**2.3**) crystallized from THF collected in CDCl₃. Asterisks indicate exogenous solvent species present. Reproduced by permission of The Royal Society of Chemistry.

Synthesis of Li₃(py)₆[La(Onaph)₆] (2.4). The synthesis of 2.4 was identical to that of 2.1, except that La[N(SiMe₃)₂]₃ (0.10 g, 0.16 mmol, 1 equiv) was dissolved in hexanes and layered over a pyridine solution of 2-naphthol (0.14 g, 0.97 mmol, 6 equiv) and Li[N(SiMe₃)₂] (0.082 g, 0.434 mmol, 3 equiv). Yield 0.18 g, 0.12 mmol, 74%. ¹H NMR (400 MHz, CDCl₃) δ : 8.13 (singlet, 12H), 7.53 (singlet, 6H), 7.43 (triplet, *J* = 7.0 Hz, 6H), 7.20 (singlet, 7H) 7.08 (singlet, 13H), 6.84 (singlet, 28H); ¹³C NMR (75 MHz, CDCl₃) δ : 163.51, 149.61, 136.35, 136.10, 128.80, 127.38, 126.86, 125.72, 125.01, 124.09, 123.81, 120.68, 111.88; ⁷Li NMR (194 MHz, CDCl₃) δ : 2.04 (1Li), 1.95 (0.84 Li), 1.61 (0.24 Li). The CHN combustion analysis for compound **2.4** was within ±0.5 % for the H and N values but the carbon value was low. We attribute the problem with the 71

carbon value to incomplete combustion for this complex. The same result was obtained for complex **2.1**, the cerium analogue of complex **2.4**.



Figure 2.4.26. ¹H NMR spectrum of Li₃(py)₆[La(Onaph)₆] (2.4) collected in CDCl₃.

Asterisks indicate exogenous solvent peaks. Reproduced by permission of The Royal Society of Chemistry.



Figure 2.4.27. ⁷Li NMR spectrum (left) and ¹³C NMR spectrum (right) of $Li_3(py)_6[La(Onaph)_6]$ (**2.4**) collected in CDCl₃. Asterisks indicate exogenous solvent peaks. Reproduced by permission of The Royal Society of Chemistry.

Synthesis of Li₄(DME)₄[La₂(Onaph)₁₀] (2.5). The synthesis of 2.5 was identical to that of 2.2, except that La[N(SiMe₃)₂]₃ (1.00 g, 0.16 mmol, 2 equiv) was dissolved in hexanes and layered over a DME solution of 2-naphthol (0.12 g, 0.81 mmol, 10 equiv) and LiN(SiMe₃)₂ (0.054 g, 0.32 mmol, 4 equiv). Yield 0.087 g, 0.041 mmol, 51%. ¹H NMR (400 MHz, CDCl₃) δ : 7.58 (singlet, 8H), 7.33 (singlet, 8H), 7.17 (multiplet, 16H), 7.11 (triplet, *J* = 7.0 Hz, 13H), 6.84 (singlet, 7H), 6.71 (singlet, 6H), 3.20 (singlet, 16H), 2.94 (singlet, 24H). ⁷Li NMR (194 MHz, CDCl₃) δ : 0.37 (1Li), 0.17 (0.7Li). Analysis calculated for C₁₁₆H₁₁₀O₁₈La₂Li₄: C, 66.42; H, 5.29. Found: C, 66.20; H, 5.70.



Asterisks indicate exogenous solvent species. Reproduced by permission of The Royal Society of Chemistry.



Figure 2.4.29. ⁷Li NMR (left) and ¹³C NMR (right) spectra of Li₄(DME)₄[La₂(Onaph)₁₀] (2.5) collected in CDCl₃. Asterisks indicate exogenous solvent species. Reproduced by permission of The Royal Society of Chemistry.

Synthesis of [HTMG]₃[La₂(Onaph)₉]·(DME)₂ (2.6). The synthesis of 2.6 was identical to that of 2.3, except that La[N(SiMe₃)₂]₃ (0.11 g, 0.16 mmol, 2 equiv) was reacted with 2-naphthol (0.11 g, 0.73 mmol, 9 equiv) and 1,1,3,3-tetramethylguanidine (33 μ L, 0.24 mmol, 3 equiv) in either THF or DME. Yield 0.11 g, 0.050 mmol, 62%. ¹H NMR (360 MHz, CDCl₃) δ : 7.60 (doublet, *J* = 7.6 Hz, 9H), 7.50 (doublet, *J* = 7.6 Hz, 9H), 7.29 (multiplet, 21H), 7.21 (triplet, *J* = 6.7 Hz, 15H), 7.10 (triplet, *J* = 7.2 Hz, 9H), 1.89 (singlet, 36H); ¹³C NMR (360 MHz, CDCl₃) δ : 163.63, 161.42, 136.27, 128.73, 127.47, 126.96, 125.86, 125.22, 124.70, 120.72, 112.04, 38.51. Analysis calculated for C₁₁₃H₁₂₅O₁₃N₉La₂: C, 64.78; H, 6.01; N, 6.02. Found: C, 64.60; H, 5.75; N, 5.78.



Figure 2.4.30. ¹H NMR spectrum of [HTMG]₃[La₂(Onaph)₉] (**2.6**) crystallized from DME collected in CDCl₃. Asterisks indicate exogenous solvent species present. Reproduced by permission of The Royal Society of Chemistry.



220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)

Figure 2.4.31. ¹³C NMR spectrum of [HTMG]₃[La₂(Onaph)₉] (**2.6**) crystallized from THF collected in CDCl₃. Asterisks indicate exogenous solvent species present. Reproduced by permission of The Royal Society of Chemistry.

Synthesis of Na₃(py)₆[Ce(Onaph)₆] (2.7). In a 20 mL scintillation vial, 2-naphthol (0.13 g, 0.88 mmol, 6 equiv) was dissolved in 2 mL of THF. Once dissolved, Na[N(SiMe₃)₂] (0.081 g, 0.44 mmol, 3 equiv) was added to the vial and the clear yellow solution was stirred for half an hour. After stirring, the THF was removed under reduced pressure to form a white solid. The white solid was then dissolved in 2 mL of pyridine. Ce[N(SiMe₃)₂]₃ (0.10 g, 0.15 mmol, 1 equiv) was added to the pyridine solution and the resulting yellow solution was stirred for 2 hours. After stirring, the pyridine was removed under reduced pressure to form a yellow solution was stirred for 2 hours. After stirring, the pyridine was removed under reduced pressure to form a yellow oil. The oil was then triturated with pentane to form a yellow solid. A few drops of pyridine were added to the yellow solid and 3 mL of toluene were added to completely dissolve the yellow solid. 6 mL of hexanes were

layered over the pyridine/toluene solution to form a white microcrystalline powder which was collected by filtration, washed with hexanes and dried under reduced pressure. Yield 0.17 g, 0.11 mmol, 77 %. ¹H NMR (400 MHz, CDCl₃) δ : 8.47 (broad singlet, 12 H), 7.59 (broad singlet, 8 H), 7.17 (broad singlet, 20 H); ¹³C NMR (91 MHz, CDCl₃) δ : 159.71, 136.11, 128.62, 126.01, 124.65, 120.27, 113.56, 99.45. Analysis calculated for C₉₀H₇₂O₆CeNa₃N₆: C, 70.07; H, 4.70; N, 5.45. Found: C, 69.91; H, 4.93; N, 5.39.



Figure 2.4.32. ¹H NMR of Na₃(py)₆[Ce(Onaph)₆] (**2.7**) in CDCl₃.



Figure 2.4.33. ¹³C NMR of Na₃(py)₆[Ce(Onaph)₆] (**2.7**) in CDCl₃.

Synthesis of Na₄(DME)₄[Ce₂(Onaph)₁₀] (2.8). In a 20 mL scintillation vial, 2-naphthol (0.085 g, 0.59 mmol, 5 equiv) was dissolved in 2 mL of DME. Once dissolved, Na[N(SiMe₃)₂] (0.043 g, 0.23 mmol, 2 equiv) was added to the vial and the clear yellow solution was stirred for half an hour. After stirring, the DME was removed under reduced pressure to form a white solid. The white solid was then re-dissolved in 2 mL of DME. Ce[N(SiMe₃)₂] (0.080 g, 0.12 mmol, 1 equiv) was added to the DME solution and the resulting yellow solution was stirred for 2 hours. After stirring, the DME was removed under reduced under reduced pressure to form a white solid. The white solid. A few drops of DME were added to the yellow solid and toluene was added to completely dissolve the yellow solid. 6 mL of hexanes were layered over the DME/toluene solution to crystallize the complex, producing yellow crystals which were collected by filtration, washed with hexanes and

dried under reduced pressure. Yield 0.088 g, 0.040 mmol, 69 %. ¹H NMR (360 MHz, CDCl₃) δ : 6.57 and 6.39 (broad overlapping singlets, 30 H), 5.65 and 5.43 (broad, 18 H), 4.72 (broad singlet, 18 H, DME), 3.87 (broad singlet, 24 H, DME), 2.45 (extremely broad, 6 H); ¹³C NMR (91 MHz, CDCl₃) δ : 133.13, 126.40, 126.27, 125.93, 125.91, 124.78, 123.90, 122.21, 120.49, 109.05, 73.11 (DME), 60.68 (DME). Analysis calculated for C₁₁₆H₁₁₀O₁₈Ce₂Na₄: C, 64.37; H, 5.12. Found: C, 64.03; H, 4.89.



Figure 2.4.34. ¹H NMR of Na₄(DME)₄[Ce₂(Onaph)₁₀] (2.8) in CDCl₃.



Synthesis of $K_3(py)_6[Ce_2(Onaph)_9(py)_2]$ (2.9). In a 20 mL scintillation vial, 2-naphthol (0.076 g, 0.53 mmol, 9 equiv) was dissolved in 3 mL of THF to form a clear, colorless solution. Once dissolved, K[N(SiMe_3)_2] (0.035 g, 0.18 mmol, 3 equiv) was added to the vial and stirred over a period of 0.5 hour. After stirring, the THF was removed under reduced pressure, and the resulting white solid was re-dissolved in 2 mL of pyridine to form a pale yellow solution. A bright yellow solution of Ce[N(SiMe_3)_2] (0.080 g, 0.12 mmol, 2 equiv) was prepared from in 8 mL hexanes and then layered over the yellow pyridine solution. After two days, yellow block crystals formed. The yellow crystals of the product were collected by filtration, washed with hexanes and dried under reduced pressure. Yield 0.11 g, 0.048 mmol, 83%. ¹H NMR (500 MHz, CDCl_3) δ : 14.27 (singlet, 3 H), 13.74 (singlet, 3 H), 10.16 (singlet, 7 H), 9.92 (singlet, 4 H), 9.68 (singlet, 6 H),

9.01 (singlet, 6 H), 8.22 (doublet, 6 H), 8.04 (singlet, 6 H), 7.74 (singlet, 12 H), 7.42 (singlet, 6 H), 7.22 (singlet, 6 H), 6.68 (singlet, 9 H), 5.98 (broad singlet, 19 H), 5.04 (broad singlet, 15 H); ¹³C NMR (126 MHz, CDCl₃) δ : 181.88, 152.39, 143.57, 138.68, 137.62, 134.49, 132.73, 130.61, 129.66, 129.46, 129.04, 127.89, 127.75, 126.46, 126.38, 125.89, 123.66, 121.96, 121.55, 116.85. Analysis calculated for C₂₆₅H₂₁₁O₁₈N₁₇K₆Ce₄: C, 67.48; H, 4.51; N, 5.05. Found: C, 67.36; H, 4.39; N, 5.08.



Figure 2.4.36. ¹H NMR of K₃(py)₆[Ce₂(Onaph)₉(py)₂] (2.9) in CDCl₃.



Figure 2.4.37. ¹³C NMR of K₃(py)₆[Ce₂(Onaph)₉(py)₂] (2.9) in CDCl₃.

Synthesis of {K₆(DME)]₄[Ce₂(Onaph)₁₂]}_n (2.10). In a 20 mL scintillation vial, 2naphthol (0.111 g, 0.773 mmol, 6 equiv) was dissolved in 2 mL of DME to form a clear, colorless solution. Once dissolved, K[N(SiMe₃)₂] (0.077 g, 0.39 mmol, 3 equiv) was added to the vial and stirred over a period of 0.5 hour. After stirring, the DME was removed under reduced pressure, and the white solid was re-dissolved in 2 mL of DME. A bright yellow solution of Ce[N(SiMe₃)₂]₃ (0.088 g, 0.13 mmol, 1 equiv) was prepared from in 10 mL hexanes and then layered over the clear, colorless DME solution. After two days, yellow needle-like crystals formed. The yellow crystals of the product were collected by filtration, washed with hexanes and dried under reduced pressure. Yield 0.12 g, 0.045 mmol, 69%. ¹H NMR (300 MHz, CDCl₃) δ : 7.16 (broad singlet, 12H), 6.82 and 6.69 (broad overlapping singlets, 36 H), 6.27 (broad singlet, 7 H), 5.05 (broad singlet, 12 H), 4.41 (broad singlet, 12 H), 3.49 (singlet, 18 H, DME), 3.30 (singlet, 24 H, DME); ¹³C 82

NMR spectrum of this complex gave too weak a signal because of its relative insolubility in CDCl₃. Analysis calculated for $C_{136}H_{124}O_{20}K_6Ce_2$: C, 62.99; H, 4.82. Found: C, 62.76; H, 4.80.



Figure 2.4.38. ¹H NMR of K₆(DME)₄[Ce₂(Onaph)₁₂] (2.10) in CDCl₃.

Diffusion Coefficient Experiments:

The NMR experiments for the determination of the self-diffusion coefficients and hydrodynamic radii were performed at 300 K on a Bruker Avance DRX 600 MHz spectrometer equipped with a 5 mm TXI probe with a z-axis gradient coil. The gradient system was calibrated with a doped water sample. In Bipolar-LED experiments, diffusion time (Δ) was 100 ms for all samples, and the duration (δ) of the sine shaped gradients was set to 1.4 ms. Data processing was accomplished with Bruker TOPSPIN 1.3 DOSY

software and Bruker TOPSPIN 1.3 T1/T2 software. The experiments were run in CDCl₃ with benzene used as an internal standard.^[21] The diffusion coefficient for benzene in CDCl₃ was determined to be $2.2 \times 10^{-9} \text{ m}^2 \text{s}^{-1}$ with a standard deviation of $0.1 \times 10^{-9} \text{ m}^2 \text{s}^{-1}$, which is in good agreement with literature values.^[21, 22] The hydrodynamic radii (*r*) of **3–6** were determined using the ratios of the diffusion constant of benzene (D_0 reference) with that of the samples (D_0 sample) and the hydrodynamic radius of benzene ($r_{reference}$), which was set to 2.54 Å (Eq 1).^[22]

$$r = \left(\frac{D_{0 \ reference}}{D_{0 \ sample}}\right) \times r_{reference} \tag{1}$$

This relationship is derived from the Stokes-Einstein equation (Eq 2),^[21, 23] by referencing against the internal standard to minimize errors due to variations in viscosity and temperature within the samples.^[21, 23, 24]

$$D_0 = \frac{kT}{6\pi\eta r} \qquad (2)$$

Following Stokes-Einstein relation, D_0 is the diffusion coefficient, k is Boltzmann's constant, T is the temperature, η is the viscosity of the solution, and r is the hydrodynamic radius.



Figure 2.4.39. Representative ¹H DOSY NMR spectrum of [HTMG]₃[Ce₂(Onaph)₉] (**2.3**) in CDCl₃ with benzene as an internal reference. Reproduced by permission of The Royal Society of Chemistry.



Figure 2.4.40. Representative ¹H DOSY NMR spectrum of $Li_3(py)_6[La(Onaph)_6]$ (**2.4**) in CDCl₃ with benzene as an internal reference. Reproduced by permission of The Royal Society of Chemistry.



Figure 2.4.41. Representative ¹H DOSY NMR spectrum of Li₄(DME)₄[La₂(Onaph)₁₀] (2.5) in CDCl₃ with benzene as an internal reference. Reproduced by permission of The Royal Society of Chemistry.



Figure 2.4.42. Representative ¹H DOSY NMR spectrum of [HTMG]₃[La₂(Onaph)₉] (**2.6**) in CDCl₃ with benzene as an internal reference. Reproduced by permission of The Royal Society of Chemistry.



Figure 2.4.43. Stacked plot of the ¹H NMR spectra in CDCl₃ of lanthanum naphtholate complexes with the following hydrogen bonded aminiums: ^{*t*}BuNH₃⁺ (top), diisopropylaminium (middle), and piperidinium (bottom). These reactions took place in toluene.



Figure 2.4.44. ¹H NMR spectrum in CDCl₃ of the piperidinium cerium naphtholate complex. The reaction took place in toluene.



Figure 2.4.45. ¹H NMR spectrum in CDCl₃ of an attempt to synthesize

diisopropylaminium cerium naphtholate complex. The reaction took place in toluene.



Figure 2.4.46. ¹H NMR spectrum in CDCl₃ of the (H-DBU)⁺ cerium naphtholate complex.



Figure 2.4.47. ¹H NMR spectrum in CDCl₃ of the attempt to form a (1,3-

diphenylguanidinium)⁺ cerium naphtholate complex.



Figure 2.4.48. ¹H NMR spectrum in C_6D_6 of the attempt to oxidize $Li_3(py)_6[Ce(Onaph)_6]$ (2.1) with I_2 .



Figure 2.4.49. ¹H NMR spectrum in CDCl₃ of the attempt to oxidize

 $(HTMG)_3[Ce_2(Onaph)_9]$ (2.3) with Ph₃CCl.



Figure 2.4.50. ¹H NMR spectrum (left) and ¹⁹F NMR spectrum (right) in pyridine- d_5 of the attempt to oxidize (HTMG)₃[Ce₂(Onaph)₉] (**2.3**) with FcBAr^F₄.



Figure 2.4.51. ¹H NMR spectrum in C_6D_6 of the attempt to synthesize a (HTMG)⁺ cerium mentholate complex.



Figure 2.4.52. ¹H NMR spectrum in pyridine- d_5 of the attempt to synthesize a Li⁺ cerium mentholate complex.



Figure 2.4.53. ¹H NMR spectrum in C_6D_6 of the attempt to synthesize a cerium

mentholate complex.



Figure 2.4.54. Stacked plot of ¹H NMR spectrum in C_6D_6 of the attempt to synthesize an $(HTMG)^+$ Ce(III) ^{*t*}OBu complex. The number of equivalents of TMG added increases from 0–3 from the bottom to the top.

2.5 BIBLIOGRAPHY

- G. B. Deacon, C. M. Forsyth, R. Harika, P. C. Junk, J. W. Ziller, W. J. Evans, J. Mat. Chem. 2004, 14, 3144-3149; T. J. Boyle, L. J. Tribby, S. D. Bunge, Eur. J. Inorg. Chem. 2006, 4553-4563.
- M. R. Bürgstein, H. Berberich, P. W. Roesky, *Chem. Eur. J.* 2001, *7*, 3078-3085;
 M. Shibasaki, M. Kanai, S. Matsunaga, N. Kumagai, *Acc. Chem. Res.* 2009, *42*, 1117-1127.

- [3] D. L. Clark, G. B. Deacon, T. Feng, R. V. Hollis, B. L. Scott, B. W. Skelton, J. G. Watkin, A. H. White, *Chem. Commun.* 1996, 1729-1730; T. J. Boyle, L. A. M. Ottley, *Chem. Rev.* 2008, *108*, 1896-1917.
- [4] W. J. Evans, *New J. Chem.* 1995, *19*, 525-533; L. S. Natrajan, J. J. Hall, A. J.
 Blake, C. Wilson, P. L. Arnold, *J. Solid State Chem.* 2003, *171*, 90-100.
- [5] A. J. Lewis, U. J. Williams, J. M. Kikkawa, P. J. Carroll, E. J. Schelter, *Inorg. Chem.* 2012, 51, 37-39.
- [6] A. R. Stefankiewicz, J. Harrowfield, A. Madalan, K. Rissanen, A. N. Sobolev, J. M. Lehn, *Dalton Trans.* 2011, 40, 12320-12332.
- [7] W. Runde, M. P. Neu, C. Van Pelt, B. L. Scott, *Inorg. Chem.* 2000, *39*, 1050-1051; G. S. Goff, M. R. Cisneros, C. Kluk, K. Williamson, B. Scott, S. Reilly, W. Runde, *Inorg. Chem.* 2010, *49*, 6558-6564.
- [8] R. E. Marsh, F. H. Herbstein, *Acta Cryst. B* **1988**, *44*, 77-88.
- [9] T. E. Janini, R. Rakosi, Iii, C. B. Durr, J. A. Bertke, S. D. Bunge, *Dalton Trans*.
 2009, 10601-10608.
- [10] J. R. Robinson, X. Fan, J. Yadav, P. J. Carroll, A. J. Wooten, M. A. Pericas, E. J.
 Schelter, P. J. Walsh, *J. Am. Chem. Soc.* 2014, *136*, 8034-8041.
- [11] P. B. Hitchcock, Q. Huang, M. F. Lappert, M. Zhou, *Dalton Trans.* 2005, 2988-2993; J. R. Robinson, Z. Gordon, C. H. Booth, P. J. Carroll, P. J. Walsh, E. J. Schelter, *J. Am. Chem. Soc.* 2013, *135*, 19016-19024; B. D. Mahoney, N. A. Piro, P. J. Carroll, E. J. Schelter, *Inorg. Chem.* 2013, *52*, 5970-5977; J. Robinson, P. J. Carroll, P. J. Walsh, E. J. Schelter, *Angew. Chem. Int. Ed.* 2012, *51*, 10159-10163.

- [12] A. Shokri, J. Schmidt, X.-B. Wang, S. R. Kass, J. Am. Chem. Soc. 2012, 134, 2094-2099.
- [13] E. M. Broderick, N. Guo, T. Wu, C. S. Vogel, C. Xu, J. Sutter, J. T. Miller, K. Meyer, T. Cantat, P. L. Diaconescu, *Chem. Commun.* 2011, 47, 9897-9899.
- [14] C. Wakai, M. Nakahara, J. Chem. Phys. 1997, 106, 7512-7518.
- [15] D. C. Bradley, J. S. Ghotra, F. A. Hart, J. Chem. Soc., Dalton Trans. 1973, 1021-1023.
- [16] Bruker, Bruker AXS Inc., Madison, Wisconsin, USA, 2009.
- [17] Bruker, Bruker AXS Inc., Madison, Wisconsin, USA, 2009.
- [18] G. M. Sheldrick, University Of Gottingen, Germany, 2008.
- [19] G. M. Sheldrick, University Of Gottingen, Germany, 2007.
- [20] G. M. Sheldrick, Acta Cryst. 2008, A64, 112-122.
- [21] D. Li, G. Kagan, R. Hopson, P. Williard, J. Am. Chem. Soc. 2009, 131, 5627-2634.
- [22] C. Wakai, M. Nakahara, J. Chem. Phys. 1997, 106, 7512-7518.
- [23] E. J. Cabrita, S. Berger, Magn. Reson. Chem. 2001, 39, S142-S148.
- [24] E. M. Lane, T. W. Chapp, R. P. Hughes, D. S. Glueck, B. C. Feland, G. M.
 Bernard, R. E. Wasylishen, A. L. Rheingold, *Inorg. Chem.* 2010, 49, 3950-3957;
 D. Zuccaccia, A. Macchioni, *Organometallics* 2005, 24, 3476-3486.

CHAPTER 3

Comparison of Lanthanide(III) Naphtholate Solution Structures

Abstract:

The series of alkali metal lanthanide naphtholate complexes, $M_x(sol)_y[Ln_z(Onaph)_a]$, M = Li, Na, and K; sol = DME or py; and Ln = Ce, Pr, or Eu described in Chapter 2 were compared to lanthanide naphtholate complexes with (HTMG)⁺ cations in the secondary coordination sphere through a series of competition experiments. The (HTMG)⁺ Ce(III) naphtholate complex was favored compared to the Na⁺ or K⁺ Ce(III) naphtholate structures. This stability indicated that the hydrogen bonding of (HTMG)⁺ cations led to the preferred cerium naphtholate solution structure. Therefore, hydrogen bonding motifs could be useful templates to organize lanthanide complexes into stable structures. When Li⁺ cations were compared to (HTMG)⁺ cations, the very Lewis acidic Li⁺ cations dominated the organization of the resulting products in solution.

Adapted from work to be submitted to Inorg. Chem.

3.1 Introduction

Piguet and Bünzli pioneered the induced fit principle for the self-assembly of lanthanide complexes.^[1-3] The induced fit principle is based on protein binding interactions, where the decreased entropy upon binding a substrate is compensated by increased enthalpic contributions in the secondary coordination sphere. In the context of lanthanide coordination chemistry, Piguet, Bünzli, Raymond, and others have designed multidentate ligands that encapsulate lanthanide metal ions.^[1, 3-7] Part of the driving force for this encapsulation is additional interactions in the secondary coordination sphere, such as π - π stacking or hydrogen bonding.^[4]

Secondary coordination sphere interactions either through use of additives, hydrogen bonding solvents, or through ligand design have also been leveraged in lanthanide catalysis.^[8-10] For example, Hatanaka and Morokuma proposed that the addition of water in the Mukaiayama-Aldol reaction catalyzed by $Ln(OTf)_3$, (OTf =trifluoromethanesulfonate) imparts selectivity through directed hydrogen bonding interactions with water as well as increases yield by stabilizing the resulting products after trimethylsilyl dissociation (Scheme 3.1.1).^[10]Our group has used hydrogen bonding interactions to stabilize lanthanide BINOLate (BINOLate = 1,1'-bi-2-naphtholate) complexes in the presence of air and water.^[9]


Scheme 3.1.1. Importance of hydrogen bonding interactions of water in the Mukaiayama-Aldol reaction catalyzed by Ln(OTf)₃. Reprinted with permission from Miho Hatanaka, Keiji Morokuma, *J. Am. Chem. Soc.* 2013, *135*, 13972-13979 (Ref. 11). Copyright 2013 American Chemical Society.

Despite the importance of both the primary and secondary coordination sphere interactions in these systems, solution structures of lanthanide cations can be difficult to predict because of their kinetic labilities.^[11] Controlling the lanthanide primary coordination sphere through pre-organization in the secondary coordination sphere could allow for rational design of lanthanide complexes with unique applications such as luminescence,^[3, 7, 12] catalysis,^[8-10] and lanthanide separations.^[6, 13]

Using a Ce(III) naphtholate system, we set out to systematically change the interactions in a secondary coordination sphere and observe their effect on the primary coordination sphere of a sterically unencumbered ligand. The naphtholate ligand is supported by interactions with the alkali metal cations, Li^+ , Na^+ , K^+ , as well as hydrogen bonding interactions with (HTMG)⁺ (tetramethylguanidinium cation) in the secondary coordination sphere. Even though hydrogen bond strengths, which typically range from ~3–15 kcal/mol,^[14] are weaker than covalent or ionic bonds, we were interested in

comparing the series of alkali metal cerium complexes with the hydrogen bonded cerium complex. We expected these comparisons allowed the determination of a preferred preorganized solution structure, and would lead to a better understanding of the nature of the kinetic lability of the ligands bound to the lanthanide metal center.

3.2 Results and Discussion

In Chapter 2, Li₄(DME)₄[Ce₂(Onaph)₁₀] (**3.2**), Na₄(DME)₄[Ce₂(Onaph)₁₀] (**3.3**), K₆(DME)₄[Ce₂(Onaph)₁₂] (**3.4**), Li₃(py)₆[Ce(Onaph)₆] (**3.5**), Na₃(py)₆[Ce(Onaph)₆] (**3.6**), K₃(py)₆[Ce₂(Onaph)₉(py)₂] (**3.7**), and (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) were synthesized and characterized. In Chapter 3, the hydrogen bonding interactions of the (HTMG)⁺ cation with cerium naphtholate complexes were compared to the alkali metal cations by a series of competition experiments with MOTf (M = Li⁺, Na⁺, K⁺) or (HTMG)OTf salts, as monitored by ¹H NMR spectroscopy. The Ce₂Onaph₉ structure organized by (HTMG)⁺ was found to be the preferred structure by these competition experiments. Further investigation into the solution structures of the Ln₂Onaph₉ core (Ln = Eu, Pr) by ¹H-¹H EXSY NMR spectroscopy showed that intermolecular exchange occurred between the Ln₂Onaph₉ units. Despite the evident lability of the Ln–Onaph bonds, the net Ce₂Onaph₉ structure was maintained in solution even in the presence of Na⁺ and K⁺ cations, indicating that there was an energy barrier to change the Ce₂Onaph₉ core structure.

3.2.1 Competition Experiments between Alkali Metal Cations and (HTMG)⁺

As described in previous work (see Chapter 2),^[15] the (HTMG)⁺ cation in the secondary coordination sphere provided a more electron-rich and solvent stable environment about the Ce(III) center compared to the alkali metal cation analogues.

Despite the stability provided by the $(HTMG)^+$, we expected that the replacement of the ammonium cation with an alkali metal cation would be enthalpically favorable. Work in our group with 1,1'-bi-2-naphtholate rare earth(III) complexes,

 $(HTMG)_3[(BINOLate)_3RE]$ (RE = La, Eu, Yb, Y, BINOLate = 1,1'-bi-2-naphtholate), had shown that the ammonium cations $(HTMG)^+$ in the secondary coordination sphere were easily replaced with alkali metal cations using alkali metal salts (Scheme 3.2.1).^[9] Initial tests reacting $(HTMG)_3[Ce_2(Onaph)_9]$ (**3.1**) with MOTf or MI (M = Li, Na, and K, OTf = trifluoromethanesulfonate) salts in DME, however, showed that the framework was more robust than initially expected. Reactivity only took place with the Li⁺, forming complex mixtures by ¹H and ⁷Li NMR spectra. We had previously seen that Li⁺ cations promoted complex solution structures, likely due to the high Lewis acidity and small size of the Li⁺ cation.^[16]



Scheme 3.2.1. Cation exchange reactions of 3 or more equivalents of MX with (HTMG)₃[(BINOLate)₃Ce]. Adapted with permission from Jerome R. Robinson, Xinyuan Fan, Jagjit Yadav, Patrick J. Carroll, Alfred J. Wooten, Miquel A. Pericas, Eric

J. Schelter, and Patrick J. Walsh, *J. Am. Chem. Soc.* **2014**, *136*, 8034-8041 (Ref. 10). Copyright 2014 American Chemical Society.

To replace the (HTMG)⁺ in complex **3.1** with alkali metal cations, 3 equiv MOTf and 1 or 3 equiv MOnaph were added to obtain the correct stoichiometry of naphtholate in order to fully form the expected products $Li_4(DME)_4[Ce_2(Onaph)_{10}]$ (**3.2**), $Na_4(DME)_4[Ce_2(Onaph)_{10}]$ (**3.3**), { $K_6(DME)_4[Ce_2(Onaph)_{12}]$ }_n (**3.4**) $Li_3(py)_6[Ce(Onaph)_6]$ (**3.5**), or $Na_3(py)_6[Ce(Onaph)_6]$ (**3.6**) (Scheme 3.2.2). The reactions then were monitored by ¹H NMR spectroscopy both in CDCl₃ and either proteo DME (complexes **3.2–3.4**), or pyridine- d_5 (complexes **3.5–3.6**) to ensure that no side reactions occurred in CDCl₃. The reactions with LiOTf and LiOnaph were also monitored by ⁷Li NMR spectroscopy. The ¹H NMR spectra of the resulting mixtures from the addition of MOTf and MOnaph, however, did not correspond either to the previously synthesized alkali metal complexes or the starting material (see section 3.4, Figures 3.4.9–3.4.36). Since the addition of NaOTf and KOTf alone resulted in no apparent reaction with complex **3.1**, the addition of MOnaph facilitated the formation of the complicated spectra (section 3.4, Figures 3.4.9–3.4.36).



Scheme 3.2.2. Attempted cation exchange reactions of MOTf and MOnaph with complex3.1.

From the reaction of complex **3.1** with 3 equiv NaOTf and 1 equiv NaOnaph in DME, we were able to obtain crystals of Na₂(DME)₂(HTMG)[Ce₂(Onaph)₉(TMG)₂] (**3.12**) (Figure 3.2.1, Scheme 3.2.2). Instead of doing simple cation metathesis, an acid-base reaction occurred between the acidic (HTMG)⁺ (pK_a = 13.6 in DMSO) and the basic NaOnaph (pK_a 2-naphthol = 17.1 in DMSO) to form TMG and 2-naphthol.^[17] Similar to complexes **3.1** and **3.7**, complex **3.12** formed a dimeric Ce(III) core where each Ce(III)

cation bound to 3 terminal and 3 bridging naphtholates. Additionally, the Ce(III) cations were coordinated to the neutral TMG that formed from the acid-base reaction. In the secondary coordination sphere, two Na⁺ and one (HTMG)⁺ bridged the 6 terminal naphtholate ligands.



Figure 3.2.1. Left, Crystal structure of [Na₂(DME)₂][HTMG][Ce₂(Onaph)₉(TMG)₂] (**3.12**). Hydrogen atoms and the DME molecules coordinated to Na⁺ cations were omitted for clarity, and the carbons on the naphthyl groups were rendered in wire frame for clarity. To simplify the rendering of complex **3.12**, the skeletal formula of the complex was included at right, where naphthyl groups and the DME bound to Na⁺ were removed for clarity.



Scheme 3.2.3. Attempted cation exchange reactions of MOTf and HOnaph with complex3.1.

To avoid the initial acid-base chemistry while achieving a balanced chemical equation, MOTf and protonated naphtholate (HOnaph), instead of MOnaph, were added to complex **3.1** (Scheme 3.2.3). Given that a resulting side product would be triflic acid, these reactions only were used to test for the occurrence of any reaction. Similar to what was observed in the non-stoichiometric reactions with the addition of MI and MOTf salts, the Li^+ and pyridine-solvated K⁺ reacted with the (HTMG)⁺ framework (see section 3.4, Figures 3.4.37–3.4.52).





Scheme 3.2.4. Reactions of (HTMG)OTf with complexes (a) 3.3 Na₄(DME)₄[Ce₂(Onaph)₁₀], (b) 3.4 K₆(DME)₄[Ce₂(Onaph)₁₂], (c) 3.6 Na₃(py)₆[Ce(Onaph)₆], (d) 3.7 K₃(py)₆[Ce₂(Onaph)₉(py)₂], and (e) 3.7, K₃(py)₆[Ce₂(Onaph)₉(py)₂].

To glean more information about the reactants and products in the cation exchange reactions, the reverse reactions where $(HTMG)^+$ was added to complexes **3.2–3.7** were performed (Scheme 3.2.4). Despite observing complex NMR spectra when Li^+ was in solution previously, complexes 3.2 and 3.5 still were reacted with the salt (HTMG)OTf to better characterize the various species present in solution by ¹H and ⁷Li NMR spectroscopy (see section 3.4, Figures 3.4.53–3.4.68). We focused on the reaction of 6 equiv (HTMG)OTf with 2 equiv complex 3.5 characterized in pyridine- d_5 . At room temperature, one broad ⁷Li NMR resonance was observed for the mixture centered at 6.56 ppm, compared to 4.00 ppm for complex **3.5** (see section 3.4, Figures 3.4.74– 3.4.75).^[16] After lowering the temperature of the mixture solution to 250 K, two sharp signals were observed in the ⁷Li NMR spectrum: 18.36 ppm and 4.48 ppm, the latter resonance having approximately the same ⁷Li NMR resonance as **3.5** in pyridine, see section 3.4, Figures 3.4.74–3.4.75. Previously, we had measured ⁷Li NMR spectra of Li-Ce(III) naphtholate complexes in a variety of solvents and found that ⁷Li NMR signals at 17–18 ppm corresponded to dimeric species in solution.^[16] Thus the other major species in solution besides **3.5** was an unknown dimeric Li Ce(III) naphtholate complex.

(HTMG)OTf was also added to each of the Na⁺ or K⁺ Ce(III) naphtholate complexes (Scheme 3.2.4). Consistent with the previous results, addition of (HTMG)OTf to complexes **3.3**, **3.4**, and **3.6** formed complex **3.1**, where the (HTMG)₃[Ce₂(Onaph)₉] complex was the only Ce(III) product observed by NMR spectroscopy (see section 3.4, Figures 3.4.53–3.4.68). In the reaction with **3.4** and **3.6**, the 3 equiv (HTMG)Onaph and complex **3.1** were in fast exchange, showcasing the lability of the Ce–Onaph bonds. When (HTMG)OTf was added to **3.7** in pyridine and the ¹H NMR spectrum was measured in CDCl₃, the formation of complex **3.1** also was observed. However, the same reaction mix measured in pyridine- d_5 resulted in a complicated NMR spectrum KOTf was insoluble in CDCl₃, thus the precipitation of KOTf helped drive the reaction to form **3.1**. Despite the good solubility and greater Lewis acidity of NaOTf in pyridine, the equilibrium heavily favored formation of complex **3.1** when complex **3.6** was reacted with (HTMG)OTf in pyridine. Even with the poorer solubility and Lewis acidity of the K⁺ cations in KOTf, the K⁺ cations were able to compete with (HTMG)⁺ cationic interactions in pyridine. Thus solubility and Lewis acidity were not the only factors in determining which product would form, indicating that the conserved Ce₂Onaph₉ motif found in both **3.1** and **3.7** played a role in the formation of a mixed species containing both (HTMG)⁺ and K⁺ cations, (HTMG)_{3-x} K_x[Ce₂(Onaph)₉]. Rearrangement from the Ce₂Onaph₉ motif likely had a significant energy barrier, making the Ce₂Onaph₉ complex the preferred solution structure.

Complex ¹H NMR spectra of the reaction of **3.7** with (HTMG)OTf were also observed at low temperatures. The spectrum at 250 K was similar both to complexes **3.1** and **3.7** (see section 3.4, Figures 3.4.69–3.4.73). The similarity of the ¹H NMR spectrum to both complex **3.1** and complex **3.7** indicated that the resulting spectrum likely was a mixture of K⁺ and (HTMG)⁺ cations in the secondary coordination sphere. The formation of (HTMG)_{3-x} K_x[Ce₂(Onaph)₉] in solution was supported by electrochemistry of the mixture of (HTMG)OTf with complex **3.7** in pyridine, where only one set of waves was observed, which could suggest only one type of Ce(III) center was in solution on the electrochemical timescale (see section 3.4, Figures 3.4.76–3.4.83).

3.2.2 Solution Structure of Lanthanide Naphtholate Complexes

It was evident that naphtholate exchange and cation exchange were occurring in solution based on the fast exchange of (HTMG)Onaph with 3.1 on the NMR timescale as well as the formation of the $(HTMG)_{3-x}K_x[Ce_2(Onaph)_9]$ mixture. To better understand the dynamic solution behavior and exchange, ¹H-¹H NMR Exchange Spectroscopy (EXSY) of the Ln(III) naphtholates was performed in CDCl₃.^[18-20] Activation parameters for the exchange processes were also obtained using ¹H-¹H EXSY at multiple temperatures.^[19, 21] Complexes **3.2–3.6** had very broad, overlapping ¹H NMR spectra which precluded their analyses using ¹H-¹H EXSY. To improve ¹H NMR spectral resolution of **3.7**, $K_3(py)_6[Eu_2(Onaph)_9(py)_2]$ (**3.8**) and $K_3(py)_6[Pr_2(Onaph)_9(py)_2]$ (**3.9**), isostructural analogues of complex 3.7, were synthesized with identical procedures to complex **3.7** (see section 3.4). The paramagnetism of the Eu and Pr cations gave rise to larger ¹H NMR spectral widths for those complexes, facilitating the spectral assignment and reducing the overlap of the naphtholate resonances in the ¹H NMR spectrum. Eu and Pr analogues of complex **3.1**, (HTMG)₃[Eu₂(Onaph)₉] (**3.10**) and (HTMG)₃[Pr₂(Onaph)₉] (3.11) were also synthesized, however, all of the 2-naphtholate protons overlapped in the room temperature ¹H NMR spectrum. The ¹H NMR spectrum was only resolved for the Eu complex at 220 K (Figures 3.4.97–3.4.98, section 3.4). In addition to measuring the self-exchange of pure compound, we also attempted to measure the exchange of the following mixtures: complex 3.8 mixed with 3.9, 3.10 mixed with 3.11, and 3.8 mixed

with **3.10** (Figures 3.4.99–3.4.111 in section 3.4). In all cases, new species formed in solution that we were unable to identify by spectroscopy (Figures 3.4.99–3.4.111 in section 3.4).



Scheme 3.2.5. Depiction of proposed naphtholate self-exchange process between the terminal and bridging naphtholates in complexes 3.7–3.9, where Ln = Ce, Eu, and Pr. The remaining naphtholates and pyridine ligands bound to K⁺ were omitted for clarity. The self-exchange was evidently mediated by naphtholate association.

Complex	Mass	$\mathbf{k} (\mathbf{s}^{-1})^{a, b}$	ΔH^{\ddagger}	$\Delta S^{\ddagger} (J/K)$	ΔG^{\ddagger}	\mathbf{R}^2
	complex		(kcal/mol	mol) ^a	(kcal/mol	
	(g) ^c) ^a) ^a	
3.8	0.061	31	11.8	-51.7	15.5	0.971
3.8	0.035	7				
3.9	0.054	8	12.2	-55.9	16.2	0.956
3.9	0.033	2				

Table 3.2.1. 2D ¹H-¹H EXSY NMR spectroscopy self-exchange rate and activation parameters for complex **3.8–3.9**. The terminal and bridging naphtholates exchanged.

^{*a*} Measured at 300 K. ^{*b*} Determined using EXSYCalc.^{[22] *c*} Volume of solution was approximately 500 μL.

The terminal and bridging naphtholate protons in complexes **3.8** and **3.9** were assigned by ¹H-¹H COSY and ¹H-¹³C HSQC NMR spectroscopies (see Figures 3.4.84–3.4.94 in section 3.4).^[20] Subsequently, the rates of self-exchange of the bridging and terminal naphtholate protons were measured by ¹H-¹H EXSY NMR spectroscopy for complex **3.8** (see Figure 3.4.95 in section 3.4 for a representative ¹H-¹H EXSY spectrum and Scheme 3.2.5 for the exchange measured). At 300 K, the self-exchange of the bridging to terminal naphtholate protons appeared to be concentration dependent (Table 3.2.1), indicating that the naphtholates underwent intermolecular exchange. The ΔS^{\ddagger} was relatively large and negative as well (-52 J K⁻¹ mol⁻¹, see Table 3.2.1 and Figures 3.4.95 and 3.4.112 in section 3.4), which also suggested that the self-exchange proceeded through an intermolecular process by the association of naphtholates across at least two

sets dimers (see Scheme 3.2.5). As expected, the ¹H-¹H EXSY NMR spectra for complex **3.9** had similar activation enthalpy and activation entropy as complex **3.8** (Table 3.2.1, Figures 3.4.96 and 3.4.113 in section 3.4).

Since complexes **3.8–3.11** were model complexes for **3.1** and **3.7**, it was likely that complex **3.1** also underwent intermolecular exchange by naphtholate association of two separate dimers (see Figures 3.4.95–3.4.98 in section 3.4). Given that the geometries for both the **3.1** and **3.7** complexes were very similar, it would not be surprising if naphtholate exchange also occurred between the two structures.

3.3 Conclusions

We synthesized a series of Ce(III) naphtholate complexes with Li⁺, Na⁺, K⁺ or (HTMG)⁺ in the secondary coordination sphere. To compare the interactions of the hydrogen bonded (HTMG)⁺ Ce(III) naphtholate complex to those of the alkali metal Ce(III) naphtholate complexes, a series of competition experiments were performed. When both Li⁺ and (HTMG)⁺ were present in solution along with Ce(III) naphtholate, a complex mixture resulted in **3.5** and an unidentified Li⁺ Ce(III) naphtholate dimer. When $M^+ = Na^+$ or K^+ and (HTMG)⁺ were present in solution with Ce(III) naphtholate, the formation of complex **3.1** was favored in solution, except with complex **3.7** in pyridine. The preference for complex **3.1** formation with (HTMG)⁺ cations in the secondary coordination sphere over forming the Ce(III) naphtholate complex with alkali metal cations Na⁺ or K⁺ was likely driven by a combination of alkali metal solvation, the enthalpy of salt elimination, and the preference for the [Ce₂(Onaph)₉]³⁻ complex structure

in solution. Because complex **3.1** and complex **3.7** had the same Ce(III) naphtholate structure, the K^+ and (HTMG)⁺ cations could easily exchange, although the mechanism of the cation exchange could not be observed by ¹H NMR spectroscopy. The naphtholate ligands in complexes **3.1** and **3.7**, based on the self-exchange data, likely exchanged by the association of naphtholate from at least two Ce(III) naphtholate dimers. Regardless of the solvent, the (HTMG)⁺ cation organized the structure into the preferred geometry. Use of hydrogen bonds as a template could be a general method to obtain stable Ln(III) complex solution structures.

3.4 Experimental Section

General Methods. Unless otherwise indicated, all reactions and manipulations were performed under an inert atmosphere (N₂) using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. Nexus II drybox equipped with a molecular sieves 13X / Q5 Cu-0226S catalyst purifier system. Glassware was oven-dried overnight at 150 °C prior to use. ¹H, ¹³C, and ⁷Li NMR spectra were obtained on a Bruker DMX-300, Bruker DMX-360, Bruker UNI-400, or on a Bruker BioDRX-500 Fourier transform NMR spectrometer at 300, 360, 400, and 500 MHz respectively. Chemical shifts were recorded in units of parts per million downfield from residual proteo solvent peaks (¹H), or characteristic solvent peaks (¹³C). The ⁷Li spectra were referenced to external solution standards of LiCl in H₂O. Variable temperature ¹H NMR spectroscopy was performed on a Bruker UNI-400 Fourier transform NMR spectrometer at 400 MHz. The temperature probe was calibrated using a methanol standard. ¹H-¹H EXSY ¹H-¹H COSY and ¹H-¹³C HSQC NMR spectroscopy was performed on a Bruker BioDRX-500 Fourier transform

NMR spectrometer. Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility using a Perkin-Elmer Series II 2400 CHNS analyzer and also at Complete Analysis Laboratories Inc. in Parsippany, NJ using a Carlo Erba EA 1108 analyzer.

2D ¹**H**-¹**H EXSY NMR Spectra.** Variable temperature ¹H-¹H EXSY NMR spectroscopy was performed on a Bruker UNI-400 Fourier transform NMR spectrometer at 400 MHz with a typical NOESY sequence using CDCl₃ as the NMR solvent. 2048 and 512 data points were used in the t_2 and t_1 domain respectively, and 8 scans were collected for each increment. t_{mix} ranging from 5–150 ms were used for EXSY experiments performed at 300 K to determine the optimal value (15 ms) for complexes **3.8** and **3.9**. Similarly, a range of t_{mix} times were used when the temperature was lowered. At 250 K, t_{mix} ranged from 15 ms to 60 ms, where t_{mix} was optimized to 25 ms. Finally, 260, 270, 280, and 290 K temperatures were collected with $t_{mix} = 0$, 15, and 25 ms. $t_{mix} = 25$ ms was optimal below 300 K. In addition, a reference was recorded at $t_{mix} = 0$ ms at each temperature. Pseudo-first order rate constants (k, s⁻¹) were calculated using EXSYCale 1.0 (Mestrelab Research)^[22] from volume intensities obtained from the 2D spectra. Activation parameters were determined using Eyring plots generated from rate data obtained at several temperatures.

Materials. Tetrahydrofuran, dimethoxyethane, toluene, fluorobenzene, hexane, and pentane were purchased from Fisher Scientific. The solvents were sparged for 20 min with dry N_2 and dried using a commercial two-column solvent purification system comprising columns packed with Q5 reactant and neutral alumina respectively (for

hexane and pentane), or two columns of neutral alumina (for THF, DME, and toluene). Pyridine was freeze-pump-thawed for 4 cycles and stored over 4 Å molecular sieves for three days before use. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. CDCl₃ was freeze-pump-thawed for 4 cycles and stored over 4 Å molecular sieves for three days before use or was stirred over calcium hydride for 3 days, distilled, and then freeze-pump-thawed for 4 cycles. Pyridine-d₅ was stored over 4 Å molecular sieves for three days before use. $Ln[N(SiMe_3)_2]_3$ (Ln = La, Ce, Pr, Eu) was prepared following published procedures.^[23] Li[N(SiMe₃)₂] (Acros) was recrystallized from hot pentane prior to use. Na[N(SiMe₃)₂] (Acros) and K[N(SiMe₃)₂] (Sigma Aldrich) were used as received. 2-naphthol (Acros, Sigma Aldrich) was sublimed under reduced pressure prior to use. 1,1,3,3-tetramethylguanidine (Acros, Sigma Aldrich) was freezepump-thawed for 4 cycles and stored over 4 Å molecular sieves for three days before use. LiOTf (Acros), NaOTf (Acros), and KOTf (Acros) were dried under vacuum at 150 °C for 12 hours. (HTMG)OTf was prepared by slowly adding 1 equiv neat triflic acid (HOTf) to 1.01 equiv neat tetramethylguanidine (TMG). A precipitate immediately formed which was then dried under vacuum overnight. Detailed synthetic details for complexes **3.1–3.7** can be found in Chapter 2.^[16]

X-Ray Crystallography. X-ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at a temperature of 143(1) or 100(1) K. In all cases, rotation frames were integrated using SAINT,^[24] producing a listing of unaveraged F² and σ (F²) values which were then passed to the SHELXTL^[25] program package for further processing and structure solution on a

Dell Pentium 4 computer. The intensity data were corrected for Lorentz and polarization effects and for absorption using TWINABS^[26] or SADABS.^[27] The structures were solved by direct methods (SHELXS-97).^[28] Refinement was by full-matrix least squares based on F² using SHELXL-97.^[28] All reflections were used during refinements. The weighting scheme used was w=1/[$\sigma^2(F_o^2)$ + (0.0907P)² + 0.3133P] where P = (F_o² + 2F_c²)/3. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model.

Electrochemistry. Voltammetry experiments (CV and DPV) were performed using a CH Instruments 620D Electrochemical Analyzer/Workstation and the data were processed using CHI software v 9.24. All experiments were performed in an N₂ atmosphere drybox using electrochemical cells that consisted of a 4 mL vial, glassy carbon (3 mm diameter) working electrode, a platinum wire counter electrode, and a silver wire plated with AgCl as a quasi-reference electrode. The working electrode surfaces were polished prior to each set of experiments, and were periodically replaced to prevent the buildup of oxidized product on the electrode surfaces. Potentials were reported versus ferrocene (Fc). Solutions employed during CV studies were ~3 mM in analyte and 150 mM in $[^nBu_4N][B(3,5-(CF_3)_2-C_6H_3)_4]$ ($[^nBu_4N][BAr^F_4]$) in pyridine. All data were collected in a positive-feedback IR compensation mode. Scan rate dependences of 25–1000 mV/s were performed to determine electrochemical reversibility.

Competition Experiments. 10.0 mg or more of the initial Ce(III) naphtholate starting material (complexes **3.1–3.7**) was weighed in a 20 mL scintillation vial. Stock solutions of LiOTf, NaOTf, KOTf, (HTMG)OTf, 2-naphthol, LiN(SiMe₃)₂, NaN(SiMe₃)₂, and

KN(SiMe₃)₂ were prepared in either DME or pyridine. Stoichiometric quantities were added of the triflate salt, naphtholate salt, or 2-naphthol by microliter syringe to the initial Ce(III) naphtholate starting material. The reactions were stirred in either DME (for DME solvated alkali metal cations) or pyridine (for pyridine solvated alkali metal cations) for one hour. Subsequently, the reaction was dried under vacuum for one hour. The results of the experiments were monitored both by CDCl₃ in all cases, and either in proteo DME (for DME solvated alkali metal cations) or pyridine- d_5 (for pyridine solvated alkali metal cations). Each competition reaction was performed at least twice to ensure that the results of the reactions were consistent and reproducible.

Na₂(DME)₂(HTMG)[Ce₂(Onaph)₉(TMG)₂] (**3.12**) was crystallized by reacting (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) with 3 equiv NaOTf and 1 equiv NaOnaph in DME for 1 hr followed by layering the reaction mixture with hexanes.

Synthetic Details and characterization of complexes 3.8–3.11.

Synthesis of $K_3(py)_6[Eu_2(Onaph)_9(py)_2]$ (3.8). In a 20 mL scintillation vial, 2-naphthol (0.23 g, 1.62 mmol, 9 equiv.) was dissolved in 3 mL of THF to form a clear, colorless solution. Once dissolved, $K[N(SiMe_3)_2]$ (0.11 g, 0.54 mmol, 3 equiv.) was added to the vial and stirred over a period of 0.5 hour. After stirring, the THF was removed under reduced pressure, and the resulting white solid was re-dissolved in 2 mL of pyridine to form a pale yellow solution. A bright orange solution of Eu[N(SiMe_3)_2]_3 (0.25 g, 0.36 mmol, 2 equiv.) was prepared in 5 mL hexanes and then layered over the yellow pyridine solution. After two days, yellow block crystals formed. The yellow crystals of the product were collected by filtration, washed with hexanes and dried under reduced pressure.

Complex 5 had the same unit cell as complex 4b, verifying the solid state structure. Yield 0.319 g, 0.134 mmol, 74%. ¹H NMR (300 MHz, CDCl₃) δ: 10.85 (py), 8.22 (py), 7.83 (py), 7.66 (multiplet, 9 H), 7.28 (singlet, 9 H), 6.90 (multiplet, 18 H), 6.10 (singlet, 9 H), 5.83 (singlet, 9 H), 5.47 (singlet, 3 H), 4.36 (broad singlet, 9 H), 3.86 (singlet, 3 H), -5.63 (singlet, 3 H), -6.84 (singlet, 3 H); ¹³C NMR (126 MHz, CDCl₃) δ: 192.93, 159.32, 138.74, 132.14, 129.39, 127.85, 127.76, 127.60, 126.64, 125.48, 125.28, 124.73, 124.33, 124.14, 122.87, 121.53, 121.15, 120.88, 114.35, 104.68, 99.17, 94.48. Analysis calculated for C₂₆₅H₂₁₁O₁₈N₁₇K₆Eu₄: C, 66.81; H, 4.46; N, 5.00. Found: C, 66.77; H, 4.72; N, 4.96.



Figure 3.4.1. ¹H NMR of K₃(py)₆[Eu₂(Onaph)₉(py)₂] (**3.8**) in CDCl₃.



Figure 3.4.2. ¹³C NMR of K₃(py)₆[Eu₂(Onaph)₉(py)₂] (3.8) in CDCl₃.

Synthesis of $K_3(py)_6[Pr_2(Onaph)_9(py)_2]$ (3.9). In a 20 mL scintillation vial, 2-naphthol (0.24 g, 1.65 mmol, 9 equiv.) was dissolved in 3 mL of THF to form a clear, colorless solution. Once dissolved, $K[N(SiMe_3)_2]$ (0.11 g, 0.55 mmol, 3 equiv.) was added to the vial and stirred over a period of 0.5 hour. After stirring, the THF was removed under reduced pressure, and the resulting white solid was re-dissolved in 2 mL of pyridine to form a pale yellow solution. A green solution of $Pr[N(SiMe_3)_2]_3$ (0.25 g, 0.37 mmol, 2 equiv.) was prepared in 4 mL hexanes and then layered over the yellow pyridine solution. After two days, green block crystals formed. The green crystals of the product were collected by filtration, washed with hexanes and dried under reduced pressure. Complex 6 had the same unit cell as complex 4b, verifying the solid state structure. Yield 0.34 g, 0.14 mmol, 78%. ¹H NMR (400 MHz, CDCl₃) δ : 26.14 and 25.83 (overlapping singlets, 6 H), 13.42 (singlet, 6H), 13.16 (singlet, 3 H), 11.01 (singlet, 9 H), 10.84 (multiplet, 3 H),

9.46 (multiplet, 3 H), 9.37 (singlet, 3 H), 8.54 (singlet, 6 H), 7.78 (singlet, 6 H), 7.37 (singlet, 15 H), 7.36 (singlet, 6 H), 5.63 (py), 4.71 (py), 1.18 (py); ¹³C NMR (126 MHz, CDCl₃) δ: 206.68, 148.71, 144.10, 139.18, 137.72, 133.71, 132.14, 132.08, 132.05, 131.89, 130.99, 130.19, 129.96, 128.77, 127.78, 127.35, 126.15, 124.74, 121.87, 120.79. Analysis calculated for C₂₆₅H₂₁₁O₁₈N₁₇K₆Pr₄: C, 67.44; H, 4.51; N, 5.04. Found: C, 67.39; H, 4.33; N, 4.89.



Figure 3.4.3. ¹H NMR of K₃(py)₆[Pr₂(Onaph)₉(py)₂] (**3.9**) in CDCl₃.



Figure 3.4.4. ¹³C NMR of K₃(py)₆[Pr₂(Onaph)₉(py)₂] (3.9) in CDCl₃.

Synthesis of (HTMG)₃[**Eu**₂(**Onaph**)₉] (**3.10**). In a 20 mL scintillation vial, 2-naphthol (0.093 g, 0.65 mmol, 9 equiv.) was dissolved in 3 mL of THF to form a clear, colorless solution. Once dissolved, tetramethylguanidine (TMG) (0.025 g, 27 μ L, 0.22 mmol, 3 equiv.) was added to the vial and stirred over a period of 1 hour. A yellow solution of Eu[N(SiMe₃)₂]₃ (0.10 g, 0.14 mmol, 2 equiv.) was prepared in 10 mL hexanes and then layered over the colorless THF solution. After two days, green block crystals formed. The green crystals of the product were collected by filtration, washed with hexanes and dried under reduced pressure. Complex 7 had the same unit cell as complex 2, verifying the solid state structure. Yield 0.13 g, 0.067 mmol, 93%. ¹H NMR (300 MHz, CDCl₃) δ : 8.35, 7.62, 6.74, 5.78, 3.77 (THF), 3.14, 1.87 (THF), 0.75 (TMG); ¹³C NMR (360 MHz, CDCl₃) δ : 159.71, 136.11, 128.62, 126.01, 124.65, 120.27, 113.56, 99.45, 37.87. Analysis

calculated for C₁₀₅H₁₀₅O₉N₉Eu₂: C, 64.98; H, 5.45; N, 6.49. Found: C, 64.60; H, 5.64; N, 6.59.



Figure 3.4.5. ¹H NMR of (HTMG)₃[Eu₂(Onaph)₉] (**3.10**) in CDCl₃.



Figure 3.4.6. ¹³C NMR of (HTMG)₃[Eu₂(Onaph)₉] (3.10) in CDCl₃.

Synthesis of (HTMG)₃[**Pr**₂(**Onaph**)₉] (**3.11**). In a 20 mL scintillation vial, 2-naphthol (0.24 g, 1.65 mmol, 9 equiv.) was dissolved in 3 mL of THF to form a clear, colorless solution. Once dissolved, TMG (0.063 g, 69 μ L, 0.55 mmol, 3 equiv.) was added to the vial and stirred over a period of 1 hour. A green solution of Pr[N(SiMe₃)₂]₃ (0.25 g, 0.37 mmol, 2 equiv.) was prepared in 10 mL hexanes and then layered over the colorless THF solution. After two days, green block crystals formed. The green crystals of the product were collected by filtration, washed with hexanes and dried under reduced pressure. Complex 8 had the same unit cell as complex 2, verifying the solid state structure. Yield 0.32 g, 0.17 mmol, 91%. ¹H NMR (400 MHz, CDCl₃) δ : 13.11, 7.80, 7.39, 7.22, 6.23, 3.68 (THF), 2.79 (TMG), 1.82 (THF); ¹³C NMR (360 MHz, CDCl₃) δ : 161.83, 136.61,

131.05, 128.99, 127.46, 126.50, 125.36, 121.12, 118.11, 39.10. Analysis calculated for C₁₀₅H₁₀₅O₉N₉Pr₂: C, 65.72; H, 5.52; N, 6.57. Found: C, 65.78; H, 5.31; N, 6.58.



Figure 3.4.7. ¹H NMR of (HTMG)₃[Pr₂(Onaph)₉] (**3.11**) in CDCl₃.



Figure 3.4.8. ¹³C NMR of (HTMG)₃[Pr₂(Onaph)₉] (3.11) in CDCl₃.

X-ray Structural Parameters.

	3.8 (Penn4774)	3.9 (Penn3779)
Empirical formula	C ₂₆₅ H ₂₁₁ N ₁₇ O ₁₈ K ₆ Eu ₄	C ₂₆₅ H ₂₁₁ N ₁₇ O ₁₈ K ₆ Pr ₄
Formula weight	4763.95	4719.74
Temperature (K)	100(1)	100(1)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Cell constants		
a (Å)	26.5595(7)	26.5977(9)
b (Å)	18.4461(5)	18.4629(6)
c (Å)	23.4805(6)	23.5457(2)
α (°)	90.00	90.00
β (°)	106.406(2)	106.532(2)

Table 3.4.1. Crystallographic parameters for compounds 3.8 and 3.9.

γ (^o)	90.00	90.00
$V(Å^3)$	11035.2(5)	11084.6(6)
Ζ	2	2
$\rho_{calc} (mg/cm^3)$	1.434	1.414
μ (Mo K α) (mm ⁻¹)	1.305	1.046
F(000)	4860	4828
Crystal size (mm ³)	0.22 x 0.18 x 0.08	0.25 x 0.25 x 0.08
Theta range for data collection	1.60 to 27.53°	1.36 to 27.65°
Index ranges	$\label{eq:23} \begin{array}{l} -34 \leq h \leq 34, -23 \leq k \leq 23, \\ -30 \leq l \leq 30 \end{array}$	$\label{eq:second} \begin{array}{l} \textbf{-34} \leq h \leq \textbf{34}, \ \textbf{-24} \leq k \leq \textbf{24}, \\ \textbf{-30} \leq \textbf{l} \leq \textbf{30} \end{array}$
Reflections collected	413990	302003
Independent collections	25403 [R(int) = 0.0423]	25641 [R(int) = 0.0228]
Completeness to theta = 27.53° and 27.52°	99.9%	99.2%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max and min. transmission	0.7456 and 0.7010	0.7456 and 0.6604
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	25403 / 0 / 1439	25641 / 0 / 1438
Goodness-of-fit on F ²	1.138	1.022
Final R indices	R1 = 0.0283, wR2 =	R1 = 0.0324, wR2 =
[I>2sigma(I)]	0.0567	0.0757
R indices (all data)	R1 = 0.0404, wR2 = 0.0645	R1 = 0.0412, wR2 = 0.0896
Largest diff. peak and hole $(e.Å^{-3})$	1.684 and -0.737	1.487 and -0.805

	3.12 (Penn4705)
Empirical formula	$C_{113}H_{123}N_9O_{13}Ce_2Na_2$
Formula weight	2141.42
Temperature (K)	100(1)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	Pbca
Cell constants	
a (Å)	25.9599(7)
b (Å)	24.9788(7)
c (Å)	33.1117(10)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
$V(Å^3)$	21471.2(11)
Z	8
$\rho_{calc} (mg/cm^3)$	1.325
μ (Mo K α) (mm ⁻¹)	0.909
F(000)	8848
Crystal size (mm ³)	0.30 x 0.25 x 0.25
Theta range for data collection	1.23 to 27.55°
T 1	$\textbf{-33} \leq h \leq \textbf{33}, \textbf{-32} \leq k \leq \textbf{32}, \textbf{-43} \leq l \leq$
Index ranges	42
Reflections collected	403452
Independent collections	24741 [R(int) = 0.0344]
Completeness to theta = 27.55°	99.9%
Absorption correction	Semi-empirical from equivalents
Max and min. transmission	0.7456 and 0.6982

 Table 3.4.2. Crystallographic parameters for compound 3.12.

Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	24741 / 1064 / 1404
Goodness-of-fit on F ²	0.822
Final R indices [I>2sigma(I)]	R1 = 0.0586, wR2 = 0.1529
R indices (all data)	R1 = 0.0721, wR2 = 0.1656
Largest diff. peak and hole $(e.Å^{-3})$	1.654 and -0.896

¹H and ⁷Li NMR spectra of Complex 3.1 + MOTf + MOnaph



Figure 3.4.9. Stacked plot of ¹H NMR spectra in CDCl₃ of (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) at the top, complex **3.1** with 3 equiv LiOTf and 1 equiv LiOnaph stirred for 1 hr in DME at the middle, and $\text{Li}_4(\text{DME})_4[\text{Ce}_2(\text{Onaph})_{10}]$ (**3.2**) shown at the bottom.



Figure 3.4.10. Stacked plot of ⁷Li NMR spectra in CDCl₃ of Li₄(DME)₄[Ce₂(Onaph)₁₀] (**3.2**) at the top with a peak at 17 ppm, and complex **3.1** with 3 equiv LiOTf and 1 equiv LiOnaph stirred for 1 hr in DME at the bottom, with a major resonance at 15 ppm.



Figure 3.4.11. Stacked plot of ¹H NMR spectra in CDCl₃ of (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) with 3 equiv LiOTf and 1 equiv LiOnaph stirred for 1 hr in DME at the top, and complex **3.1** mixed with 1 equiv LiOnaph stirred for 1 hr in DME at the bottom.



Figure 3.4.12. Stacked plot of ⁷Li NMR spectra in CDCl₃ of (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) with 3 equiv LiOTf and 1 equiv LiOnaph stirred for 1 hr in DME at the top, and complex **3.1** mixed with 1 equiv LiOnaph stirred for 1 hr in DME at the bottom.



Figure 3.4.13. Stacked plot of ¹H NMR spectra in proteo DME of

 $(HTMG)_3[Ce_2(Onaph)_9]$ (**3.1**) at the top, complex **3.1** with 3 equiv LiOTf and 1 equiv LiOnaph stirred for 1 hr in DME at the middle, and Li₄(DME)₄[Ce₂(Onaph)₁₀] (**3.2**) shown at the bottom.



Figure 3.4.14. Stacked plot of ⁷Li NMR spectra in proteo DME of

 $Li_4(DME)_4[Ce_2(Onaph)_{10}]$ (3.2) at the top, and complex 3.1 with 3 equiv LiOTf and 1 equiv LiOnaph stirred for 1 hr in DME at the bottom.



Figure 3.4.15. Stacked plot of ¹H NMR spectra in proteo DME of

(HTMG)₃[Ce₂(Onaph)₉] (**3.1**) with 3 equiv LiOTf and 1 equiv LiOnaph stirred for 1 hr in DME at the top, and complex **3.1** mixed with 1 equiv LiOnaph stirred for 1 hr in DME at the bottom.



Figure 3.4.16. Stacked plot of ⁷Li NMR spectra in proteo DME of

(HTMG)₃[Ce₂(Onaph)₉] (**3.1**) with 3 equiv LiOTf and 1 equiv LiOnaph stirred for 1 hr in DME at the top, and complex **3.1** mixed with 1 equiv LiOnaph stirred for 1 hr in DME at the bottom.



Figure 3.4.17. Stacked plot of ¹H NMR spectra in CDCl₃ of (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) at the top, complex **3.1** with 3 equiv NaOTf and 1 equiv NaOnaph stirred for 1 hr in DME at the middle, and Na₄(DME)₄[Ce₂(Onaph)₁₀] (**3.3**) shown at the bottom.



Figure 3.4.18. Stacked plot of ¹H NMR spectra in CDCl₃ of (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) with 3 equiv NaOTf and 1 equiv NaOnaph stirred for 1 hr in DME at the top, and complex **3.1** mixed with 1 equiv NaOnaph stirred for 1 hr in DME at the bottom.



Figure 3.4.19. Stacked plot of ¹H NMR spectra in proteo DME of

 $(HTMG)_3[Ce_2(Onaph)_9]$ (3.1) at the top, complex 3.1 with 3 equiv NaOTf and 1 equiv NaOnaph stirred for 1 hr in DME at the middle, and Na₄(DME)₄[Ce₂(Onaph)₁₀] (3.3) shown at the bottom.



Figure 3.4.20. Stacked plot of ¹H NMR spectra in proteo DME of

(HTMG)₃[Ce₂(Onaph)₉] (**3.1**) with 3 equiv NaOTf and 1 equiv NaOnaph stirred for 1 hr in DME at the top, and complex **3.1** mixed with 1 equiv NaOnaph stirred for 1 hr in DME at the bottom.



Figure 3.4.21. Stacked plot of ¹H NMR spectra in CDCl₃ of (HTMG)₃[Ce₂(Onaph)₉] (3.1) at the top, complex 3.1 with 3 equiv KOTf and 3 equiv KOnaph stirred for 1 hr in DME at the middle, and $K_6(DME)_4[Ce_2(Onaph)_{12}]$ (3.4) shown at the bottom.


Figure 3.4.22. Stacked plot of ¹H NMR spectra in CDCl₃ of (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) with 3 equiv KOTf and 3 equiv KOnaph stirred for 1 hr in DME at the top, and (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) with 3 equiv KOnaph stirred for 1 hr in DME shown at the bottom.



Figure 3.4.23. Stacked plot of ¹H NMR spectra in proteo DME of

 $(HTMG)_3[Ce_2(Onaph)_9]$ (**3.1**) at the top, complex **3.1** with 3 equiv KOTf and 3 equiv KOnaph stirred for 1 hr in DME at the middle, and $K_6(DME)_4[Ce_2(Onaph)_{12}]$ (**3.4**) shown at the bottom.



Figure 3.4.24. Stacked plot of ¹H NMR spectra in proteo DME of

 $(HTMG)_3[Ce_2(Onaph)_9]$ (**3.1**) with 3 equiv KOTf and 3 equiv KOnaph stirred for 1 hr in DME at the top, and $(HTMG)_3[Ce_2(Onaph)_9]$ (**3.1**) with 3 equiv KOnaph stirred for 1 hr in DME shown at the bottom.



Figure 3.4.25. Stacked plot of ¹H NMR spectra in CDCl₃ of (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) at the top, complex **3.1** with 3 equiv LiOTf and 3 equiv LiOnaph stirred for 1 hr in pyridine at the middle, and Li₃(py)₃[Ce(Onaph)₆] (**3.5**) shown at the bottom.



Figure 3.4.26. Stacked plot of ⁷Li NMR spectra in CDCl₃ of Li₃(py)₃[Ce(Onaph)₆] (**3.5**) shown at the top, and (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) with 3 equiv LiOTf and 3 equiv LiOnaph stirred for 1 hr in pyridine at the bottom.



Figure 3.4.27. Stacked plot of ¹H NMR spectra in CDCl₃ of (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) with 3 equiv LiOTf and 3 equiv LiOnaph stirred for 1 hr in pyridine at the top, and HTMG)₃[Ce₂(Onaph)₉] (**3.1**) with 3 equiv LiOnaph stirred for 1 hr in pyridine shown at the bottom.



Figure 3.4.28. Stacked plot of ⁷Li NMR spectra in CDCl₃ of (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) with 3 equiv LiOTf and 3 equiv LiOnaph stirred for 1 hr in pyridine at the top, and HTMG)₃[Ce₂(Onaph)₉] (**3.1**) with 3 equiv LiOnaph stirred for 1 hr in pyridine shown at the bottom.



Figure 3.4.29. Stacked plot of ¹H NMR spectra in pyridine- d_5 of (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) at the top, complex **3.1** with 3 equiv LiOTf and 3 equiv LiOnaph stirred for 1 hr in pyridine at the middle, and Li₃(py)₃[Ce(Onaph)₆] (**3.5**) shown at the bottom.



Figure 3.4.30. Stacked plot of ⁷Li NMR spectra in pyridine-*d*₅ of Li₃(py)₃[Ce(Onaph)₆]
(3.5) shown at the top, and (HTMG)₃[Ce₂(Onaph)₉] (3.1) with 3 equiv LiOTf and 3 equiv LiOnaph stirred for 1 hr in pyridine at the bottom.



Figure 3.4.31. Stacked plot of ¹H NMR spectra in pyridine- d_5 of (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) with 3 equiv LiOTf and 3 equiv LiOnaph stirred for 1 hr in pyridine at the top, and (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) with 3 equiv LiOnaph stirred for 1 hr in pyridine shown at the bottom.



Figure 3.4.32. Stacked plot of ⁷Li NMR spectra in pyridine- d_5 of

 $(HTMG)_3[Ce_2(Onaph)_9]$ (**3.1**) with 3 equiv LiOTf and 3 equiv LiOnaph stirred for 1 hr in pyridine at the top, and $(HTMG)_3[Ce_2(Onaph)_9]$ (**3.1**) with 3 equiv LiOnaph stirred for 1 hr in pyridine shown at the bottom.



Figure 3.4.33. Stacked plot of ¹H NMR spectra in CDCl₃ of (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) at the top, complex **3.1** with 3 equiv NaOTf and 3 equiv NaOnaph stirred for 1 hr in pyridine at the middle, and Na₃(py)₆[Ce(Onaph)₆] (**3.6**) shown at the bottom.



Figure 3.4.34. Stacked plot of ¹H NMR spectra in CDCl₃ of (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) with 3 equiv NaOTf and 3 equiv NaOnaph stirred for 1 hr in pyridine at the top, and (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) with 3 equiv NaOnaph stirred for 1 hr in pyridine shown at the bottom.



Figure 3.4.35. Stacked plot of ¹H NMR spectra in pyridine- d_5 of (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) at the top, complex **3.1** with 3 equiv NaOTf and 3 equiv NaOnaph stirred for 1 hr in pyridine at the middle, and Na₃(py)₆[Ce(Onaph)₆] (**3.6**) shown at the bottom.



Figure 3.4.36. Stacked plot of ¹H NMR spectra in pyridine- d_5 of (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) with 3 equiv NaOTf and 3 equiv NaOnaph stirred for 1 hr in pyridine at the top, and (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) with 3 equiv NaOnaph stirred for 1 hr in pyridine shown at the bottom.

¹H and ⁷Li NMR spectra of Complex 3.1 + MOTf + HOnaph



Figure 3.4.37. Stacked plot of ¹H NMR spectra in CDCl₃ of (HTMG)₃[Ce₂(Onaph)₉]
(3.1) at the top, complex 3.1 with 4 equiv LiOTf and 1 equiv HOnaph stirred for 1 hr in DME at the middle, and Li₄(DME)₄[Ce₂(Onaph)₁₀] (3.2) shown at the bottom.



Figure 3.4.38. Stacked plot of ⁷Li NMR spectra in CDCl₃ of Li₄(DME)₄[Ce₂(Onaph)₁₀] (**3.2**) at the top, and (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) with 4 equiv LiOTf and 1 equiv HOnaph stirred for 1 hr in DME at the bottom.



Figure 3.4.39. Stacked plot of ¹H NMR spectra in proteo DME of

 $(HTMG)_3[Ce_2(Onaph)_9]$ (**3.1**) at the top, complex **3.1** with 4 equiv LiOTf and 1 equiv HOnaph stirred for 1 hr in DME at the middle, and Li₄(DME)₄[Ce₂(Onaph)₁₀] (**3.2**) shown at the bottom.



Figure 3.4.40. Stacked plot of ⁷Li NMR spectra in proteo DME of

 $Li_4(DME)_4[Ce_2(Onaph)_{10}]$ (3.2) at the top, and $(HTMG)_3[Ce_2(Onaph)_9]$ (3.1) with 4 equiv LiOTf and 1 equiv HOnaph stirred for 1 hr in DME at the bottom.



Figure 3.4.41. Stacked plot of ¹H NMR spectra in CDCl₃ of (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) at the top, complex **3.1** with 4 equiv NaOTf and 1 equiv HOnaph stirred for 1 hr in DME at the middle, and Na₄(DME)₄[Ce₂(Onaph)₁₀] (**3.3**) shown at the bottom.



Figure 3.4.42. Stacked plot of ¹H NMR spectra in proteo DME of

 $(HTMG)_3[Ce_2(Onaph)_9]$ (3.1) at the top, complex 3.1 with 4 equiv NaOTf and 1 equiv HOnaph stirred for 1 hr in DME at the middle, and Na₄(DME)₄[Ce₂(Onaph)₁₀] (3.3) shown at the bottom.



Figure 3.4.43. Stacked plot of ¹H NMR spectra in CDCl₃ of (HTMG)₃[Ce₂(Onaph)₉]
(3.1) at the top, complex 3.1 with 6 equiv KOTf and 1 equiv HOnaph stirred for 1 hr in DME at the middle, and K₆(DME)₄[Ce₂(Onaph)₁₂] (3.4) shown at the bottom.



Figure 3.4.44. Stacked plot of ¹H NMR spectra in proteo DME of

(HTMG)₃[Ce₂(Onaph)₉] (**3.1**) at the top, complex **3.1** with 6 equiv KOTf and 1 equiv HOnaph stirred for 1 hr in DME at the middle, and $K_6(DME)_4[Ce_2(Onaph)_{12}]$ (**3.4**) shown at the bottom.



Figure 3.4.45. Stacked plot of ¹H NMR spectra in CDCl₃ of (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) at the top, complex **3.1** with 6 equiv LiOTf and 3 equiv HOnaph stirred for 1 hr in pyridine at the middle, and Li₃(py)₆[Ce(Onaph)₆] (**3.5**) shown at the bottom.



Figure 3.4.46. Stacked plot of ⁷Li NMR spectra in CDCl₃ of Li₃(py)₆[Ce(Onaph)₆] (**3.5**) at the top, and (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) with 6 equiv LiOTf and 3 equiv HOnaph stirred for 1 hr in pyridine shown at the bottom.



Figure 3.4.47. Stacked plot of ¹H NMR spectra in pyridine- d_5 of (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) at the top, complex **3.1** with 6 equiv LiOTf and 3 equiv HOnaph stirred for 1 hr in pyridine at the middle, and Li₃(py)₆[Ce(Onaph)₆] (**3.5**) shown at the bottom.



Figure 3.4.48. Stacked plot of ⁷Li NMR spectra in pyridine- d_5 of Li₃(py)₆[Ce(Onaph)₆] (**3.5**) at the top, and (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) with 6 equiv LiOTf and 3 equiv HOnaph stirred for 1 hr in pyridine shown at the bottom.



Figure 3.4.49. Stacked plot of ¹H NMR spectra in CDCl₃ of (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) at the top, complex **3.1** with 6 equiv NaOTf and 3 equiv HOnaph stirred for 1 hr in

pyridine at the middle, and $Na_3(py)_6[Ce(Onaph)_6]$ (3.6) shown at the bottom.



Figure 3.4.50. Stacked plot of ¹H NMR spectra in pyridine- d_5 of (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) at the top, complex **3.1** with 6 equiv NaOTf and 3 equiv HOnaph stirred for 1 hr in pyridine at the middle, and Na₃(py)₆[Ce(Onaph)₆] (**3.6**) shown at the bottom.



Figure 3.4.51. Stacked plot of ¹H NMR spectra in CDCl₃ of (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) at the top, complex **3.1** with 3 equiv KOTf stirred for 1 hr in pyridine at the middle, and $K_3(py)_6[Ce_2(Onaph)_9(py)_2]$ (**3.7**) shown at the bottom.



Figure 3.4.52. Stacked plot of ¹H NMR spectra in pyridine- d_5 of (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) at the top, complex **3.1** with 3 equiv KOTf stirred for 1 hr in pyridine at the middle, and K₃(py)₆[Ce₂(Onaph)₉(py)₂] (**3.7**) shown at the bottom.

¹H and ⁷Li NMR spectra of the reactions described in Scheme 3.2.1, MCeOnaph + (HTMG)OTf



Figure 3.4.53. Stacked plot of ¹H NMR spectra in CDCl₃ of Li₄(DME)₄[Ce₂(Onaph)₁₀] (**3.2**) at the top, complex **3.2** with 4 equiv (HTMG)OTf stirred for 1 hr in DME next, and $(HTMG)_3[Ce_2(Onaph)_9]$ (**3.1**) shown at the bottom.



Figure 3.4.54. ⁷Li NMR spectrum in CDCl₃ of $Li_4(DME)_4[Ce_2(Onaph)_{10}]$ (**3.2**) with 4 equiv (HTMG)OTf stirred for 1 hr in DME.



Figure 3.4.55. Stacked plot of ¹H NMR spectra in proteo DME of

 $Li_4(DME)_4[Ce_2(Onaph)_{10}]$ (**3.2**) at the top, complex **3.2** with 4 equiv (HTMG)OTf stirred for 1 hr in DME next, and (HTMG)_3[Ce_2(Onaph)_9] (**3.1**) shown at the bottom.



Figure 3.4.56. Stacked plot of ⁷Li NMR spectra in proteo DME of Li₄(DME)₄[Ce₂(Onaph)₁₀] (**3.2**) at the top, and complex **3.2** with 4 equiv (HTMG)OTf

stirred for 1 hr in DME shown at the bottom.



Figure 3.4.57. Stacked plot of ¹H NMR spectra in CDCl₃ of Na₄(DME)₄[Ce₂(Onaph)₁₀] (**3.3**) at the top, complex **3.3** with 4 equiv (HTMG)OTf stirred for 1 hr in DME next, and (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) shown at the bottom.



Figure 3.4.58. Stacked plot of ¹H NMR spectra in proteo DME of

 $Na_4(DME)_4[Ce_2(Onaph)_{10}]$ (3.3) at the top, complex 3.3 with 4 equiv (HTMG)OTf stirred for 1 hr in DME next, and (HTMG)_3[Ce_2(Onaph)_9] (3.1) shown at the bottom.



Figure 3.4.59. Stacked plot of ¹H NMR spectra in CDCl₃ of K₆(DME)₄[Ce₂(Onaph)₁₂] (**3.4**) at the top, complex **3.4** with 6 equiv (HTMG)OTf stirred for 1 hr in DME next, (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) with 3 equiv (HTMG)Onaph second from the bottom, and complex **3.1** shown at the bottom.



Figure 3.4.60. Stacked plot of ¹H NMR spectra in proteo DME of

 $K_6(DME)_4[Ce_2(Onaph)_{12}]$ (3.4) at the top, complex 3.4 with 6 equiv (HTMG)OTf stirred for 1 hr in DME next, (HTMG)_3[Ce_2(Onaph)_9] (3.1) with 3 equiv (HTMG)Onaph second from the bottom, and complex 3.1 shown at the bottom.



Figure 3.4.61. Stacked plot of ¹H NMR spectra in CDCl₃ of Li₃(py)₆[Ce(Onaph)₆] (**3.5**) at the top, 2 equiv complex **3.5** with 6 equiv (HTMG)OTf stirred for 1 hr in pyridine in the middle, and (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) shown at the bottom.



Figure 3.4.62. ⁷Li NMR spectrum in CDCl₃ of Li₃(py)₆[Ce(Onaph)₆] (**3.5**) with 3 equiv (HTMG)OTf stirred for 1 hr in pyridine.



Figure 3.4.63. Stacked plot of ¹H NMR spectra in pyridine- d_5 of Li₃(py)₆[Ce(Onaph)₆] (**3.5**) at the top, 2 equiv complex **3.5** with 6 equiv (HTMG)OTf stirred for 1 hr in pyridine in the middle, and (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) shown at the bottom.



Figure 3.4.64. Stacked plot of ⁷Li NMR spectra in pyridine- d_5 of Li₃(py)₆[Ce(Onaph)₆] (3.5) at the top, and 2 equiv complex 3.5 with 6 equiv (HTMG)OTf stirred for 1 hr in pyridine shown at the bottom.



Figure 3.4.65. Stacked plot of ¹H NMR spectra in CDCl₃ of Na₃(py)₆[Ce(Onaph)₆] (**3.6**) at the top, complex **3.6** with 6 equiv (HTMG)OTf stirred for 1 hr in pyridine next, (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) with 3 equiv (HTMG)Onaph second to the bottom, and complex **3.1** shown at the bottom.



Figure 3.4.66. Stacked plot of ¹H NMR spectra in pyridine- d_5 of Na₃(py)₆[Ce(Onaph)₆] (**3.6**) at the top, complex **3.6** with 6 equiv (HTMG)OTf stirred for 1 hr in pyridine next, (HTMG)₃[Ce₂(Onaph)₉] (**3.1**) with 3 equiv (HTMG)Onaph second to the bottom, and complex **3.1** shown at the bottom.



Figure 3.4.67. Stacked plot of ¹H NMR spectra in CDCl₃ of $K_3(py)_6[Ce_2(Onaph)_9(py)_2]$ (3.7) at the top, complex 3.7 with 3 equiv (HTMG)OTf stirred for 1 hr in pyridine at the middle, and (HTMG)₃[Ce₂(Onaph)₉] (3.1) shown at the bottom.



Figure 3.4.68. Stacked plot of ¹H NMR spectra in pyridine- d_5 of

 $K_3(py)_6[Ce_2(Onaph)_9(py)_2]$ (3.7) at the top, complex 3.7 with 3 equiv (HTMG)OTf stirred for 1 hr in pyridine at the middle, and (HTMG)_3[Ce_2(Onaph)_9] (3.1) shown at the bottom.

VT NMR Spectra



Figure 3.4.69. Variable temperature ¹H NMR spectra of $(HTMG)_3[Ce_2(Onaph)_9]$ (**3.1**) in pyridine- d_5 .

	h	340 K
	h	330 K
		320 K
		310 K
		300 K
		290 K
	linh	280 K
	linh	270 K
	Imital	260 K
	rml	250 K
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.(δ (ppm)	0 8.5 8.0 7.5 7.0 6.5	6.0 5.5 5.0

Figure 3.4.70. Variable temperature ¹H NMR spectra of $K_3(py)_6[Ce_2(Onaph)_9(py)_2]$ (**3.7**) in pyridine- d_5 .


Figure 3.4.71. Variable temperature ¹H NMR spectra of the reaction of

 $K_3(py)_6[Ce_2(Onaph)_9(py)_2]$ (3.7) with 3 equiv (HTMG)OTf in pyridine- d_5 .



Figure 3.4.72. Overlay of ¹H NMR spectra of the reaction of $K_3(py)_6[Ce_2(Onaph)_9(py)_2]$ (**3.7**) with 3 equiv (HTMG)OTf (black), $K_3(py)_6[Ce_2(Onaph)_9(py)_2]$ (**3.7**) (red), and (HTMG)_3[Ce_2(Onaph)_9] (blue) in pyridine- d_5 at 250 K.



i.0 15.5 15.0 14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 (ppm)

Figure 3.4.73. Overlay of ¹H NMR spectra of the reaction of $K_3(py)_6[Ce_2(Onaph)_9(py)_2]$ (**3.7**) with 3 equiv (HTMG)OTf (black), $K_3(py)_6[Ce_2(Onaph)_9(py)_2]$ (**3.7**) (red), and (HTMG)_3[Ce_2(Onaph)_9] (blue) in pyridine- d_5 at 300 K.



Figure 3.4.74. Variable temperature ¹H NMR spectra of the reaction of

 $Li_3(py)_6[Ce(Onaph)_6]$ (3.5) with 3 equiv (HTMG)OTf in pyridine- d_5 .



Figure 3.4.75. Variable temperature ⁷Li NMR spectra of the reaction of

 $Li_3(py)_6[Ce(Onaph)_6]$ (3.5) with 3 equiv (HTMG)OTf in pyridine- d_5 .

Electrochemistry of Complex 3.1, Complex 3.7, and the mixture of Complex 3.7 with

(HTMG)OTf in pyridine



Figure 3.4.76. Cyclic voltammetry of $K_3(py)_6[Ce_2(Onaph)_9(py)_2]$ (3.7) in pyridine and

0.15 M ([${}^{n}Bu_{4}N$][BAr ${}^{F}_{4}$]). Scan rate was 100 mV/s.



Figure 3.4.77. Scan rate dependence of the Ce^{III/IV} redox wave of

 $K_3(py)_6[Ce_2(Onaph)_9(py)_2]$ (3.7) in pyridine and 0.15 M ([ⁿBu₄N][BAr^F₄]). Scan rates ranged from 50–1000 mV/s.



Figure 3.4.78. Cyclic voltammetry of $(HTMG)_3[Ce_2(Onaph)_9]$ (3.1) in pyridine and 0.15 M $([^nBu_4N][BAr^F_4])$. Scan rate was 100 mV/s.



Figure 3.4.79. Scan rate dependence of the Ce^{III/IV} redox wave of

 $(HTMG)_3[Ce_2(Onaph)_9]$ (**3.1**) in pyridine and 0.15 M ([ⁿBu₄N][BAr^F₄]). Scan rates ranged from 25–1000 mV/s.



Figure 3.4.80. Cyclic voltammetry of $K_3(py)_6[Ce_2(Onaph)_9(py)_2]$ (**3.7**) and 3 equiv (HTMG)OTf in pyridine and 0.15 M ([ⁿBu₄N][BAr^F₄]). Scan rate was 100 mV/s.



Figure 3.4.81. Cyclic voltammetry of $K_3(py)_6[Ce_2(Onaph)_9(py)_2]$ (**3.7**) and 3 equiv (HTMG)OTf in pyridine and 0.15 M ([ⁿBu₄N][BAr^F₄]). Scan rate was 100 mV/s.



Figure 3.4.82. Scan rate dependence of the Ce^{III/IV} redox wave of

 $K_3(py)_6[Ce_2(Onaph)_9(py)_2]$ (3.7) and 3 equiv (HTMG)OTf in pyridine and 0.15 M

([$^{n}Bu_{4}N$][BAr $^{F}_{4}$]). Scan rates ranged from 25–1000 mV/s.

rate was 100 mV/s.



Figure 3.4.83. Cyclic voltammetry of $K_3(py)_6[Ce_2(Onaph)_9(py)_2]$ (**3.7**) and 3 equiv (HTMG)OTf (top), (HTMG)_3[Ce_2(Onaph)_9] (**3.1**) (middle), and $K_3(py)_6[Ce_2(Onaph)_9(py)_2]$ (**3.7**) (bottom) in pyridine and 0.15 M ([ⁿBu₄N][BAr^F₄]). Scan

¹H NMR Spectra assignment of complexes 3.8 and 3.9



Figure 3.4.84. ^{1}H - ^{1}H COSY NMR spectrum of $K_{3}(py)_{6}[Eu_{2}(Onaph)_{9}(py)_{2}]$ (3.8) in

CDCl₃.



Figure 3.4.85. 1 H- 1 H COSY NMR spectrum of K₃(py)₆[Eu₂(Onaph)₉(py)₂] (3.8) in CDCl₃.



Figure 3.4.86. ${}^{1}H{}^{-13}C$ HSQC NMR spectrum of $K_{3}(py)_{6}[Eu_{2}(Onaph)_{9}(py)_{2}]$ (3.8) in CDCl₃.



Figure 3.4.87. 1 H- 13 C HSQC NMR spectrum of K₃(py)₆[Eu₂(Onaph)₉(py)₂] (3.8) in CDCl₃.



Figure 3.4.88. 1 H- 1 H COSY NMR spectrum of K₃(py)₆[Pr₂(Onaph)₉(py)₂] (3.9) in

CDCl₃.



Figure 3.4.89. 1 H- 1 H COSY NMR spectrum of K₃(py)₆[Pr₂(Onaph)₉(py)₂] (3.9) in CDCl₃.



Figure 3.4.90. ${}^{1}\text{H}{-}^{13}\text{C}$ HSQC NMR spectrum of $K_{3}(py)_{6}[\Pr_{2}(\text{Onaph})_{9}(py)_{2}]$ (3.9) in CDCl₃.



Figure 3.4.91. ¹H-¹³C HSQC NMR spectrum of $K_3(py)_6[Pr_2(Onaph)_9(py)_2]$ (3.9) in CDCl₃.



Figure 3.4.92. ¹H NMR spectrum of $K_3(py)_6[Eu_2(Onaph)_9(py)_2]$ (**3.8**) in CDCl₃ (top) and $K_3(py)_6[Eu_2(Onaph)_9(py)_2]$ (**3.8**) first dissolved in pyridine-*d*₅, solvent removed under reduced pressure, and then ¹H NMR spectrum in CDCl₃ (bottom).



Figure 3.4.93. ¹H NMR spectrum of $K_3(py)_6[Pr_2(Onaph)_9(py)_2]$ (**3.9**) in CDCl₃ (top) and $K_3(py)_6[Pr_2(Onaph)_9(py)_2]$ (**3.9**) first dissolved in pyridine-*d*₅, solvent removed under reduced pressure, and then ¹H NMR spectrum in CDCl₃ (bottom).



Figure 3.4.94. Assigned ¹H NMR spectrum of $K_3(py)_6[Eu_2(Onaph)_9(py)_2]$ (**3.8**) (top) and $K_3(py)_6[Pr_2(Onaph)_9(py)_2]$ (**3.9**) (bottom) in CDCl₃.



Figure 3.4.95. Representative 2D ¹H-¹H EXSY NMR spectrum of

 $K_3(py)_6[Eu_2(Onaph)_9(py)_2]$ (3.8) in CDCl₃ at 300 K, where $t_{mix} = 15$ ms.



Figure 3.4.96. Representative ¹H-¹H 2D EXSY spectrum of $K_3(py)_6[Pr_2(Onaph)_9]$ (**3.9**) at 300 K in CDCl₃, $t_{mix} = 15$ ms.



Figure 3.4.97. ¹H-¹H 2D EXSY spectrum of (HTMG)₃[Eu₂(Onaph)₉] (**3.10**) at 220 K in CDCl₃, t_{mix} = 25 ms.



Figure 3.4.98. ¹H-¹H 2D EXSY spectrum of (HTMG)₃[$Pr_2(Onaph)_9$] (3.11) at 220 K in CDCl₃, $t_{mix} = 25$ ms.



Figure 3.4.99. ¹H-¹H 2D EXSY spectrum of the mixture of $K_3(py)_6[Eu_2(Onaph)_9(py)_2]$ (3.8) and $K_3(py)_6[Pr_2(Onaph)_9(py)_2]$ (3.9) at 300 K in CDCl₃, $t_{mix} = 25$ ms.



Figure 3.4.100. Overlay of the ¹H NMR spectra of $K_3(py)_6[Eu_2(Onaph)_9(py)_2]$ (**3.8**) (red), $K_3(py)_6[Pr_2(Onaph)_9(py)_2]$ (**3.9**) (blue), and the mixture of $K_3(py)_6[Eu_2(Onaph)_9(py)_2]$ (**3.8**) and $K_3(py)_6[Pr_2(Onaph)_9(py)_2]$ (**3.9**) (black).



Figure 3.4.101. Overlay of the ¹H NMR spectra of $K_3(py)_6[Eu_2(Onaph)_9(py)_2]$ (3.8) (red), $K_3(py)_6[Pr_2(Onaph)_9(py)_2]$ (3.9) (blue), and the mixture of $K_3(py)_6[Eu_2(Onaph)_9(py)_2]$ (3.8) and $K_3(py)_6[Pr_2(Onaph)_9(py)_2]$ (3.9) (black).



Figure 3.4.102. Overlay of the ¹H NMR spectra of $K_3(py)_6[Eu_2(Onaph)_9(py)_2]$ (**3.8**) (red), $K_3(py)_6[Pr_2(Onaph)_9(py)_2]$ (**3.9**) (blue), and the mixture of

 $K_3(py)_6[Eu_2(Onaph)_9(py)_2]$ (3.8) and $K_3(py)_6[Pr_2(Onaph)_9(py)_2]$ (3.9) (black).



Figure 3.4.103. ¹H-¹H COSY NMR spectrum of the mixture of

 $K_3(py)_6[Eu_2(Onaph)_9(py)_2]$ (3.8) and $K_3(py)_6[Pr_2(Onaph)_9(py)_2]$ (3.9).



Figure 3.4.104. ¹H-¹H COSY NMR spectrum of the mixture of

 $K_3(py)_6[Eu_2(Onaph)_9(py)_2]$ (3.8) and $K_3(py)_6[Pr_2(Onaph)_9(py)_2]$ (3.9).



Figure 3.4.105. ¹H-¹³C HSQC NMR spectrum of the mixture of

 $K_3(py)_6[Eu_2(Onaph)_9(py)_2]$ (3.8) and $K_3(py)_6[Pr_2(Onaph)_9(py)_2]$ (3.9).



Figure 3.4.106. ¹H-¹³C HSQC NMR spectrum of the mixture of

 $K_3(py)_6[Eu_2(Onaph)_9(py)_2]$ (3.8) and $K_3(py)_6[Pr_2(Onaph)_9(py)_2]$ (3.9).



Figure 3.4.107. ¹H-¹H TOCSY NMR spectrum of the mixture of

 $K_3(py)_6[Eu_2(Onaph)_9(py)_2]$ (3.8) and $K_3(py)_6[Pr_2(Onaph)_9(py)_2]$ (3.9).



Figure 3.4.108. ¹H-¹H TOCSY NMR spectrum of the mixture of

 $K_3(py)_6[Eu_2(Onaph)_9(py)_2]$ (3.8) and $K_3(py)_6[Pr_2(Onaph)_9(py)_2]$ (3.9).



Figure 3.4.109. UV-Vis spectra of K₃(py)₆[Eu₂(Onaph)₉(py)₂] (3.8) (yellow),

 $K_3(py)_6[Pr_2(Onaph)_9(py)_2]$ (3.9) (green), and the mixture of 3.8 and 3.9 (black).



Figure 3.4.110. ${}^{1}\text{H} {}^{-1}\text{H} 2D \text{ EXSY}$ spectrum of the mixture of (HTMG)₃[Eu₂(Onaph)₉] (3.10) and (HTMG)₃[Pr₂(Onaph)₉] (3.11) at 300 K in CDCl₃, t_{mix} = 50 ms.



Figure 3.4.111. ¹H-¹H 2D EXSY spectrum of the mixture of $K_3(py)_6[Eu_2(Onaph)_9(py)_2]$ (**3.8**) and (HTMG)₃[Eu₂(Onaph)₉] (**3.10**) at 300 K in CDCl₃, $t_{mix} = 50$ ms.



Figure 3.4.112. Eyring plot of $K_3(py)_6[Eu_2(Onaph)_9(py)_2]$ (**3.8**) bridging to terminal selfexchange obtained from variable temperature 2D ¹H-¹H EXSY NMR spectra in CDCl₃.



Figure 3.4.113. Eyring plot of $K_3(py)_6[Pr_2(Onaph)_9(py)_2]$ (**3.9**) bridging to terminal selfexchange obtained from variable temperature 2D ¹H-¹H EXSY NMR spectra in CDCl₃.

3.5 BIBLIOGRAPHY

- [1] J.-C. G. Bunzli, C. Piguet, *Chem. Rev.* 2002, *102*, 1897-1928; C. Piguet, E. Rivara-Minten, G. Bernardinelli, J.-C. G. Bunzli, G. Hopfgartner, *J. Chem. Soc., Dalton Trans.* 1997, 421-433.
- [2] C. Piguet, J.-C. G. Bunzli, *Chem. Soc. Rev.* **1999**, *28*, 347-358.
- [3] C. Edder, C. Piguet, J.-C. G. Bunzli, G. Hopfgartner, J. Chem. Soc., Dalton Trans. 1997, 4657-4663.
- [4] G. Lu, Y. Chen, Y. Zhang, M. Bao, Y. Bian, X. Li, J. Jiang, J. Am. Chem. Soc. 2008, 130, 11623-11630; S. Rigault, C. Piguet, G. Bernardinelli, G. Hopfgartner, Angew. Chem. Int. Ed. 1998, 37, 169-172; C. Piguet, J.-C. G. Bunzli, G. Bernardinelli, C. G. Bochet, P. Froidevaux, J. Chem. Soc. Dalton Trans. 1995, 83-97; F. Renaud, C. Piguet, G. Bernardinelli, G. Hopfgartner, J.-C. G. Bunzli, Chem. Commun. 1999, 457-458; P. E. Ryan, G. Canard, S. Koeller, B. Bocquet, C. Piguet, Inorg. Chem. 2012, 51, 10012-10024; S. Petoud, Seth M.Bunzli, Jean-Claude G.Raymond, Kenneth N., J. Am. Chem. Soc. 2003, 125, 13324-13325; E. J. D. Werner, AnkonaJocher, Christoph J.Raymond, Kenneth N., Angew. Chem. Int. Ed. 2008, 47, 8568-8580; A. E. V. Gorden, J. Xu, G. Szigethy, A. Oliver, D. K. Shuh, K. N. Raymond, J. Am. Chem. Soc. 2007, 129, 6674-6675; N. Dalla Favera, L. Guenee, G. Bernardinelli, C. Piguet, Dalton Trans. 2009, 7625-7638; G. Bernardinelli, C. Piguet, A. F. Williams, Angew. Chem. Int. Ed. Engl. 1992, 31, 1622-1624; G. Muller, J.-C. G. Bunzli, K. J. Schenk, C. Piguet, G. Hopfgartner, Inorg. Chem. 2001, 40, 2642-2651; A. Escande, L. Guenee, K.-L. Buchwalder, C. Piguet, Inorg. Chem. 2009, 48, 1132-1147.
- [5] T. Riis-Johannessen, N. Dupont, G. Canard, G. Bernardinelli, A. Hauser, C. Piguet, *Dalton Trans.* 2008, 3661-3677.

- [6] N. Andre, T. B. Jensen, R. Scopelliti, D. Imbert, M. Elhabiri, G. Hopfgartner, C. Piguet,
 J.-C. G. Bunzli, *Inorg. Chem.* 2004, 43, 515-529; S. Petoud, J.-C. G. Bunzli, F. Renaud,
 C. Piguet, K. J. Schenk, G. Hopfgartner, *Inorg. Chem.* 1997, 36, 5750-5760; N. Andre, R.
 Scopelliti, G. Hopfgartner, C. Piguet, J.-C. G. Bunzli, *Chem. Commun.* 2002, 214-215.
- [7] C. Piguet, J.-C. G. Bunzli, G. Bernardinelli, G. Hopfgartner, A. F. Williams, J. Am. Chem. Soc. 1993, 115, 8197-8206; F. Renaud, C. Piguet, G. Bernardinelli, J.-C. G.
 Bunzli, G. Hopfgartner, J. Am. Chem. Soc. 1999, 121, 9326-9342; C. Piguet, J.-C. G.
 Bunzli, G. Bernardinelli, G. Hopfgartner, S. Petoud, O. Schaad, J. Am. Chem. Soc. 1996, 118, 6681-6697.
- [8] M. Shibasaki, M. Kanai, S. Matsunaga, N. Kumagai, Acc. Chem. Res. 2009, 42, 1117-1127; Y. Horiuchi, V. Gnanadesikan, T. Ohshima, H. Masu, K. Katagiri, Y. Sei, K. Yamaguchi, M. Shibasaki, Chem. Eur. J. 2005, 11, 5195-5204; N. Yoshikawa, Y. M. A. Yamada, J. Das, H. Sasai, M. Shibasaki, J. Am. Chem. Soc. 1999, 121, 4168-4178; T. Yukawa, B. Seelig, Y. Xu, H. Morimoto, S. Matsunaga, A. Berkessel, M. Shibasaki, J. Am. Chem. Soc. 2010, 132, 11988-11992; S. Handa, V. Gnanadesikan, S. Matsunaga, M. Shibasaki, J. Am. Chem. Soc. 2010, 132, 11988-11992; S. Handa, V. Gnanadesikan, S. Matsunaga, M. Shibasaki, J. Am. Chem. Soc. 2010, 132, 4925-4934; M. Shibasaki, N. Kumagai, Angew. Chem. Int. Ed. 2013, 52, 223-234; T. N. Parac-Vogt, S. Pachini, P. Nockemann, K. Van Hecke, L. Van Meervelt, K. Binnemans, Eur. J. Org. Chem. 2004, 4560-4566; L. Cunha-Silva, S. Lima, D. Ananias, P. Silva, L. Mafra, L. D. Carlos, M. Pillinger, A. A. Valente, F. A. Almeida Paz, J. Rocha, J. Mater. Chem. 2009, 19, 2618-2632.
- [9] J. R. Robinson, X. Fan, J. Yadav, P. J. Carroll, A. J. Wooten, M. A. Pericas, E. J. Schelter, P. J. Walsh, J. Am. Chem. Soc. 2014, 136, 8034-8041.
- [10] K. Morokuma, M. Hatanaka, J. Am. Chem. Soc. 2013, 135, 13972-13979.

- [11] L. S. Natrajan, J. J. Hall, A. J. Blake, C. Wilson, P. L. Arnold, J. Sol. State Chem. 2003, 171, 90-100; W. J. Evans, New J. Chem. 1995, 19, 525-533; S. Cotton, Lanthanide and Actinide Chemistry, John Wiley and Sons Inc., Hoboken, NJ, 2006.
- X. Yang, D. Schipper, R. A. Jones, L. A. Lytwak, B. J. Holliday, S. Huang, J. Am. Chem. Soc. 2013, 135, 8468-8471; S. Koeller, G. Bernardinelli, C. Piguet, Dalton Trans. 2003, 2395-2404; T. B. Jensen, E. Terazzi, K.-L. Buchwalder, L. Guenee, H. Nozary, K. Schenk, B. Heinrich, B. Donnio, D. Guillon, C. Piguet, Inorg. Chem. 2010, 49, 8601-8619.
- [13] A. M. Johnson, M. C. Young, X. Zhang, R. R. Julian, R. J. Hooley, J. Am. Chem. Soc.
 2013, 135, 17723-17726.
- [14] E. Peris, J. C. Lee Jr., J. R. Rambo, O. Eisenstein, R. H. Crabtree, J. Am. Chem. Soc.
 1995, 117, 3485-3491; P. Gilli, V. Bertolasi, V. Ferretti, G. Gilli, J. Am. Chem. Soc.
 2000, 122, 10405-10417; C. L. Perrin, J. B. Nielson, Annu. Rev. Phys. Chem. 1997, 48, 511-544; S. J. Grabowski, J. Phys. Org. Chem. 2004, 17, 18-31.
- [15] J. R. Levin, E. J. Schelter, *CIM Proceedings of the Annual Conference of Metallurgists* 2012.
- [16] J. R. Levin, J. Gu, P. J. Carroll, E. J. Schelter, *Dalton Trans.* 2012, 41, 7870-7872.
- [17] F. G. Bordwell, Acc. Chem. Res. 1988, 21, 456-463.
- [18] C. L. Perrin, T. J. Dwyer, *Chem. Rev.* 1990, 90, 935-967; J. Jeener, B. H. Meier, P. Bachmann, R. R. Ernst, *J. Chem. Phys.* 1979, 71, 4546-4553.
- [19] J. R. Robinson, J. Gu, P. J. Carroll, E. J. Schelter, P. J. Walsh, J. Am. Chem. Soc. 2015, 137, 7135-7144.
- [20] Coord. Chem. Rev. 1996, 150, 185-220.
- J. D. Heise, D. Raftery, B. K. Breedlove, J. Washington, C. P. Kubiak, Organometallics
 1998, 17, 4461-4468; S. P. Babailov, Prog. Nucl. Magn. Reson. Spectrosc. 2008, 52, 1-199

21; S. Fischer, P. D. J. Grootenhuis, L. C. Groenen, W. P. van Hoorn, F. C. J. M. van
Veggel, D. N. Reinhoudt, M. Karplus, *J. Am. Chem. Soc.* 1995, *117*, 1611-1620; M.-C.
Chen, J. A. S. Roberts, T. J. Marks, *J. Am. Chem. Soc.* 2004, *126*, 4605-4625; F. A.
Dunand, S. Aime, A. E. Merbach, *J. Am. Chem. Soc.* 2000, *122*, 1506-1512; S. Aime, M.
Botta, G. Ermondi, *Inorg. Chem.* 1992, *31*, 4291-4299; L. Di Bari, S. Di Pietro, G.
Pescitelli, F. Tur, J. Mansilla, J. M. Saa, *Chem. Eur. J.* 2010, *16*, 14190-14201.

- [22] J. C. Cobas, M. Martin-Pastor, 1.0 ed., Mestrelab Research, Santiago de Compostela.
- [23] D. C. Bradley, J. S. Ghotra, F. A. Hart, J. Chem. Soc., Dalton Trans. 1973, 1021-1023.
- [24] Bruker, Bruker AXS Inc., Madison, Wisconsin, USA, 2009.
- [25] Bruker, Bruker AXS Inc., Madison, Wisconsin, USA, 2009.
- [26] G. M. Sheldrick, University of Gottingen, Germany, 2008.
- [27] G. M. Sheldrick, University of Gottingen, Germany, 2007.
- [28] G. M. Sheldrick, Acta Cryst. 2008, A64, 112-122.

CHAPTER 4

Control of cerium oxidation state through metal complex secondary structures

Abstract:

A series of alkali metal cerium diphenylhydrazido complexes, $M_x(sol)_y[Ce(PhNNPh)_4]$, M = Li, Na, and K; x = 4 (Li and Na) or 5 (K); y = 4 (Li), 8 (Na), or 7 (K); sol = py (Li, Na, and K) or Et₂O (Li), were synthesized to probe how the secondary coordination sphere would modulate electronic structures at a cerium cation. The resulting electronic structures of the heterobimetallic cerium diphenylhydrazido complexes were found to be strongly dependent on the identity of the alkali metal cations. When $M = Li^+$ or Na⁺, the cerium(III) starting material was oxidized with concomitant reduction of 1,2diphenylhydrazine to aniline. Reduction of 1,2-diphenylhydrazine was not observed when $M = K^+$, and the complex remained in the cerium(III) oxidation state. Oxidation of the cerium(III) diphenylhydrazido complex to the Ce(IV) diphenylhydrazido was achieved through a cation exchange with simple alkali metal salts. UV-Vis spectroscopy, FTIR spectroscopy, XAS spectroscopy, electrochemistry, magnetic susceptibility, and

DFT were used to probe the oxidation state and the electronic changes that occurred at the metal center.

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4.1 Introduction

Electron transfer (ET) processes at metal cations are a fundamental tenet of natural and synthetic inorganic chemistry. The lanthanides predominantly form complexes in the Ln(III) oxidation state, and for most of the lanthanides, electron transfer processes are energetically inaccessible.^[1] Cerium is unique among the lanthanides because of its accessible +4 oxidation state ($E^{\circ}(Ce^{IV/III}) = 1.40 \text{ V vs. Fc/Fc}^+$).^[1-3] Considering its standard reduction potential, Ce(IV) complexes are best known as oneelectron oxidants in inorganic and organic syntheses, as well as in materials chemistry.^{[4-} ^{7]} For example, ceric ammonium nitrate (CAN), has been employed in water oxidation, oxidation of alcohols, oxidative carbon-carbon coupling reactions, and in oxidative deprotection of ketones and acetals.^[4] While most molecular inorganic and organic applications have focused on the use of Ce(IV) as an oxidant, materials chemistry has successfully utilized cerium in both oxidative and reductive contexts. For instance, cerium(IV) dioxide (ceria) and related materials are applied in catalytic redox cycling devices, such as fuel cells,^[7, 8] catalytic converters,^[9] and the water-gas-shift reaction,^[10] and also in heterogeneous catalysis for organic reactions and fuel production.^[6, 11]

We have studied the electrochemical behavior of a variety of cerium complexes, and have found that, despite the isolated nature of the cerium $4f^4$ electron, electron donating ligands shift the Ce^{IV/III} redox potential to more reducing values, e.g. $E^{\circ}(Ce^{IV/III}[2-({}^{t}BuNO)py]_4) = -1.95 V vs. Fc/Fc^+$, where 2-(${}^{t}BuNO$)py is *N-tert*-butyl-*N*-2pyridylnitroxide.^[12] Depending on the nature of the ligand environment, Ce(III) has been shown to act as a mild reductant in some cases.^[13]

To further expand molecular cerium redox chemistry, we recently have focused on understanding the thermodynamic and kinetic factors that underlie cerium redox reactions. We demonstrated that in the cerium heterobimetallic frameworks, $[M_3(THF)_n][Ce(BINOLate)_3] M = Li$, Na, K, Cs and BINOL = (S)-1,1'-bi-2-naphthol, the secondary coordination sphere, namely the identity of M⁺, impacted the rates, thermodynamic potentials, and product outcomes of electron transfer (ET) reactions.^[14, 15] Furthermore, natural redox systems modulate the thermodynamic potentials and rates of electron transfer using secondary coordination sphere interactions.^[16] Given these observations, we were compelled to investigate cerium heterobimetallic complexes with redox active ligands to express and modulate cerium-ligand intramolecular redox chemistry.

Zdilla and coworkers recently reported a Li^+ heterobimetallic diphenylhydrazido complex that effectively stabilized high valent Mn(IV) cations despite the reducing character of the ligand and the oxidizing character of Mn(IV) (see Scheme 4.1.1).^[17-19] Intrigued by these results and the relative scarcity of electrochemical properties reported for anionic nitrogen donors at cerium,^[20] we initiated studies of a series of heterobimetallic alkali metal- cerium diphenylhydrazido complexes. Herein, we report that the choice of alkali metal cation in the complexes $M_x(sol)_y[Ce(PhNNPh)_4]$, M = Li, Na, and K; x = 4 (Li and Na) or 5 (K); y = 4 (Li), 8 (Na), or 7 (K); and sol = py (Li, Na, K) or Et₂O (Li), resulted in variable electronic structures. Our results showed the smaller, harder alkali metal cations Li⁺ and Na⁺ stabilized the tetravalent cerium cation whereas the larger, softer K⁺ formed a thermally unstable cerium(III) complex. To the best of our knowledge, these results are the first examples of the use of secondary coordination sphere effects to modulate the oxidation state of a lanthanide cation.



Scheme 4.1.1. Synthesis of the lithium manganese diphenylhydrazido complex.^[18, 19] Reproduced by permission of The Royal Society of Chemistry.

4.2 Results and Discussion

4.2.1 Synthesis of M_{4.5}(sol)[Ce(PhNNPh)₄]

Dark purple $Li_4(Et_2O)_4[Ce(PhNNPh)_4]$ (4.1.1) was synthesized by a layered reaction of $Ce(N(SiMe_3)_2)_3$ with 4 equiv 1,2-diphenylhydrazine in diethyl ether and 4 equiv $LiN(SiMe_3)_2$ dissolved in hexanes affording crystals in 71 % yield (Scheme 4.2.1). The potassium analogue, however, did not react after three days in diethyl ether because of the reactant and product's insolubility in the poorly coordinating solvent. To stabilize the potassium product, the coordinating solvent pyridine needed to be used for the synthesis and crystallization of polymeric $K_5(py)_7[Ce(PhNNPh)_4]$ (4.3).

 $K_5(py)_7[Ce(PhNNPh)_4]$ (4.3) was synthesized in pyridine by reaction of Ce[N(SiMe_3)_2]_3 with 4 equiv 1,2-diphenylhydrazine and 5 equiv KN(SiMe_3)_2. Complex 4.3 was isolated as dark brown needles in 65 % yield following crystallization from a concentrated pyridine solution of the reaction mixture that had been layered with hexanes (Scheme 4.2.1). Initial attempts to isolate analogous cerium products with Li⁺ or Na⁺ cations in 100% pyridine resulted in poor crystalline yield. Thus, the synthesis was modified to improve isolated yield. Dark purple Li₄(py)₄[Ce(PhNNPh)₄] (4.1.2) and Na₄(py)₈[Ce(PhNNPh)₄] (4.2) were synthesized by a layered reaction of Ce[N(SiMe_3)_2]_3 with 4 equiv 1,2-diphenylhydrazine in a mixture of Et₂O and stoichiometric pyridine and 4 equiv MN(SiMe_3)₂, M = Li or Na, in 75 % and 63 % yield respectively (Scheme 4.2.1).

Alternatively, to improve solubility of polymeric $\{K_5(py)_7[Ce(PhNNPh)_4]\}_n$ in poorly coordinating solvents as well as form a better comparison to the Li and Na analogues **4.1.2** and **4.2**, 1 equiv 18-crown-6 dissolved in Et₂O was layered over 1 equiv complex **4.3** dissolved in pyridine to crystallize a complex similar to "K(py)₂(crown)K₄(py)₈[Ce(PhNNPh)₄]" (see Figure 4.4.27). Powder formed, and the resulting complex was not able to be crystallized. In addition, Li₄(DME)₄[Ce(PhNNPh)₄] and Na₄(Et₂O)₄[Ce(PhNNPh)₄] were also crystallized from DME and Et₂O respectively, but no further characterization was made (Table 4.4.13 and Figure 4.4.28).


Scheme 4.2.1. Syntheses of complexes 4.1.1, 4.1.2, 4.2, and 4.3. Reproduced by permission of The Royal Society of Chemistry.

Dissolution of the isolated product **4.1.1** in pyridine changed the solution structure dramatically, just like the alkali metal cerium naphtholate complexes in chapters two and three (Figure 4.2.1). The ¹H and ⁷Li NMR spectra of Li₄(Et₂O)₄[Ce(PhNNPh)₄] (**4.1.1**) in non-coordinating solvents like benzene- d_6 showed resonances only in the diamagnetic region, whereas the ¹H and ⁷Li NMR spectra of the complex **4.1.1** in strongly coordinating solvents like pyridine- d_5 had broad resonances in the paramagnetic region (Figure 4.2.1). For example, complex **4.1.1** had one ⁷Li NMR resonance at 0.57 ppm in C₆D₆, and when the same complex was dissolved in pyridine- d_5 , the ⁷Li NMR resonance shifted to 36.27 ppm. This indicated that the solvation environment at the Li⁺ cation played a large role in determining the products in solution. While the least soluble product in 100 % pyridine, complex **4.1.2**, crystallized from the product mixture, it obviously was not the only product in solution. It was likely this solvent dependence that impacted isolated yields of complexes **4.1.2** and **4.2.1** in 100 % pyridine.



Figure 4.2.1. ¹H and ⁷Li spectra of complex **4.1.1** in benzene- d_6 (top) and pyridine- d_5 (bottom).

Alkali metal cluster formation in pyridine also impacted yield. The formation of the alkali metal clusters was dependent on the crystallization conditions of complexes **4.1.2** and **4.2**. Orange crystals of $\text{Li}(\text{py})_4[\text{Li}_5(\text{PhNNPh})_3(\text{py})_3]$ were collected from the product mixture to form complex **4.1.2** (Figure 4.2.2). The isolation of the insoluble orange crystals exemplified the complex equilibria that existed in the formation and isolation of the desired product, complex **4.1.2**. The solvent polarity was able to shift the solution equilibrium to favor formation of the alkali metal clusters along with the formation of an unidentified Ce(III) product.



Figure 4.2.2. Thermal ellipsoid plot of the complex Li(py)₄[Li₅(PhNNPh)₃(py)₃], an unintended side product from the reaction to form complex **4.1.2**.

4.2.2 Structural characterization of M_{4.5}(sol)[Ce(PhNNPh)₄]

X-ray crystal structures revealed that **4.1.1**, **4.1.2**, and **4.2** formed formally Ce(IV) complexes by charge balance, with dianionic diphenylhydrazido ligands and four alkali metal cations per cerium cation in the formula unit (Figures 4.2.3 and 4.2.4). Within the structures, the alkali metal cations bridged neighboring 1,2-diphenylhydrazido units. Surprisingly, **4.3** formed an extended coordination polymer in which the potassium ions interacted both intramolecularly through bridging neighboring hydrazido ligands and intermolecularly through K–arene interactions within the ligands at K(4) and K(5) (Figure 4.2.5). The most notable difference in the structure of **4.3**, however, was the

presence of an additional K^+ cation per formula unit, suggesting that **4.3** was a formally Ce(III) complex.

The N–N bond lengths in complexes **4.1.1**, **4.1.2**, **4.2**, and **4.3** were consistent with single bonds ranging from 1.451(2)–1.466(3) Å.^[18, 21] The Ce–N distances for **4.1.2** ranged from 2.4408(14)–2.4199(13) Å while those for **4.2** were slightly shorter at 2.373(2)–2.398(2) (Table 4.2.1). The shortened Ce–N distances for **4.2** compared to **4.1.2** were consistent with the stronger Lewis acidity of Li⁺ cations in **4.1.2** versus Na⁺ cations in **4.2**. The Li⁺ cations reduced the relative charge density at the nitrogen atoms for binding with the cerium cation, compared to the Na⁺ cation in **4.2**. This effect was reversed in **4.3**, however, with Ce–N bonds ranging from 2.449(3)–2.636(4), in support of bonding to the larger cerium(III) cation in that complex. This set of bond distances also indicated that a change in secondary coordination sphere caused a change in cerium electronic structure.



Figure 4.2.3. 30 % thermal ellipsoid plots of $Li_4(Et_2O)_4[Ce(PhNNPh)_4]$ **4.1.1** (left) and $Li_4(py)_4[Ce(PhNNPh)_4]$ **4.1.2** (right). Hydrogen atoms are omitted for clarity. Selected bond distances for $Li_4(Et_2O)_4[Ce(PhNNPh)_4]$ (Å): Ce(1)-N(1) 2.4665(10), Ce(1)-N(2) 2.3915(10), N(1)-N(2) 1.4578(13), Li(1)-N(1) 1.984(2), Li(2)-N(1) 2.639(2), Li(2)-N(2) 2.018(2). Selected bond distances for $Li_4(py)_4[Ce(PhNNPh)_4]$ (Å): Ce(1)-N(1) 2.4408(13), Ce(1)-N(2) 2.4199(13), N(1)-N(2) 1.451(2), Li(2)-N(1) 2.018(3), Li(2)-N(1) 2.018(3), Li(1)-N(2) 1.995(3). Adapted by permission of The Royal Society of Chemistry.



Figure 4.2.4. 30 % thermal ellipsoid plots of $Na_4(py)_8[Ce(PhNNPh)_4]$ (4.2). Hydrogen atoms are omitted for clarity. Selected bond distances for $Na_4(py)_8[Ce(PhNNPh)_4]$ (Å): Ce(1)-N(1) 2.390(3), Ce(1)-N(2) 2.373(2), N(1)-N(2) 1.462(3), Na(1)-N(1) 2.853(3),Na(1)-N(2) 2.630(3), Na(1)-N(3) 2.535(3). Adapted by permission of The Royal Society of Chemistry.



Figure 4.2.5. 30 % thermal ellipsoid plots of $K_5(py)_7[Ce(PhNNPh)_4]$ (**4.3**). Hydrogen atoms, coordinated pyridine, and potassium-arene interactions are omitted for clarity. Selected bond distances (Å): Ce(1)–N(1) 2.564(3), Ce(1)–N(2) 2.480(4), N(1)–N(2) 1.465(5), K(2)–N(1) 3.044(4), K(2)–N(2) 2.877(4). Adapted by permission of The Royal Society of Chemistry.

To better understand the differences between complexes **4.1–4.3**, we established the geometrical changes to the Ce primary coordination sphere using shape parameters for eight coordinate complexes (Table 4.4.5 in section 4.4).^[22] The shape parameters showed that each structure could be described by distinct eight-coordinate geometries with complexes **4.1.2** and **4.2** resembling dodecahedra (D_{2d}) and complex **4.3** resembling

a square antiprism (D_{4d}). However, complexes **4.1–4.3** were heavily distorted from the idealized structures described by shape parameters which made it difficult to express the three-dimensional structural differences between each of the complexes. Because of the distortions, the parameter τ_4 , which typically indicated the degree of planarity in four-coordinate structures, was found to be a more convenient metric to describe the system (Figure 4.2.6, Table 4.2.1).^[23] The four centroids between the N–N bonds of the ligands were used to calculate the τ_4 parameters, where a τ_4 value of 0 indicated a planar distribution of the centroids and a value of 1 indicated a tetrahedral distribution of the centroids and a value of 1 indicated a tetrahedral distribution of the structure changed from pseudo-planar (**4.1**) $\tau_4 = 0.199$ (**4.1.1**) and 0.110 (**4.1.2**) to pseudo-tetrahedral (**4.3**) $\tau_4 = 0.773$ (Figure 4.2.6, Table 4.2.1). By the τ_δ parameter, a modified τ_4 parameter that defined a numeric region for the sawhorse geometry,^[24] also described complex **4.1.1** as distorted square planar and complexes **4.2–4.3** as distorted tetrahedra (Table 4.2.1).



Figure 4.2.6. Comparison of the core structures of complexes **4.1.2**, **4.2**, and **4.3**. Adapted by permission of The Royal Society of Chemistry.

Table 4.2.1. Unique Ce(1)–N and N–N bonds of complexes **4.1.1**, **4.1.2**, **4.2**, and **4.3** measured by X-ray crystallography or DFT calculations. Reproduced by permission of The Royal Society of Chemistry.

Complex	Ce(1)–N(x)	Ce(1)–N(x)	N–N	N–N	$ au_4$	$ au_4$	$ au_\delta$
	(exp, Å)	$(\text{calc}, \text{\AA})^a$	(exp, Å)	$(\text{calc}, \text{\AA})^a$	(expt.)	(calc.) ^a	(expt.)
4.1.1	2.4408(14)	2.464	1.451(2)	1.441	0.199	0.000	0.199
	2.4199(13)						
4.1.2	2.4665(10)	2.464	1.4578(13)	1.441	0.110	0.000	0.110
	2.3915(10)						
4.2	2.390(3)	2.439	1.462(3)	1.441	0.663	0.498	0.660
	2.373(2)	2.443	1.461(3)				
	2.380(3)		1.457(3)				
	2.381(2)		1.466(3)				
	2.398(2)						
	2.374(2)						
	2.397(2)						
	2.394(2)						
4.3	2.564(3)	2.582	1.465(5)	1.448	0.773	0.709	0.772
	2.480(4)	2.488	1.449(5)				
	2.415(4)		1.459(5)				
	2.636(4)		1.456(5)				
	2.499(3)						
	2.482(4)						
	2.449(3)						
	2.494(3)						

^{*a*} Pyridine was replaced with OMe₂ in the calculated structures, resulting in the following calculated complexes: $Li_4(OMe_2)_4[Ce(PhNNPh)_4]$, $Na_4(OMe_2)_4[Ce(PhNNPh)_4]$, and $K_4(OMe_2)_4[Ce(PhNNPh)_4]^-$.

4.2.3 Balancing the chemical equation

Because the structural analyses seemed to indicate that a spontaneous oxidation from Ce(III) to Ce(IV) occurred to form complexes **4.1.1**, **4.1.2**, and **4.2**, we examined the reaction mixtures to determine the species that had been reduced. Reductive cleavage of 1,2-diphenylhydrazine ($E_{1/2} = -1.7$ V versus Fc/Fc⁺ in DMSO)^[25] by metal complexes, including f-block metals, has been well-established to yield aniline, metal anilides, and metal diphenylamides.^[17-19, 26] We postulated the balanced equation in Scheme 4.2.2 was at work in the synthesis of complexes **4.1** and **4.2**, where the electron transfer occurred from a Ce(III) cation to 0.5 equiv 1,2-diphenylhydrazinato to form aniline.^[19] Indeed, aniline was detected by ¹H NMR spectroscopy of the reaction mixture of complex **4.1.2** (Figure 4.2.7). As expected, the reaction mixture for complex **4.3** did not show any evidence of aniline formation (Figure 4.2.8).



Scheme 4.2.2. The balanced chemical equation to form complex 4.3 (top) and complexes4.1 and 4.2 (bottom). Reproduced by permission of The Royal Society of Chemistry.



Figure 4.2.7. ¹H NMR spectra of (top) the filtrate from the reaction to synthesize $Li_4(py)_4[Ce(PhNNPh)_4]$ (**4.1.2**) collected in C_6D_6 (middle) the filtrate spiked with aniline, and (bottom) the filtrate spiked with aniline and 1,2-diphenylhydrazine. Reproduced by permission of The Royal Society of Chemistry.



Figure 4.2.8. ¹H NMR spectrum of the filtrate from the reaction to synthesize $K_5(py)_7[Ce(PhNNPh)_4]$ (**4.3**) collected in C₆D₆. Reproduced by permission of The Royal Society of Chemistry.

The reduction of 1,2-diphenylhydrazine by Ce(III) was surprising as the reduction potential of 1,2-diphenylhydrazine was thermodynamically inaccessible.^[3, 25] However, coordination of substrates to one or more Lewis acids had been shown to promote electron transfer.^[13, 27, 28] Fukuzumi and coworkers quantified the effect of Lewis acid coordination to O₂ and its reduction with (TPP)Co (TPP = tetra-*p*-tolylporphyrin).^[28] Similarly, the reduction of 1,2-diphenylhydrazine by Ce(III) in the formation of complexes **4.1–4.3** was determined to be dependent on the Lewis acidity of the countercation, where K⁺ was not sufficiently Lewis acidic to promote the reduction of 1,2-diphenylhydrazine.

4.2.4 Oxidation state assignment using magnetic measurements and XAS spectroscopy

Since the X-ray crystal structures and the species identified in the reaction mix suggested that the formal oxidation state varied with the alkali metal in the secondary coordination sphere, we decided to further investigate the electronic structure at the metal center by performing magnetic and Ce L_{III} -edge XAS spectroscopic measurements on complexes **4.1.2–4.3**. The oxidation state of complex **4.3** was corroborated with room temperature magnetic susceptibility measurements using Evans' method^[29] and solid state SQUID magnetometry (Table 4.4.1 in section 4.4 and Figure 4.2.9). The room temperature γT products measured by both techniques, $\gamma T = 0.57$ emu K mol⁻¹ by Evans' method and $\chi T = 0.70$ emu K mol⁻¹ by SQUID magnetometry, were similar to other reported Ce(III) complexes.^[30] Temperature dependent susceptibility plots of Ce(III) complexes typically show a decrease in the χT product at low temperatures due to thermal depopulation of crystal field levels,^[31] which we also observed in our data (Figure 4.2.9). The low temperature χT product was also similar to previously reported Ce(III) complexes.^[30] Complexes **4.1.2** and **4.2** showed only a small paramagnetic shift when Evans' method was applied (0.01 ppm compared to 0.1 ppm seen in complex 4.3, see section 4.4, Table 4.4.1). Similarly, room temperature χ T products obtained by SQUID magnetometry were small, $\gamma T = 0.18$ emu K mol⁻¹ and $\gamma T = 0.089$ emu K mol⁻¹ for complexes 4.1.2 and 4.2 respectively (Figure 4.2.9). The small paramagnetic responses from complexes 4.1.2 and 4.2 were attributed to a small amount of

paramagnetic impurity that was consistent over multiple measurements (<5 % since the impurity was unobserved by NMR spectroscopy).



Figure 4.2.9. Temperature dependent magnetic data measured by SQUID magnetometry for complexes **4.1.2** (blue circles), **4.2** (red diamonds), and **4.3** (green squares). Reproduced by permission of The Royal Society of Chemistry.

Further examination of the cerium oxidation state in complexes **4.1–4.3** was attempted by XAS spectroscopy. However, complex **4.3** was thermally unstable in the

solid state and decomposed prior to measurement of the Ce L_{III} -edge XAS spectroscopy data (Figure 4.4.4, section 4.4), resulting in a low signal measurement and a measured Ce(IV) character. Complexes **4.1.2** and **4.2** were also thermally unstable and partially decomposed prior to measurement of the Ce L_{III} -edge. Because of the measureable product decomposition of complexes **4.1.2** and **4.2**, we could not reliably assign oxidation state based on these results.

4.2.5 Spectroscopic and electrochemical characterization

To support the assignment of **4.1** and **4.2** as formally Ce(IV) complexes and **4.3** as a formally Ce(III) complex, UV-Vis spectroscopy, FTIR spectroscopy, and electrochemistry were performed on each of these complexes. UV-Vis spectroscopy of complexes **4.1.2** and **4.2** in non-coordinating solvent showed broad ligand-to-metal charge transfer bands which are defining features in many Ce(IV) complexes, corroborating the oxidation state assignment from the magnetic data (Figures 4.2.10–4.2.11).^[14, 32] When complexes **4.1.2** and **4.2** were dissolved in coordinating solvents, however, the UV-Vis spectra drastically changed (Figures 4.2.10–4.2.11). The UV-Vis spectra of complexes **4.1.2** and **4.2** dissolved in pyridine were similar to those of complex **4.3**, as well as the ligand that had been deprotonated by MN(SiMe₃)₂ where M = Li, Na, K (Figures 4.2.10–4.2.13). The absence of the ligand to metal charge transfer band in pyridine indicated that the solution structure and electronic structure of complexes **4.1** and **4.2** were strongly solvent dependent, reflecting what already was observed by NMR spectroscopy (Figure 4.2.1).



Figure 4.2.10. UV-Vis spectra of Li₄(py)₄[Ce(PhNNPh)₄] (**4.1.2**) collected in pyridine (blue) and fluorobenzene (red). Reproduced by permission of The Royal Society of Chemistry.



Figure 4.2.11. UV-Vis spectra of $Na_4(py)_8[Ce(PhNNPh)_4]$ (**4.2**) collected in pyridine (blue) and fluorobenzene (red). Reproduced by permission of The Royal Society of Chemistry.



Figure 4.2.12. UV-Vis spectrum of K₅(py)₇[Ce(PhNNPh)₄] (4.3) collected in pyridine.

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Figure 4.2.13. UV-Vis spectra of 1,2-diphenylhydrazine deprotonated with KN(SiMe₃)₂ (red), NaN(SiMe₃)₂ (blue) or LiN(SiMe₃)₂ (green) collected in pyridine. Reproduced by permission of The Royal Society of Chemistry.

FTIR spectroscopy was also performed to probe the changes in Ce-N and N-N stretching frequencies that were expected to accompany a change in formal oxidation state. We expected that the Ce-N would decrease in energy and the N-N stretching modes would increase in energy from complex 4.1 to 4.3 based on the Lewis acidity of both the Ce ion and the alkali metal in each complex. Compared to Ce(III) cations, the more Lewis acidic Ce(IV) cation was expected to accept more electron density from the diphenylhydrazido ligands through σ -bonding with the N–N units (see Figure 4.4.22 in section 4.4), increasing the Ce–N energy and reducing the electron density in the N–N bonds. We also expected that the alkali metals would similarly withdraw more electron density in the N–N bonds with increasing Lewis acidity. To identify the vibrational modes in the experimental spectra, DFT calculations were used (see section 4.4 for further details). DFT computed vibrational spectra typically overestimate the energies of the vibrational modes,^[33, 34] but apart from this overestimation, the calculated and experimental spectra were in good agreement (Table 4.2.2, see Figures 4.4.11, 4.4.15, and 4.4.19 in the section 4.4).

Table 4.2.2. Energies of the N–N stretch vibrational modes of **4.1**, **4.2**, and **4.3** determined experimentally and by calculations. Spectrometer errors for the experimental spectra = ± 0.034 cm⁻¹.^[35] Reported calculated values were not scaled, see text for details.^[33, 34] Reproduced by permission of The Royal Society of Chemistry.

Complex	N–N stretch	N–N stretch
	$(\mathrm{cm}^{-1},\mathrm{sol}=\mathrm{py})$	$(\mathrm{cm}^{-1},\mathrm{sol} =$
		OMe ₂)
Li ₄ (sol)[Ce(PhNNPh) ₄] (4.1)	1255	1284
Na ₄ (sol)[Ce(PhNNPh) ₄] (4.2)	1257	1289
$K_4(OMe_2)_4[Ce(PhNNPh)_4]^-$ (4.3.2 ⁻)		1303
$\{K_5(py)_7[Ce(PhNNPh)_4]\}_n$ (4.3)	1265	

The intense absorption band of the N–N stretch in complexes **4.1.2**, **4.2**, and **4.3** in both the experimental and calculated spectra allowed for assignment of that vibrational mode (see section 4.4, Figures 4.4.11, 4.4.15, and 4.4.19). The Ce–N vibrational modes, however, were difficult to unambiguously assign because of their low intensities and overlap with ligand features. Complex **4.3** showed a ~10 cm⁻¹ increase in energy of the N–N stretching mode from complexes **4.1.2** and **4.2**, consistent with a change in cerium oxidation state. Because the N–N stretching mode found in complexes **4.1.2** and **4.2** differed by only 2 cm⁻¹ despite the change in Lewis acidity between Li⁺ and Na⁺, the

more significant factor to the increase in energy between these complexes was evidently the variable oxidation state at the central Ce cation (Table 4.2.2). Overall, based on the spectroscopic and magnetic measurements, the oxidation state of the cerium metal center was evidently impacted by the identity of the alkali metal cation in the secondary coordination sphere.

To better understand how the alkali metal cation in the secondary coordination sphere influenced the redox properties of the cerium metal center, cyclic voltammetry was performed on complexes **4.1.2–4.3** (see Figures 4.2.14–4.2.16, and Figures 4.4.1– 4.4.3 in section 4.4). Because of the instability of complexes **4.1.2** and **4.2** in coordinating solvents and the insolubility of complex **4.3** in non-coordinating solvents, the electrochemistry of complexes **4.1.2** and **4.2** was performed in fluorobenzene, and in THF for complex **4.3**. Beginning the scans from their rest potentials in each case, the $Ce^{IV/III}$ reductions (in complexes **4.1 and 4.2**) and the $Ce^{III/IV}$ oxidation waves (complex **4.3**) were reversible for complexes **4.1.2–4.3**, where $\Delta E = 50$ mV for complex **4.3** in THF, and $\Delta E = 60–70$ mV for complexes **4.1.2** and **4.2** in fluorobenzene. The electrochemical reversibility of the Ce^{IV/III} redox event indicated that outer sphere electron transfer between cerium and the electrode was rapid in all three complexes, and that there would be little ligand reorganization upon oxidation or reduction of the cerium cation in any geometry.

In order to compare the electrochemical potentials of complexes **4.1.2–4.3**, we used 1,2-diphenylhydrazine, which was measured in both solvents, to normalize the

influence of the solvent on the electron transfer between the electrode and the analyte. Based on the normalization, the $E_{1/2}$ of the Ce^{IV/III} reduction potential of complexes **4.1.2** and **4.2**, and the $E_{1/2}$ of the Ce^{III/IV} oxidation potential of complex **4.3** were centered at – 1.93 V versus Fc/Fc⁺, –1.88 V versus Fc/Fc⁺, and –2.02 V versus Fc/Fc⁺ respectively in fluorobenzene, indicating that the 1,2-diphenylhydrazido ligand strongly stabilized the Ce(IV) oxidation state.



Figure 4.2.14. Cyclic voltammetry of 1,2-diphenylhydrazine (red, top) and $Li_4(py)_4[Ce(PhNNPh)_4]$ (**4.1.2**) (black, bottom) in a solution of [NBu₄][BAr^F₄] in fluorobenzene, v = 100 mV/s. Reproduced by permission of The Royal Society of Chemistry.



Figure 4.2.15. Cyclic voltammetry of 1,2-diphenylhydrazine (red, top) and $Na_4(py)_8[Ce(PhNNPh)_4]$ (4.2) (black, bottom) in a solution of $[NBu_4][BAr^F_4]$ in fluorobenzene, v = 100 mV/s. Reproduced by permission of The Royal Society of Chemistry.



Figure 4.2.16. Cyclic voltammetry of 1,2-diphenylhydrazine (red, top) and $K_5(py)_7[Ce(PhNNPh)_4]$ (**4.3**) (black, bottom) in a solution of $[NPr_4][BAr^F_4]$ in THF, v = 100 mV/s. Reproduced by permission of The Royal Society of Chemistry.

4.2.6 Ce(IV) and alkali metal cation exchange reactions

Considering the oxidation potential of complex 4.3, we reasoned that a potassiumsupported Ce(IV) diphenylhydrazido analogue should be accessible. In an effort to isolate a Ce(IV) diphenylhydrazido complex with K^+ cations in the secondary coordination sphere, we reacted 1,2-diphenylhydrazine with a formally Ce(IV) protonolysis starting material, $Ce[N(SiHMe_2)_2]_4$.^[36, 37] The addition of 1,2-diphenylhydrazine to the Ce(IV) starting material however resulted in immediate reduction (Scheme 4.2.3) and subsequent reaction with $KN(SiMe_3)_2$ formed complex 4.3, which was detected by ¹H NMR spectroscopy. Adding 1,2-diphenylhydrazine to a mixture of KH and Ce[N(SiHMe₂)₂]₄ also resulted in the formation of complex 4.3. Presumably, 0.5 equiv azobenzene was the other product that formed in the course of the redox reaction, but this side product was not detected by ¹H NMR spectroscopy (see Figure 4.4.21 in section 4.4). Thus, the presence of alkali metal cations in the secondary coordination sphere were essential in stabilizing the Ce(IV) oxidation state. The alkali metals in solution structurally supported the resultant cerium diphenylhydrazido complex as well as modulated the electronics of the ligands in order to stabilize Ce(IV) and destabilize the ligand oxidation. These observations were consistent with those of Zdilla and coworkers, who discovered that, upon removing the Li⁺ cations in the cluster Li₄Mn₄(μ_3 -N^tBu)₃(N^tBu)(N), the Mn(V) cations reductively eliminated azo-tert-butane.^[38] Oxidation of complex **4.3** also was attempted unsuccessfully using the following oxidants: Ph₃CCl, FcPF₆, CuCl₂, and I₂. In

these cases, either no reaction occurred, azobenzene was produced, or new unidentified products formed (see section 4.4, Figures 4.4.23–4.4.26).



Scheme 4.2.3. Attempted synthesis of $K_4(sol)_2[Ce(PhNNPh)_4]$ starting from a Ce(IV) precursor. Instead, $K_5(py)_7[Ce(PhNNPh)_4]$ (4.3) formed as a result of this reaction (Figure 4.4.21, section 4.4). Reproduced by permission of The Royal Society of Chemistry.

Based on the similar cerium electrochemistry of complexes **4.1.2** and **4.3** and the Ce–N and M–N ($M = Li^+$ and K^+) bond enthalpies, we expected that complex **4.3** should convert to complex **4.1.2** through a cation exchange reaction (Scheme 4.2.4). The successful metathesis of LiI with complex **4.3** in diethyl ether demonstrated that the oxidation state of cerium could be influenced by a change in the secondary coordination sphere (Figure 4.2.17). This reaction likely occurred through a Li⁺ promoted reduction of the 1,2-diphenylhydrazido ligand as well. By ¹H NMR spectroscopy, the reaction appeared to proceed cleanly, but the percent conversion was consistently overestimated. Presumably the resonances of side-products present in the reaction overlapped with the

desired products' resonances. Cation exchange reactions of **4.2** with KI were also successful, where complex **4.3** was the only product evident by ¹H NMR spectroscopy (Figures 4.2.20–4.2.21). In this case, the 1,2-diphenylhydrazido ligand presumably acted as the reductant to form Ce(III) and azobenzene. A complex mixture formed when a cation exchange reaction was attempted with complex **4.1.2** and KI (Figures 4.2.18– 4.2.19). The complex mixture in this case could be as a result of the smaller lattice energy of LiI formation, the poorer solubility of KI, and the weaker M–N interactions with larger alkali metal cations.^[39]

$$K_{5}(py)_{7} \begin{bmatrix} Ph & Ph \\ Ph & Ph \\ N & N \\ I & Ce & N \\ Ph & N & Ph \\ Ph & N & N & N & Ph \\ Ph & N & N & N & Ph \\ Ph & N & N & N & Ph \\ Ph & N & N & N & Ph \\ Ph & N & N & N & Ph \\ Ph & N & N & N & Ph \\ Ph & N & N & N & Ph \\ Ph & N & N & N & Ph \\ Ph & N & N & N & Ph \\ Ph & N & N & N & Ph \\ Ph & N & N & N & Ph \\ Ph & N & N & N & Ph \\ Ph & N & N & N & Ph \\ Ph & N & N & N & N \\ Ph & N & N & N & N \\ Ph & N & N & N & N \\ Ph & N & N & N & N \\ Ph & N & N & N & N \\ Ph & N & N & N & N \\ Ph & N & N & N & N \\ Ph & N & N & N & N \\ Ph & N & N & N & N \\ Ph & N & N \\ Ph & N & N \\ Ph & N &$$

Scheme 4.2.4. Metathesis reaction of complex **4.3** with 4 equiv LiI. Reproduced by permission of The Royal Society of Chemistry.



Figure 4.2.17. ¹H NMR spectrum of the metathesis reaction of complex **4.3** with LiI in C_6D_6 , where 2.0 µL of TMS₂O was used as an internal standard to determine percent conversion (top). To compare the products, the ¹H NMR spectrum of crystals of complex **4.1.2** in C_6D_6 was included (bottom). Reproduced by permission of The Royal Society of Chemistry.



Figure 4.2.18. ¹H (left) and ⁷Li (right) NMR spectra of the metathesis reaction of complex **4.1.2** with 5 equiv KI in pyridine- d_5 . Reproduced by permission of The Royal Society of Chemistry.



Figure 4.2.19. ¹H (left) and ⁷Li (right) NMR spectra of the metathesis reaction of complex **4.1.2** with 5 equiv KI and 0.5 equiv PhNHNHPh in pyridine-*d*₅. Reproduced by permission of The Royal Society of Chemistry.



Figure 4.2.20. ¹H NMR spectrum of the metathesis reaction of complex **4.2** with 5 equiv KI and in pyridine- d_5 (top). To compare products, the ¹H NMR spectrum of pure complex **4.3** in pyridine- d_5 was provided at bottom. Reproduced by permission of The Royal Society of Chemistry.



Figure 4.2.21. ¹H NMR spectrum of the metathesis reaction of complex **4.2** with 5 equiv KI and 0.5 equiv PhNHNHPh in pyridine- d_5 . Reproduced by permission of The Royal Society of Chemistry.

4.3 Conclusions

We have shown that the secondary coordination sphere about cerium 1,2diphenylhydrazido complexes influenced both the primary coordination geometry and the oxidation state of the cerium metal center, making these complexes the first example of a secondary coordination sphere influencing the oxidation state of f-element complexes. The alkali metals in the secondary coordination sphere both facilitated the reduction of the 1,2-diphenylhydrazine to produce a high-valent Ce(IV) complex, and structurally stabilized the high-valent Ce(IV) complexes. Furthermore, alkali metal metathesis had changed the oxidation state at the cerium ion. The use of multiple Lewis acids could be a general strategy to access high valent metal oxidation states.

4.4 Experimental Section

General Methods. Unless otherwise indicated all reactions and manipulations were performed under an inert atmosphere (N_2) using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. Nexus II drybox equipped with a molecular sieves 13X / Q5 Cu-0226S catalyst purifier system. Glassware was oven-dried overnight at 150 °C prior to use. ¹H, ¹³C, and ⁷Li NMR spectra were obtained on a Bruker DMX-300, on a Bruker DMX-360, or on a Bruker DRX-400 Fourier transform NMR spectrometer at 300, 360, and 400 MHz respectively. Chemical shifts were recorded in units of parts per million downfield from residual proteo solvent peaks (¹H), or characteristic solvent peaks (¹³C). The ⁷Li spectra were referenced to external solution standards of LiCl in H₂O. Evans' method was performed on a Bruker BioDRX-500 Fourier transform NMR spectrometer at 500 MHz. Hexamethylcyclotrisiloxane was used as the internal standard for Evans's method experiments. Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility using a Perkin-Elmer Series II 2400 CHNS analyzer. UV-vis-NIR absorption measurements of complexes were performed using a PerkinElmer 950 UV-vis/NIR Spectrophotometer. One mm path length screw cap quartz cells were used with a blank measured before each run. The infrared spectra were obtained from 400–4000 cm⁻¹ using a PerkinElmer 1600 series infrared spectrometer.

Solution spectra were first collected with a background of air, and then the solvent spectrum was subtracted using PerkinElmer software. GC/MS Spectrometry was performed using an Agilent 5937 GC/MS spectrometer with the CI method of ionization. Diethyl ether was used as the volatile solvent, and He as the carrier gas. Materials. Tetrahydrofuran, diethyl ether, hexane, and pentane were purchased from Fisher Scientific. The solvents were sparged for 20 min with dry N₂ and dried using a commercial two-column solvent purification system comprising columns packed with Q5 reactant and neutral alumina respectively (for hexane and pentane), or two columns of neutral alumina (for THF and diethyl ether). Pyridine, also purchased from Fisher Scientific, was freeze-pump-thawed for 4 cycles and stored over 4 Å molecular sieves for three days before use. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. Pyridine-d₅ was stored over 4 Å molecular sieves for three days before use, and benzene- d_6 was dried and stored over potassium for 2 days before use. $Ce[N(SiMe_3)_2]_3^{[40]}$ and $Ce[N(SiHMe_2)_2]_4^{[36, 37]}$ were prepared following published procedures. Li[N(SiMe₃)₂] (Acros) was recrystallized from hot pentane prior to use. $K[N(SiMe_3)_2]$ (Acros) and $Na[N(SiMe_3)_2]$ (Acros) were used as purchased. Hydrazobenzene (Sigma Aldrich, MP Biochemicals, Alfa Aesar) was sublimed under reduced pressure first at 60° C to remove azobenzene, and then at 105° C for further purification prior to use. Alternatively, the hydrazobenzene was purified by fractional recrystallization in toluene layered with pentane.

Electrochemistry. Voltammetry experiments (CV and DPV) were performed using a CH Instruments 620D Electrochemical Analyzer/Workstation and the data were processed using CHI software v 9.24. All experiments were performed in an N2 atmosphere drybox using electrochemical cells that consisted of a 4 mL vial, glassy carbon (3 mm diameter) working electrode, a platinum wire counter electrode, and a silver wire plated with AgCl as a quasi-reference electrode. The working electrode surfaces were polished prior to each set of experiments, and were periodically replaced to prevent the buildup of oxidized product on the electrode surfaces. Potentials were reported versus ferrocene (Fc), which was converted from cobaltocene for calibration at the end of each run.^[3] Solutions employed during CV studies were ~3 mM in analyte. For electrochemistry collected in fluorobenzene, the solution was 100 mM in $[nBu_4N][B(3,5-(CF_3)_2-C_6H_3)_4]$ ([*n*Bu₄N][BAr^F₄]). The electrolyte was changed to 100 mM in [*n*Pr₄N][B(3,5-(CF₃)₂- $C_6H_3_4$] ([*n*Pr₄N][BAr^F₄]) when the solvent was THF. All data were collected in a positive-feedback IR compensation mode. Scan rate dependences of 25–1000 mV/s were performed to determine electrochemical reversibility.



Figure 4.4.1. Isolation scans of $Li_4(py)_4[Ce(PhNNPh)_4]$ (**4.1.2**) in a solution of $[NBu_4][BAr^F_4]$ in fluorobenzene at varying scan rates (top). At bottom, i_p vs. $v^{1/2}$ plot. Reproduced by permission of The Royal Society of Chemistry.



Figure 4.4.2. Isolation scans of Na₄(py)₈[Ce(PhNNPh)₄] (**4.2**) in a solution of [NBu₄][BAr^F₄] in fluorobenzene at varying scan rates (top). At bottom, i_p vs. $v^{1/2}$ plot. Reproduced by permission of The Royal Society of Chemistry.



Figure 4.4.3. Isolation scans of $K_5(py)_7[Ce(PhNNPh)_4]$ (**4.3**) in a solution of $[NPr_4][BAr^F_4]$ in THF at varying scan rates (top). At bottom, i_p vs. $v^{1/2}$ plot. Reproduced by permission of The Royal Society of Chemistry.

Magnetism. Magnetic data were collected on a Quantum Design Multi-Property Measurement System (MPMS-7) with a Reciprocating Sample Option at 1 T from 2 to 300 K and at 2 K and 300 K from 0 to 7 T. Quartz wool was dried at 250 °C prior to use,
plastic drinking straws were evacuated overnight prior to use. The plastic drinking straws themselves were used as the sample holders through heat sealing the plastic tubing. The plastic drinking straws were sealed at one end in a glovebox. Then a ground sample was loaded into the straw and capped with ~10 mg of quartz wool. The other end of the plastic drinking straw was then sealed through application of heat, forming a pouch that contained the sample and the quartz wool. The sample and wool were weighed to the nearest 0.1 mg on a calibrated and levelled Mettler-Toledo AL-204 analytical balance. Corrections for the intrinsic diamagnetism of the samples were made using Pascal's constants.^[41] Data were collected on two independently prepared samples to ensure reproducibility. Evans' method magnetism was collected on complexes **4.1.2** and **4.2** in C₆D₆ and on complex **4.3** in pyridine-*d*₅. The internal standard in all cases was hexamethylcyclotrisiloxane. Each duplicate measurement was run on an independently prepared sample. **Table 4.4.1.** Evans' method results for complexes **4.1.2**, **4.2**, and **4.3**, with hexamethylcyclotrisiloxane as the internal standard. The μ_{eff} found for complexes **4.1.2** and **4.2** are not within the range of Ce(III) complex magnetic moments whereas complex **4.3** is well within the range.^[30] Reproduced by permission of The Royal Society of Chemistry.

Complex	Solvent	Concentration	Δδ (ppm)	μ_{eff} (μ_B)
		(M)		
4.1.2	Toluene- <i>d</i> ₈	0.014	0.011	1.46
4.1.2	Toluene- <i>d</i> ₈	0.020	0.013	1.48
4.2	Toluene- d_8	0.012	0.010	1.54
4.2	Toluene- d_8	0.026	0.015	1.55
4.3	Pyridine-d ₅	0.028	0.126	2.14
4.3	Pyridine-d ₅	0.036	0.148	2.10

X-ray Absorption Spectroscopy. Ce L_{III} -edge XANES data were collected at the Stanford Synchrotron Radiation Lightsource, beamline 11-2, using a Si 220 (phi=0) double monochromator that was detuned to 20 % in order to reduce harmonic contamination. The resulting data have an energy resolution of 3.2 eV. Data were collected in transmission, using a CeO₂ reference to calibrate the energy scale, setting the first inflection point of the CeO₂ absorption to 5723 eV. A linear pre-edge background was subtracted and the data were subsequently normalized at 5800 eV.

Since the compounds are extremely sensitive to oxygen, each sample was ground into a powder, mixed with dry boron nitride as a diluent, and then packed into the slots of a machined aluminum sample holder. Aluminized mylar was affixed to the holder with an indium-wire seal. After packaging, the samples were transported in dry nitrogen-filled containers to the beamline. Sample holders were quickly transferred to the vacuum chamber, exposing the sealed holders to air for less than thirty seconds before pumping out the chamber and collecting the data under vacuum.



Figure 4.4.4. Normalized absorption (A) as a function of the incident X-ray energy (E) in the Ce L_{III} near-edge region at T = 30 K for complexes **4.1.2** (top), **4.2** (bottom left), and **4.3** (bottom right). Red and black traces represent 2 different measurements. Reproduced by permission of The Royal Society of Chemistry.

X-ray Crystallography. X-ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at a temperature of 143(1) K. In all cases, rotation frames were integrated using SAINT,^[42]

producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the SHELXTL^[43] program package for further processing and structure solution on a Dell Pentium 4 computer. The intensity data were corrected for Lorentz and polarization effects and for absorption using TWINABS^[44] or SADABS.^[45] The structures were solved by direct methods (SHELXS-97).^[46] Refinement was by full-matrix least squares based on F² using SHELXL-97.^[46] All reflections were used during refinements. The weighting scheme used was w=1/[$\sigma^2(F_o^2)$ + (0.0907P)² + 0.3133P] where P = (F_o^2 + $2F_c^2$)/3. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model.

Table 4.4.2. Crystallographic parameters for compounds **4.1.1** and **4.1.2**. Reproduced bypermission of The Royal Society of Chemistry.

	4.1.1 (Penn4344)	4.1.2 (Penn4376)
Empirical formula	C ₆₄ H ₈₀ CeLi ₄ N ₈ O ₄	C ₆₈ H ₆₀ N ₁₂ Li ₄ Ce
Formula weight	1193.24	1213.16
Temperature (K)	143(1)	143(1)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	Fddd	Fddd
Cell constants		
a (Å)	11.362(2)	11.4483(7)
b (Å)	41.867(8)	43.060(2)
c (Å)	26.271(5)	24.5220(14)
α (°)	90.00	90.00
β (°)	90.00	90.00

γ (°)	90.00	90.00
V (Å ³)	12497(4)	12088.5(12)
Ζ	8	8
$\rho_{calc} (mg/cm^3)$	1.268	1.333
μ (Mo K α) (mm ⁻¹)	0.780	0.805
F(000)	4976	4976
Crystal size (mm ³)	0.50 x 0.45 x 0.35	0.15 x 0.15 x 0.04
Theta range for data collection	2.44 to 27.49°	1.89 to 27.53°
T	$-14 \le h \le 14, -54 \le k \le 49,$	-14 \leq h \leq 14, -55 \leq k \leq
Index ranges	$-34 \le 1 \le 34$	55, $-31 \le 1 \le 31$
Reflections collected	93774	74593
Independent collections	3580 [R(int) = 0.0212]	3485 [R(int) = 0.0381]
Completeness to theta = 27.49°	99.6%	99.7%
A1 /* /*	Semi-empirical from	Semi-empirical from
Absorption correction	equivalents	equivalents
Max and min. transmission	0.7456 and 0.6730	0.7456 and 0.6883
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	3580 / 0 / 189	3485 / 366 / 257
Goodness–of–fit on F ²	1.128	1.078
Final R indices	R1 = 0.0164, wR2 =	R1 = 0.0248, wR2 =
[I>2sigma(I)]	0.0421	0.0610
D indiana (all data)	R1 = 0.0171, wR2 =	R1 = 0.0300, wR2 =
K mulces (an data)	0.0430	0.0639
Largest diff. peak and hole	0.315 and -0.187	0.589 and -0.187

Tab	ole	4.4.3.	Crys	tallog	raphi	c para	ameter	s for co	mpoun	ds 4.2	and 4 .	3. Re	produ	iced b	y
				-	. ~		0.01								

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	4.2 (Penn4364)	4.3 (Penn4331)
Empirical formula	C ₈₈ H ₈₀ CeN ₁₆ Na ₄	C ₈₃ H ₇₅ CeN ₁₅ K ₅
Formula weight	1593.76	1618.20
Temperature (K)	143(1)	143(1)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	P1	Pt
Cell constants		
a (Å)	13.9504(7)	15.2003(12)
b (Å)	16.2467(9)	15.4668(12)
c (Å)	19.0053(11)	18.0353(14)
α (°)	83.136(3)	93.849(5)
β (°)	83.696(3)	101.333(5)
γ (°)	84.993(3)	107.292(5)
$V(Å^3)$	4238.8(4)	3933.7(5)
Ζ	2	2
ρ_{calc} (mg/cm ³)	1.249	1.366
μ (Mo K α) (mm ⁻¹)	0.611	0.897
F(000)	1644	1662
Crystal size (mm ³)	0.25 x 0.05 x 0.03	0.42 x 0.12 x 0.02
Theta range for data collection	1.42 to 27.61°	1.63 to 27.61°

Inday ranges	$-18 \le h \le 18, -21 \le k \le 21,$	-19 \leq h \leq 19, -20 \leq k \leq	
lindex failges	$-24 \le l \le 24$	19, $-23 \le l \le 23$	
Reflections collected	147398	95153	
Independent collections	19328 [R(int) = 0.0680]	17890 [R(int) = 0.0544]	
Completeness to theta = 27.61°	98.2%	97.9%	
Absorption correction	Semi-empirical from	Semi-empirical from	
	equivalents	equivalents	
Max and min. transmission	0.7456 and 0.6611	0.7456 and 0.6772	
Refinement method	Full-matrix least-squares	Full-matrix least-squares	
Remement method	on F ²	on F ²	
Data / restraints /	19328 / 0 / 983	17890 / 456 / 968	
parameters	1)520707905	170707 1507 700	
Goodness-of-fit on F ²	1.053	1.030	
Final R indices	R1 = 0.0487, wR2 =	R1 = 0.0556, wR2 =	
[I>2sigma(I)]	0.1125	0.1380	
D indiana (all data)	R1 = 0.0649, wR2 =	R1 = 0.0879, wR2 =	
K mulces (an data)	0.1184	0.1570	
Largest diff. peak and hole $(e.Å^{-3})$	2.833 and -1.046	2.264 and -2.044	

 Table 4.4.4. Crystallographic parameters for the lithium cluster

 $Li(py)_4[Li_5(PhNNPh)_3(py)_3]$ (Penn4392).

	Li(py) ₄ [Li ₅ (PhNNPh) ₃ (py) ₃]
	(Penn4392)
Empirical formula	C ₇₁ H ₆₅ N ₁₃ Li ₆

Formula weight	1142.00		
Temperature (K)	143(1)		
Wavelength (Å)	0.71073		
Crystal system	Triclinic		
Space group	Pt		
Cell constants			
a (Å)	15.035(3)		
b (Å)	15.032(3)		
c (Å)	15.266(3)		
α (°)	90.773(9)		
β (°)	99.217(10)		
γ (°)	109.331(9)		
$V(Å^3)$	3205.5(11)		
Z	2		
$\rho_{calc} (mg/cm^3)$	1.183		
μ (Mo K α) (mm ⁻¹)	0.070		
F(000)	1200		
Crystal size (mm ³)	0.40 x 0.28 x 0.10		
Theta range for data collection	1.46 to 27.79°		
Index ranges	-19 \leq h \leq 19, -19 \leq k \leq 17, -19 \leq l \leq		
index ranges	19		
Reflections collected	103708		
Independent collections	14701 [R(int) = 0.0269]		
Completeness to theta = 27.61°	97.0%		
Absorption correction	Semi-empirical from equivalents		
Max and min. transmission	0.7456 and 0.7105		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	14701 / 0 / 812		

Goodness–of–fit on F ²	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0437, wR2 = 0.1156
R indices (all data)	R1 = 0.0547, wR2 = 0.1270
Largest diff. peak and hole $(e.Å^{-3})$	0.534 and -0.403

Calculating τ_4 and τ_{δ} :

The centroids between the four N–N bonds were calculated using Mercury software.^[23]

$$\tau_4 = \frac{360^\circ - (\alpha + \beta)}{141^\circ}$$

 α and β represent the two largest angles θ between one N–N centroid, Ce, and another N– N centroid calculated using Mercury. τ_{δ} is calculated by multiplying the τ_4 parameter by the second to largest angle β divided by the largest angle α .^[24] τ_4 values of 0 indicates a square planar structure ($\tau_{\delta} = 0-0.2$) while 1 implicates a tetrahedral structure ($\tau_{\delta} = 0.63-$ 1). Similar results are obtained when τ is calculated using the largest angles from M–Ce– M, where M = Li, Na, or K.

Shape Parameters:

Table 4.4.5. Shape parameters for complexes **4.1.2**, **4.2**, and **4.3**. ^aIndicates the idealized shape parameters for a rigorous dodecahedron (D_{2d}), square antiprism (D_{4d}), and cube.^[22, 47] Reproduced by permission of The Royal Society of Chemistry.

	$\mathbf{\Phi}_{1}$	Φ_2	δ_1	δ_2	δ_3	δ_4	θ_{A}	θ_{B}	
4.1.2	4.0	4.0	15.0	15.0	40.9	40.9	72.1	79.8	-
4.2	2.0	3.8	30.0	32.4	34.1	35.2	48.8	48.7	
4.3	12.6	25.3	20.2	32.7	35.3	36.8	45.7	45.8	
D_{2d}^{a}	0.0	0.0	29.5	29.5	29.5	29.5	35.2	73.5	
$\boldsymbol{D_{4d}}^{\mathrm{a}}$	24.5	24.5	0.0	0.0	52.4	52.4	57.3	57.3	
<i>Cube</i> ^a	0.0	0.0	0.0	0.0	90.0	90.0	54.7	54.7	

Complex	Ce(1)–N	Ce(1)–N	τ ₄ (exp)	$\tau_4^{(calc)}$
	(avg., Å)	(avg., Å)		
	(exp, sol =	(calc, sol =		
	py)	OMe ₂)		
$Li_4(sol)[Ce(PhNNPh)_4]$ (4.1)	2.430(11)	2.464	0.110	0.000
$Na_4(sol)[Ce(PhNNPh)_4]$ (4.2)	2.386(10)	2.441	0.663	0.498
$K_4(OMe_2)_4[Ce(PhNNPh)_4]$		2.421		0.837
(4.3.2 ⁺)				
$Li_4(OMe_2)_4[Ce(PhNNPh)_4]^-$		2.578		0.116
(4.1.3 ⁻)				
$Na_4(OMe_2)_4[Ce(PhNNPh)_4]^-$		2.559		0.514
(4.2.2 ⁻)				
$K_4(OMe_2)_4[Ce(PhNNPh)_4]^-$		2.535		0.709
(4.3.2)				
$K_{5}(py)_{7}[Ce(PhNNPh)_{4}]$ (4.3)	2.502(69)		0.773	

Table 4.4.6. Ce–N average bond lengths and τ_4 values for both the experimental and calculated complexes. Reproduced by permission of The Royal Society of Chemistry.

Computational Details. All calculations were performed with Gaussian '09 Revision C.01,^[48] with the B3LYP hybrid DFT method. A 28-electron small core effective core potential was applied to cerium with published segmented natural orbital basis set incorporating quasi-relativistic effects,^[49] while the 6-31 G* basis set was applied to all other atoms. Geometry optimizations of **4.1.3** and **4.2.2** were based on their crystal structures, while the geometry optimization of the Ce(IV) structure of 4.3.2 was based off of the crystal structure coordinates of complex **4.2.2**. The coordinates that were input for the geometry optimizations of the anionic complexes were based on the optimized geometry found for the Ce(IV) calculations 4.1.3, 4.2.2, and 4.3.2 with elongated Ce-N bonds. Geometry optimization was attempted with pyridine solvating the alkali metals. However, convergence could not be reached with this system. No other restrictions were placed on the systems besides the spin. All frequency calculations found no negative frequencies, except for the calculation of Li₄(OMe₂)₄[Ce(PhNNPh)₄] which had 4 small negative frequencies less than -17 cm^{-1} , indicating that the optimized structures found were at an energy minimum. Molecular orbitals were rendered using Chemcraft v. 1.6.^[50]

Optimized Coordinates for Ce(IV) Calculations:

Table 4.4.7. Li₄(OMe₂)₄[Ce(PhNNPh)₄] (**4.1.3**). Reproduced by permission of The RoyalSociety of Chemistry.

Ce	0.000000000	0.000000000	0.000000000
0	-5.235507867	0.000000001	0.000000000

0	0.00000001	5.235496008	0.000000000
Ν	-1.964886567	1.368167716	0.583874073
Ν	-1.368126731	1.964875015	-0.583971161
С	-2.228480291	2.200709936	1.668705336
С	-2.399592432	3.601175266	1.571997585
Н	-2.336271347	4.075837702	0.598868766
С	-2.702787622	4.365647544	2.702379372
Н	-2.842173999	5.439563282	2.591771151
С	-2.855189833	3.772061994	3.955568101
Н	-3.093964847	4.371832562	4.829137581
С	-2.707949063	2.382265517	4.061015532
Н	-2.827361063	1.895417913	5.026407854
С	-2.401902163	1.607547824	2.946900045
Н	-2.284607211	0.530323833	3.045601465
С	-2.200604805	2.228350404	-1.668881467
С	-1.607355827	2.401721619	-2.947042160
Н	-0.530115512	2.284497481	-3.045651213
С	-2.382008496	2.707632848	-4.061239924
Н	-1.895094739	2.827009023	-5.026603321
С	-3.771823181	2.854785468	-3.955910452
Н	-4.371542864	3.093454609	-4.829543778
С	-4.365494553	2.702436576	-2.702756157
Н	-5.439428289	2.841757552	-2.592240991
С	-3.601088328	2.399376628	-1.572293495
Н	-4.075823102	2.336095734	-0.599197416
С	-6.015086933	0.557059699	1.053352937
Н	-5.320434370	0.963090348	1.791348376
Н	-6.637862566	-0.215542854	1.523516852

С	0.556943052	6.015073915	1.053414253
Η	-0.215714812	6.637835419	1.523505570
Η	1.361426612	6.659215821	0.672690960
Li	-3.282905430	0.000000000	0.000000000
Li	0.000000000	3.282898297	0.000000000
С	-6.015086933	-0.557059694	-1.053352937
Н	-5.320434370	-0.963090343	-1.791348376
Н	-6.637862566	0.215542856	-1.523516852
С	-0.556943047	6.015073915	-1.053414253
Н	0.215714813	6.637835419	-1.523505570
Н	-1.361426607	6.659215821	-0.672690960
0	-0.00000001	-5.235496008	0.000000000
Ν	-1.964886567	-1.368167716	-0.583874073
Ν	-1.368126731	-1.964875015	0.583971161
С	-2.228480296	-2.200709936	-1.668705336
С	-2.399592432	-3.601175266	-1.571997585
Н	-2.336271347	-4.075837702	-0.598868766
С	-2.702787622	-4.365647544	-2.702379372
Н	-2.842174004	-5.439563229	-2.591771151
С	-2.855189833	-3.772061994	-3.955568101
Η	-3.093964847	-4.371832562	-4.829137581
С	-2.707949063	-2.382265517	-4.061015532
Н	-2.827361063	-1.895417913	-5.026407854
С	-2.401902163	-1.607547824	-2.946900045
Н	-2.284607211	-0.530323833	-3.045601465
С	-2.200604805	-2.228350404	1.668881467
С	-1.607355827	-2.401721619	2.947042160
Н	-0.530115512	-2.284497481	3.045651213

С	-2.382008496	-2.707632848	4.061239924
Н	-1.895094739	-2.827009023	5.026603321
С	-3.771823181	-2.854785468	3.955910452
Н	-4.371542864	-3.093454609	4.829543778
С	-4.365494553	-2.702436576	2.702756157
Н	-5.439428289	-2.841757552	2.592240991
С	-3.601088333	-2.399376628	1.572293495
Н	-4.075823102	-2.336095734	0.599197416
С	0.556943047	-6.015073915	-1.053414253
Н	-0.215714813	-6.637835419	-1.523505570
Н	1.361426607	-6.659215821	-0.672690960
Li	0.000000000	-3.282898297	0.000000000
С	-0.556943052	-6.015073915	1.053414253
Н	0.215714812	-6.637835419	1.523505570
Н	-1.361426612	-6.659215821	0.672690960
0	5.235507867	-0.000000001	0.000000000
Ν	1.964886567	-1.368167716	0.583874073
Ν	1.368126731	-1.964875015	-0.583971161
С	2.228480291	-2.200709936	1.668705336
С	2.399592432	-3.601175266	1.571997585
Н	2.336271347	-4.075837702	0.598868766
С	2.702787622	-4.365647544	2.702379372
Н	2.842173999	-5.439563282	2.591771151
С	2.855189833	-3.772061994	3.955568101
Н	3.093964847	-4.371832562	4.829137581
С	2.707949063	-2.382265517	4.061015532
Н	2.827361063	-1.895417913	5.026407854
С	2.401902163	-1.607547824	2.946900045

Н	2.284607211	-0.530323833	3.045601465
С	2.200604805	-2.228350404	-1.668881467
С	1.607355827	-2.401721619	-2.947042160
Н	0.530115512	-2.284497481	-3.045651213
С	2.382008496	-2.707632848	-4.061239924
Н	1.895094739	-2.827009023	-5.026603321
С	3.771823181	-2.854785468	-3.955910452
Η	4.371542864	-3.093454609	-4.829543778
С	4.365494553	-2.702436576	-2.702756157
Η	5.439428289	-2.841757552	-2.592240991
С	3.601088328	-2.399376628	-1.572293495
Η	4.075823102	-2.336095734	-0.599197416
С	6.015086933	-0.557059699	1.053352937
Η	5.320434370	-0.963090348	1.791348376
Η	6.637862566	0.215542854	1.523516852
Li	3.282905430	0.000000000	0.000000000
С	6.015086933	0.557059694	-1.053352937
Η	5.320434370	0.963090343	-1.791348376
Η	6.637862566	-0.215542856	-1.523516852
Ν	1.964886567	1.368167716	-0.583874073
Ν	1.368126731	1.964875015	0.583971161
С	2.228480296	2.200709936	-1.668705336
С	2.399592432	3.601175266	-1.571997585
Н	2.336271347	4.075837702	-0.598868766
С	2.702787622	4.365647544	-2.702379372
Η	2.842174004	5.439563229	-2.591771151
С	2.855189833	3.772061994	-3.955568101
Н	3.093964847	4.371832562	-4.829137581

С	2.707949063	2.382265517	-4.061015532
Н	2.827361063	1.895417913	-5.026407854
С	2.401902163	1.607547824	-2.946900045
Н	2.284607211	0.530323833	-3.045601465
С	2.200604805	2.228350404	1.668881467
С	1.607355827	2.401721619	2.947042160
Н	0.530115512	2.284497481	3.045651213
С	2.382008496	2.707632848	4.061239924
Н	1.895094739	2.827009023	5.026603321
С	3.771823181	2.854785468	3.955910452
Н	4.371542864	3.093454609	4.829543778
С	4.365494553	2.702436576	2.702756157
Н	5.439428289	2.841757552	2.592240991
С	3.601088333	2.399376628	1.572293495
Н	4.075823102	2.336095734	0.599197416
Н	-0.962906914	-5.320420717	1.791445951
Н	0.962906914	-5.320420717	-1.791445951
Н	-6.659216773	-1.361511614	-0.672542484
Н	-6.659216773	1.361511614	0.672542484
Н	-0.962906914	5.320420717	-1.791445951
Н	0.962906914	5.320420717	1.791445951
Н	6.659216773	-1.361511614	0.672542484
Н	6.659216773	1.361511614	-0.672542484

Lowest Energy Frequencies (cm⁻¹) –16.32, –12.12, –12.08, –11.37, 9.20, 20.57 Sum of Electronic and Thermal Free Energies (Hartrees) –3415.92

 Table 4.4.8. Na₄(OMe₂)₄[Ce(PhNNPh)₄] (4.2.2). Reproduced by permission of The

Ce	0.00000361	-0.000001339	-0.000019559
Na	-2.612491927	2.110812395	-1.058384767
Na	2.110752117	2.612446429	1.058448760
Na	2.612490409	-2.110827572	-1.058362949
Na	-2.110753392	-2.612451424	1.058451417
0	-4.039218721	2.667653316	-2.776750233
0	2.667557720	4.039087400	2.776883650
0	4.039235554	-2.667646791	-2.776719906
0	-2.667555069	-4.039085310	2.776893783
Ν	-0.245509391	1.997500195	-1.377494899
N	0.001331277	2.442631227	-0.029507024
Ν	1.997516239	0.245290331	1.377384804
Ν	2.442633222	-0.001348832	0.029368073
Ν	0.245508530	-1.997506894	-1.377488496
Ν	-0.001330441	-2.442635942	-0.029499454
Ν	-1.997513773	-0.245293049	1.377385502
Ν	-2.442633116	0.001349278	0.029370692
С	0.541120626	2.538931273	-2.383815546
С	1.385548067	3.664569679	-2.231058590
Н	1.431247428	4.165115629	-1.268668434
С	2.120358499	4.163083716	-3.308093098
Н	2.756827446	5.032293654	-3.154392905
С	2.041513237	3.576281885	-4.572016473
Н	2.612397146	3.973857001	-5.406316663
С	1.195061905	2.472610362	-4.744262282

Н	1.107452637	2.003645128	-5.722643159
С	0.457724998	1.964829204	-3.680213148
Н	-0.198582205	1.109704493	-3.824003360
С	-0.736937777	3.524771422	0.420495993
С	-0.840842767	3.752857331	1.821188633
Н	-0.408748041	3.022124125	2.500941839
С	-1.541340812	4.839885658	2.325485894
Н	-1.624331913	4.959512187	3.403231193
С	-2.177984086	5.753107946	1.469564485
Н	-2.726318779	6.599890553	1.871839770
С	-2.095507568	5.543880681	0.094517532
Н	-2.565823638	6.246336279	-0.591019474
С	-1.389994960	4.455049505	-0.433811984
Н	-1.275337231	4.358716041	-1.509509880
С	-3.517509348	2.685346236	-4.102830462
Н	-3.939144111	3.524862784	-4.672948593
Н	-3.744788272	1.745157806	-4.624759231
С	-5.450503281	2.484701633	-2.747582888
Н	-5.729234961	1.514039806	-3.178221677
Н	-5.956974222	3.290746985	-3.296701759
С	2.539061948	-0.541310156	2.383658555
С	3.664756278	-1.385650886	2.230826112
Н	4.165288787	-1.431262409	1.268424515
С	4.163352575	-2.120477426	3.307812946
Н	5.032601831	-2.756879236	3.154057740
С	3.576586368	-2.041727908	4.571757737
Н	3.974227991	-2.612621645	5.406019265
С	2.472862885	-1.195358287	4.744078419

Н	2.003925893	-1.107823469	5.722479484
С	1.964995826	-0.458010823	3.680079431
Н	1.109832268	0.198235029	3.823926883
С	3.524824313	0.736891104	-0.420553604
С	3.752897131	0.840930532	-1.821238460
Н	3.022142943	0.408925510	-2.501024179
С	4.839952070	1.541434270	-2.325469542
Н	4.959578620	1.624525502	-3.403207083
С	5.753200499	2.177962432	-1.469488882
Н	6.600001204	2.726305650	-1.871714942
С	5.543976038	2.095364558	-0.094448752
Н	6.246449417	2.565593837	0.591129411
С	4.455131580	1.389823168	0.433815094
Н	4.358754639	1.275111542	1.509502773
С	2.685230753	3.517354336	4.102955083
Н	3.524705979	3.939022020	4.673108743
Н	1.745012732	3.744573956	4.624856531
С	2.484641720	5.450379188	2.747744123
Н	1.513953783	5.729121188	3.178316759
Н	3.290658390	5.956810547	3.296940518
С	-0.541125791	-2.538935686	-2.383807323
С	-1.385561497	-3.664567621	-2.231047271
Н	-1.431261059	-4.165113729	-1.268657226
С	-2.120381184	-4.163074894	-3.308078736
Н	-2.756856683	-5.032279620	-3.154376109
С	-2.041536500	-3.576273280	-4.572002175
Н	-2.612427548	-3.973843116	-5.406299994
С	-1.195077389	-2.472608187	-4.744251052

Н	-1.107469047	-2.003642948	-5.722631993
С	-0.457732105	-1.964833173	-3.680204877
Н	0.198580615	-1.109713103	-3.823997333
С	0.736934714	-3.524779180	0.420502460
С	0.840839756	-3.752866073	1.821195094
Н	0.408747499	-3.022131782	2.500948676
С	1.541335055	-4.839896506	2.325491535
Н	1.624326346	-4.959523723	3.403236765
С	2.177975254	-5.753120487	1.469569544
Н	2.726307682	-6.599904735	1.871844358
С	2.095498783	-5.543892428	0.094522736
Н	2.565812763	-6.246348926	-0.591014770
С	1.389989028	-4.455059051	-0.433806129
Н	1.275331802	-4.358724460	-1.509503916
С	3.517533436	-2.685324561	-4.102803130
Н	3.939181942	-3.524826419	-4.672932729
Н	3.744802735	-1.745124722	-4.624715495
С	5.450517092	-2.484672571	-2.747541824
Н	5.729234537	-1.513996996	-3.178158609
Н	5.957003856	-3.290698439	-3.296674744
С	-2.539058223	0.541301933	2.383664260
С	-3.664753912	1.385642033	2.230838855
Н	-4.165286411	1.431260308	1.268437686
С	-4.163349971	2.120460508	3.307831187
Н	-5.032600434	2.756861953	3.154081362
С	-3.576581378	2.041704423	4.571774523
Н	-3.974222784	2.612592153	5.406040273
С	-2.472855858	1.195336077	4.744087997

Н	-2.003916807	1.107796264	5.722487633
С	-1.964989608	0.457995749	3.680083590
Н	-1.109824547	-0.198249399	3.823925428
С	-3.524825594	-0.736889305	-0.420551261
С	-3.752899088	-0.840928537	-1.821235894
Н	-3.022145044	-0.408924784	-2.501022915
С	-4.839955377	-1.541430958	-2.325466426
Н	-4.959581991	-1.624522210	-3.403203977
С	-5.753204256	-2.177957442	-1.469485315
Н	-6.600005755	-2.726299184	-1.871711503
С	-5.543979002	-2.095359985	-0.094445120
Н	-6.246452645	-2.565588180	0.591133496
С	-4.455133152	-1.389820660	0.433817977
Н	-4.358754587	-1.275110235	1.509505477
С	-2.685220768	-3.517350388	4.102964629
Н	-3.524693400	-3.939016754	4.673123074
Н	-1.745000270	-3.744570183	4.624861563
С	-2.484640291	-5.450377389	2.747755591
Н	-1.513948201	-5.729118965	3.178319093
Н	-3.290651887	-5.956806843	3.296961151
Н	5.761203881	-2.512840639	-1.700488018
Н	2.434049528	-2.804806793	-4.028731332
Н	-2.434024323	2.804813323	-4.028751071
Н	-5.761194991	2.512852741	-1.700530129
Н	2.804759569	2.433877005	4.028857557
Н	2.512883073	5.761101962	1.700703096
Н	-2.512892540	-5.761102597	1.700715553
Н	-2.804749123	-2.433873079	4.028866347

Lowest Energy Frequencies (cm⁻¹) 5.32, 11.99, 14.77, 14.78, 20.94, 22.52 Sum of Electronic and Thermal Free Energies (Hartrees) –4034.95

Table 4.4.9. K₄(OMe₂)₄[Ce(PhNNPh)₄] (**4.3.2**⁺). Reproduced by permission of The

Ce	0.000004542	-0.000002717	-0.000005910
K	2.396475588	-2.205177769	1.725300144
0	4.197298814	-4.231754275	1.592422541
Ν	1.480418943	0.669690245	1.727596604
N	2.306249343	0.690601599	0.550414349
С	1.414352174	1.822119742	2.491599993
С	2.294587420	2.926731020	2.364772606
Н	3.082789920	2.890652509	1.621461015
С	2.167074885	4.045915829	3.187537985
Н	2.864970976	4.871819150	3.062104191
С	1.170726446	4.125709525	4.163647226
Н	1.086830838	4.997743264	4.805984823
С	0.300812061	3.036357093	4.314617256
Н	-0.466316249	3.057808262	5.087810359
С	0.415531085	1.909530716	3.503727831
Н	-0.249230131	1.061275996	3.643984668
С	3.636757615	0.388654414	0.731359874
С	4.467038460	0.143764131	-0.403331039
Н	4.017789323	0.106682475	-1.391476408
С	5.823782107	-0.125494919	-0.266837436

Н	6.409869036	-0.319903431	-1.162833783
С	6.434973310	-0.174977870	0.995941296
Н	7.499059644	-0.370973714	1.093167328
С	5.637712644	0.042944985	2.122180578
Н	6.084896101	0.021173883	3.114827295
С	4.270956789	0.314567827	2.007984895
Н	3.689593985	0.530197529	2.897765630
С	5.602899766	-4.029545757	1.656971862
Н	6.084663898	-4.334038167	0.716439456
Н	6.046015491	-4.603797642	2.484807283
С	3.856757230	-5.579407154	1.291943332
Н	4.187027510	-6.257528695	2.093234804
Н	4.317208934	-5.896833069	0.345183821
K	2.205174970	2.396463549	-1.725320237
0	4.231753010	4.197285838	-1.592448036
Ν	-0.669693203	1.480408820	-1.727607182
Ν	-0.690601081	2.306240929	-0.550426409
С	-1.822127298	1.414338765	-2.491603962
С	-2.926740947	2.294570444	-2.364769357
Н	-2.890656060	3.082779289	-1.621464825
С	-4.045937271	2.167044675	-3.187517014
Н	-4.871841445	2.864938924	-3.062078664
С	-4.125741048	1.170685953	-4.163614904
Н	-4.997783788	1.086780116	-4.805938874
С	-3.036388897	0.300772204	-4.314589300
Н	-3.057849876	-0.466367007	-5.087771258
С	-1.909551089	0.415504094	-3.503717491
Н	-1.061299274	-0.249260582	-3.643975101

С	-0.388653890	3.636748789	-0.731374378
С	-0.143761718	4.467030946	0.403314897
Н	-0.106679465	4.017783094	1.391460596
С	0.125497582	5.823774275	0.266819105
Н	0.319907300	6.409862156	1.162814516
С	0.174979355	6.434963838	-0.995960426
Н	0.370975257	7.499050066	-1.093188114
С	-0.042945275	5.637701796	-2.122198369
Н	-0.021175569	6.084884036	-3.114845705
С	-0.314568738	4.270946205	-2.008000399
Н	-0.530200217	3.689582374	-2.897780140
С	4.029544916	5.602886960	-1.656994633
Н	4.334042078	6.084649716	-0.716463031
Н	4.603793191	6.046003425	-2.484832171
С	5.579407419	3.856743144	-1.291976829
Н	6.257524515	4.187013767	-2.093271910
Н	5.896839101	4.317193820	-0.345218755
K	-2.396460687	2.205170694	1.725307579
0	-4.197280896	4.231750914	1.592438559
Ν	-1.480411407	-0.669696277	1.727602419
Ν	-2.306239622	-0.690606351	0.550419069
С	-1.414357672	-1.822124139	2.491608724
С	-2.294618821	-2.926715907	2.364793588
Н	-3.082816094	-2.890629252	1.621476499
С	-2.167145493	-4.045886306	3.187584600
Н	-2.865061280	-4.871774276	3.062159866
С	-1.170810241	-4.125685325	4.163706764
Н	-1.086944511	-4.997707804	4.806063538

С	-0.300874720	-3.036348441	4.314669423
Н	0.466238647	-3.057799752	5.087877506
С	-0.415556654	-1.909535145	3.503756375
Н	0.249215028	-1.061288643	3.644012292
С	-3.636747228	-0.388659770	0.731367774
С	-4.467030776	-0.143768146	-0.403320736
Н	-4.017784232	-0.106686438	-1.391467274
С	-5.823773905	0.125491336	-0.266822880
Н	-6.409863321	0.319900655	-1.162817357
С	-6.434961615	0.174973037	0.995957647
Н	-7.499047685	0.370968795	1.093186797
С	-5.637698092	-0.042951700	2.122194543
Н	-6.084878903	-0.021181886	3.114842488
С	-4.270942702	-0.314574875	2.007994600
Н	-3.689576839	-0.530206562	2.897773176
С	-5.602882145	4.029544805	1.656989436
Н	-6.084647017	4.334040247	0.716458401
Н	-6.045995594	4.603795684	2.484826762
С	-3.856737370	5.579403979	1.291962192
Н	-4.187005300	6.257524039	2.093255850
Н	-4.317189941	5.896833069	0.345204176
Κ	-2.205167927	-2.396469286	-1.725317681
0	-4.231745919	-4.197291702	-1.592445846
Ν	0.669698892	-1.480410820	-1.727610437
Ν	0.690610738	-2.306245851	-0.550431854
С	1.822131119	-1.414338283	-2.491609682
С	2.926746049	-2.294568867	-2.364778924
Н	2.890663378	-3.082779459	-1.621476081

С	4.045940865	-2.167039658	-3.187528079
Н	4.871846154	-2.864933135	-3.062092724
С	4.125741767	-1.170678455	-4.163623699
Н	4.997783370	-1.086769903	-4.805948854
С	3.036388474	-0.300765421	-4.314593914
Н	3.057847373	0.466375937	-5.087773787
С	1.909552111	-0.415500752	-3.503720608
Н	1.061299401	0.249263486	-3.643974990
С	0.388665687	-3.636753673	-0.731383597
С	0.143778567	-4.467040021	0.403303041
Н	0.106697757	-4.017795662	1.391449875
С	-0.125478428	-5.823783271	0.266803225
Н	-0.319884377	-6.409874380	1.162797301
С	-0.174963451	-6.434968653	-0.995978243
Н	-0.370957665	-7.499054882	-1.093209070
С	0.042956536	-5.637702378	-2.122213911
Н	0.021185222	-6.084881178	-3.114862766
С	0.314578269	-4.270946766	-2.008011660
Н	0.530206853	-3.689579617	-2.897789993
С	-4.029537619	-5.602892728	-1.656995246
Н	-4.334032611	-6.084657072	-0.716463762
Н	-4.603787656	-6.046007923	-2.484832218
С	-5.579399693	-3.856749870	-1.291970600
Н	-6.257518694	-4.187019292	-2.093264544
Н	-5.896828835	-4.317202356	-0.345212546
Н	2.962545980	5.777334738	-1.814361612
Н	5.629562733	2.770168560	-1.191443312
Н	-5.629555112	-2.770175503	-1.191434993

Η	-2.962538994	-5.777339977	-1.814364866
Η	-5.777330823	2.962546514	1.814359532
Η	-2.770162993	5.629557600	1.191425881
Н	5.777346645	-2.962547467	1.814344053
Н	2.770182758	-5.629562309	1.191408672

Lowest Energy Frequencies (cm⁻¹) 13.02, 13.06, 13.06, 13.79, 16.74, 23.47

Sum of Electronic and Thermal Free Energies (Hartrees) –5785.36

Optimized Coordinates for Ce(III) Calculations:

Table 4.4.10. $\text{Li}_4(\text{OMe}_2)_4[\text{Ce}(\text{PhNNPh})_4]^-$ (**4.1.3**⁻). Reproduced by permission of The

Ce	-0.000108261	-0.000247107	-0.000935697
0	-5.237741101	0.019168931	0.155101624
0	-0.017817705	5.237653411	-0.151399635
N	-2.042548969	1.441937353	0.589953251
N	-1.442537064	2.043098694	-0.589481352
С	-2.353443508	2.282594406	1.639253986
С	-2.479379772	3.693620113	1.543395988
Н	-2.337609403	4.170406613	0.579978731
С	-2.825262452	4.463822745	2.656178896
Н	-2.921539146	5.542684105	2.537753372
С	-3.069053633	3.879608152	3.900423746
Н	-3.338141460	4.487105031	4.760581182
С	-2.960059021	2.485289322	4.010242599

Н	-3.138469681	2.000801409	4.968852170
С	-2.610841720	1.702747615	2.916025600
Н	-2.508864999	0.624152225	3.024803540
С	-2.284158215	2.354906509	-1.637724701
С	-1.705407636	2.613634236	-2.914730608
Н	-0.626909053	2.511758503	-3.024534173
С	-2.488912725	2.963861366	-4.007927851
Н	-2.005251885	3.143254914	-4.966770006
С	-3.883157233	3.072596792	-3.896824674
Н	-4.491408321	3.342471797	-4.756202425
С	-4.466297559	2.827474445	-2.652343276
Н	-5.545071171	2.923506251	-2.532913099
С	-3.695119214	2.480578729	-1.540541860
Н	-4.171103693	2.337816470	-0.576875365
С	-5.902935064	0.372503687	1.362562486
Н	-5.193806546	0.942245781	1.966460478
Н	-6.210788268	-0.527016636	1.912260699
С	0.722688098	6.049815618	0.749808935
Н	0.124760182	6.916328970	1.066285748
Н	1.652515888	6.403748042	0.282163204
Li	-3.270917454	0.011776630	0.020278433
Li	-0.011565971	3.270624867	-0.020648180
С	-6.051074213	-0.719873240	-0.746209968
Н	-5.436474845	-0.960870254	-1.615912893
Н	-6.918281052	-0.121647240	-1.060220811
С	-0.374876784	5.904974090	-1.356544867
Н	0.522911408	6.215395180	-1.907667837
Н	-0.995127014	6.785874977	-1.136813148

0	0.017794198	-5.238115039	-0.152416692
Ν	-2.072156278	-1.437237328	-0.573520895
Ν	-1.438605431	-2.071997540	0.569573026
С	-2.446726635	-2.246291894	-1.626029360
С	-2.608295451	-3.656015069	-1.555110544
Н	-2.437813290	-4.154090798	-0.607585828
С	-3.036820303	-4.390414335	-2.663570767
Н	-3.167266729	-5.467839021	-2.561958209
С	-3.323895278	-3.771977447	-3.881714706
Н	-3.656889428	-4.351596311	-4.738755171
С	-3.175823054	-2.379232210	-3.967606539
Н	-3.386928644	-1.867989730	-4.905374571
С	-2.749123075	-1.631715169	-2.876826462
Н	-2.621773474	-0.554553648	-2.968985855
С	-2.249093983	-2.449213700	1.619973551
С	-1.636599623	-2.751878231	2.871741873
Н	-0.559907059	-2.622367772	2.966387986
С	-2.385601911	-3.181407234	3.960410078
Н	-1.875959992	-3.392573859	4.899036202
С	-3.777854982	-3.332166482	3.871344134
Н	-4.358645819	-3.667365810	4.726729052
С	-4.394254453	-3.044887510	2.652186513
Н	-5.471176436	-3.177498863	2.548070741
С	-3.658361822	-2.613557637	1.545818165
Н	-4.154660510	-2.443132876	0.597343380
С	0.374283057	-5.905057383	-1.357955468
Н	-0.523774553	-6.214813032	-1.909006180
Н	0.994189502	-6.786329435	-1.138747217

Li	0.011325911	-3.271181027	-0.020914158
С	-0.722696094	-6.050438089	0.748660165
Н	-0.124847087	-6.917133266	1.064787304
Н	-1.652649944	-6.404092166	0.281059104
0	5.237404999	-0.020011490	0.156403940
Ν	2.042250328	-1.442504054	0.590198905
Ν	1.442366971	-2.043556650	-0.589349539
С	2.352900414	-2.283228043	1.639501800
С	2.478717284	-3.694264418	1.543608749
Н	2.337052957	-4.171003361	0.580151618
С	2.824345150	-4.464544395	2.656416301
Н	2.920541297	-5.543409819	2.537959677
С	3.067985298	-3.880410506	3.900729897
Н	3.336872493	-4.487971431	4.760904446
С	2.959097813	-2.486086829	4.010591242
Н	3.137387963	-2.001656427	4.969252858
С	2.610136184	-1.703467360	2.916348525
Η	2.508234357	-0.624866884	3.025156734
С	2.284104445	-2.355318907	-1.637511676
С	1.705499046	-2.613940873	-2.914604198
Н	0.627016222	-2.512016694	-3.024528087
С	2.489119993	-2.964130971	-4.007732309
Н	2.005569163	-3.143443095	-4.966645507
С	3.883345921	-3.072918902	-3.896468739
Н	4.491690468	-3.342762119	-4.755790297
С	4.466347942	-2.827881165	-2.651903255
Н	5.545105726	-2.923942245	-2.532355262
С	3.695052781	-2.481029894	-1.540170574

Н	4.170930128	-2.338292714	-0.576447594
С	5.901957198	-0.372659743	1.364429476
Н	5.192719711	-0.942633086	1.967978475
Н	6.208922654	0.527180255	1.914095214
Li	3.270614712	-0.012251544	0.020724643
С	6.051004150	0.719188315	-0.744537001
Н	5.436883528	0.959683029	-1.614717133
Н	6.918693704	0.121279137	-1.057818531
N	2.072091347	1.436615963	-0.573558017
N	1.438533876	2.071441317	0.569488580
С	2.446250117	2.245520623	-1.626339844
С	2.607278865	3.655321735	-1.555864600
Н	2.436673792	4.153632684	-0.608489086
С	3.035407099	4.389553539	-2.664590068
Н	3.165434929	5.467061290	-2.563322455
С	3.322599397	3.770859856	-3.882572084
Н	3.655283180	4.350349214	-4.739821008
С	3.175053318	2.378032544	-3.968027643
Н	3.386265844	1.866584855	-4.905659586
С	2.748755979	1.630682590	-2.876977907
Н	2.621824053	0.553443571	-2.968794727
С	2.249081648	2.449155723	1.619649816
С	1.636743787	2.751833415	2.871494414
Н	0.560120672	2.621924046	2.966403269
С	2.385823033	3.181856855	3.959916694
Η	1.876308280	3.393013172	4.898614326
С	3.778001458	3.333111762	3.870520432
Н	4.358851839	3.668693939	4.725714344

С	4.394247425	3.045817592	2.651283938
Η	5.471097113	3.178812662	2.546909086
С	3.658279064	2.613998537	1.545158858
Н	4.154419227	2.443581841	0.596595568
Н	-0.965353327	-5.434750309	1.617127503
Н	0.944578061	-5.196445379	-1.961943960
Н	-6.403968656	-1.650729491	-0.279845375
Н	-6.785164451	0.992030745	1.146142601
Н	-0.944985464	5.196386216	-1.960739939
Н	0.965575745	5.433896640	1.618047340
Н	6.784671152	-0.991763092	1.148773062
Н	6.403160867	1.650323808	-0.278177839

Lowest Energy Frequencies (cm⁻¹) 6.79, 14.95, 18.41, 19.81, 20.11, 23.06

Sum of Electronic and Thermal Free Energies (Hartrees) –3416.00

Table 4.4.11. $Na_4(OMe_2)_4[Ce(PhNNPh)_4]^-$ (4.2.2⁻). Reproduced by permission of The

Ce	-0.000014617	-0.000013032	-0.000018678
Na	-2.580653968	2.159335361	-0.906684583
Na	2.159330551	2.580626080	0.906666353
Na	2.580613771	-2.159373991	-0.906690531
Na	-2.159362265	-2.580643516	0.906680725
0	-4.116090130	2.703950584	-2.571805288
0	2.703966046	4.116045774	2.571795773
0	4.116034312	-2.704027145	-2.571816099

0	-2.703992807	-4.116063491	2.571811024
Ν	-0.272541848	2.091614326	-1.436148948
Ν	0.003664597	2.564367061	-0.090681911
Ν	2.091610622	0.272510949	1.436112837
Ν	2.564362024	-0.003690754	0.090644291
Ν	0.272505086	-2.091633858	-1.436146932
Ν	-0.003692374	-2.564379545	-0.090670484
Ν	-2.091629085	-0.272532100	1.436127056
Ν	-2.564382122	0.003664853	0.090654673
С	0.490148392	2.609646462	-2.455723310
С	1.368099923	3.722061332	-2.344188172
Н	1.447745825	4.235514873	-1.390528006
С	2.089005138	4.187296988	-3.444994210
Н	2.747992339	5.045154217	-3.315719061
С	1.972203109	3.587923012	-4.700672607
Н	2.535303467	3.959910360	-5.552771335
С	1.101571462	2.495082821	-4.833192725
Н	0.988205354	2.006926133	-5.800627004
С	0.379152121	2.016199128	-3.748151157
Н	-0.281082138	1.158588654	-3.860111505
С	-0.688823109	3.675328938	0.325398228
С	-0.779250145	3.950226655	1.725485425
Н	-0.352031081	3.228332185	2.418093680
С	-1.457976446	5.058942644	2.208083090
Н	-1.527014952	5.206190511	3.284529957
С	-2.095501694	5.961003430	1.337340612
Н	-2.628804832	6.825442513	1.723625478
С	-2.036868209	5.705114903	-0.031831512

Н	-2.513073635	6.390904805	-0.731786274
С	-1.355964555	4.592958896	-0.541784008
Н	-1.273965154	4.456777978	-1.615564234
С	-3.650724386	2.505388362	-3.902553277
Н	-4.115454842	3.231663144	-4.585761900
Η	-3.877649175	1.487589427	-4.249616303
С	-5.517183583	2.500427622	-2.445627185
Η	-5.786124637	1.461705859	-2.677126827
Η	-6.069389567	3.184909673	-3.106948264
С	2.609646875	-0.490183184	2.455681897
С	3.722058199	-1.368138204	2.344136847
Η	4.235507956	-1.447780057	1.390474299
С	4.187293839	-2.089054167	3.444935927
Н	5.045147835	-2.748044072	3.315653088
С	3.587923620	-1.972259752	4.700616827
Н	3.959910757	-2.535368640	5.552709950
С	2.495086377	-1.101625708	4.833146501
Η	2.006931731	-0.988266580	5.800582606
С	2.016202171	-0.379196285	3.748111834
Н	1.158592824	0.281038066	3.860079019
С	3.675312999	0.688812763	-0.325438136
С	3.950182601	0.779283372	-1.725527902
Н	3.228289925	0.352057456	-2.418133950
С	5.058863226	1.458065173	-2.208128615
Н	5.206089338	1.527135774	-3.284576530
С	5.960918338	2.095599343	-1.337386740
Η	6.825331439	2.628942831	-1.723674056
С	5.705053518	2.036927398	0.031788063
Н	6.390835694	2.513144947	0.731742135
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С	4.592928955	1.355974546	0.541743129
Н	4.456762589	1.273955967	1.615523684
С	2.505432369	3.650659594	3.902541196
Н	3.231713649	4.115389743	4.585743035
Н	1.487637026	3.877568041	4.249625188
С	2.500429612	5.517139396	2.445640631
Н	1.461709601	5.786068491	2.677162086
Н	3.184918230	6.069341518	3.106958012
С	-0.490196042	-2.609640159	-2.455730338
С	-1.368204679	-3.722013642	-2.344209640
Н	-1.447892619	-4.235463146	-1.390552252
С	-2.089124224	-4.187207943	-3.445024569
Н	-2.748154913	-5.045033326	-3.315759405
С	-1.972281713	-3.587834956	-4.700699363
Н	-2.535392511	-3.959791126	-5.552804832
С	-1.101601847	-2.495031708	-4.833204494
Н	-0.988208154	-2.006872453	-5.800634307
С	-0.379172486	-2.016185163	-3.748152982
Н	0.281098501	-1.158601778	-3.860103033
С	0.688821272	-3.675312792	0.325453852
С	0.779212144	-3.950170107	1.725551969
Н	0.351913122	-3.228289205	2.418125579
С	1.457987056	-5.058832756	2.208205859
Н	1.526983720	-5.206053883	3.284659283
С	2.095616017	-5.960867114	1.337512727
Н	2.628963268	-6.825259576	1.723841488
С	2.037040197	-5.705003723	-0.031667129

Η	2.513342833	-6.390764943	-0.731583774
С	1.356084282	-4.592905708	-0.541676278
Н	1.274163892	-4.456733363	-1.615461421
С	3.650714919	-2.505315696	-3.902558384
Н	4.115378932	-3.231590594	-4.585812050
Н	3.877759953	-1.487516130	-4.249540991
С	5.517148975	-2.500672192	-2.445593831
Н	5.786215391	-1.461963770	-2.677002460
Н	6.069288494	-3.185165371	-3.106959250
С	-2.609638905	0.490164926	2.455710827
С	-3.722027047	1.368154873	2.344193881
Η	-4.235484001	1.447830588	1.390539219
С	-4.187228645	2.089067311	3.445010128
Н	-5.045065516	2.748083622	3.315748060
С	-3.587847937	1.972236124	4.700682392
Η	-3.959809642	2.535341599	5.552788956
С	-2.495031935	1.101571711	4.833184390
Н	-2.006868415	0.988184605	5.800612875
С	-2.016179617	0.379147737	3.748131926
Н	-1.158587315	-0.281112193	3.860079305
С	-3.675323688	-0.688843969	-0.325451259
С	-3.950203858	-0.779238672	-1.725544428
Н	-3.228325671	-0.351957334	-2.418131590
С	-5.058886885	-1.457995554	-2.208176336
Н	-5.206125808	-1.526997378	-3.284626955
С	-5.960921566	-2.095599073	-1.337464577
Н	-6.825330909	-2.628931194	-1.723776203
С	-5.705039336	-2.037013802	0.031711217

Η	-6.390803256	-2.513291471	0.731642248
С	-4.592920488	-1.356075333	0.541698324
Н	-4.456737342	-1.274136756	1.615481386
С	-2.505359787	-3.650711125	3.902553214
Н	-3.231629758	-4.115411233	4.585787602
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С	-2.500541030	-5.517166490	2.445620062
Н	-1.461823151	-5.786159087	2.677075402
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Н	5.782487602	-2.715039938	-1.407280916
Н	2.568178101	-2.653006621	-3.896980522
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Н	-5.782566238	2.714681341	-1.407301914
Н	2.653258266	2.568141386	3.896913587
Н	2.714663454	5.782538879	1.407315492
Н	-2.714850217	-5.782535916	1.407302914
Н	-2.653122897	-2.568184234	3.896951687

Lowest Energy Frequencies (cm⁻¹) 8.48, 10.33, 10.33, 10.39, 18.23, 23.19

Sum of Electronic and Thermal Free Energies (Hartrees) –4035.01

Table 4.4.12. $K_4(OMe_2)_4[Ce(PhNNPh)_4]^-$ (**4.3.2**). Reproduced by permission of The

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Ce	0.001222862	0.003654966	0.000014809
K	2.317243334	-2.179369477	1.686015787
0	4.163405376	-4.162599005	1.269282507

Ν	1.633940348	0.608737127	1.776976932
Ν	2.445131616	0.602238730	0.577172567
С	1.576730874	1.783769584	2.484634967
С	2.440077682	2.902077811	2.300502600
Н	3.213742276	2.847446012	1.542966969
С	2.313083218	4.051058210	3.079292403
Н	2.998822736	4.879937550	2.904708880
С	1.334376256	4.165513877	4.071332943
Н	1.251781896	5.063374663	4.678343815
С	0.476982591	3.073087191	4.275688427
Н	-0.284532721	3.119760677	5.054776146
С	0.588767671	1.915671733	3.511093201
Н	-0.074292998	1.073627437	3.691968863
С	3.773463800	0.342902478	0.742065912
С	4.596736936	0.106922694	-0.408305513
Н	4.126986699	0.045229637	-1.386533606
С	5.961664320	-0.118340278	-0.295907220
Н	6.534834878	-0.301980485	-1.203726050
С	6.603004497	-0.141846303	0.955718459
Н	7.674833805	-0.305283173	1.033598142
С	5.815777878	0.050651078	2.095124861
Н	6.281119417	0.039195921	3.080836172
С	4.440147900	0.279213119	2.009311838
Н	3.867824105	0.476061688	2.909356030
С	5.516079296	-3.821094272	1.001713757
Н	5.724806012	-3.868145696	-0.076906889
Н	6.203472393	-4.503038314	1.527843866
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Н	4.402904993	-6.232693560	1.328528440
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С	-1.779343328	1.578781267	-2.484600576
С	-2.897563294	2.442243716	-2.300479427
Н	-2.842781087	3.216024422	-1.543072174
С	-4.046633891	2.315222448	-3.079130586
Н	-4.875442686	3.001051837	-2.904564706
С	-4.161267616	1.336377404	-4.071014785
Н	-5.059199417	1.253760542	-4.677917488
С	-3.068921497	0.478881457	-4.275370318
Н	-3.115726833	-0.282731681	-5.054354747
С	-1.911415942	0.590692951	-3.510914646
Η	-1.069422452	-0.072429683	-3.691810221
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Η	-0.039899019	4.129653202	1.385790985
С	0.123645769	5.964092132	0.294764008
Η	0.307550848	6.537423507	1.202427915
С	0.146944824	6.605182749	-0.956994051
Н	0.310479230	7.676979460	-1.035121521
С	-0.045894470	5.817752291	-2.096202706
Η	-0.034610926	6.282898670	-3.082008431
С	-0.274593078	4.442165679	-2.010065683
Н	-0.471682829	3.869676802	-2.909951931

С	3.826313774	5.518640143	-1.004858525
Н	3.874352178	5.728421880	0.073516698
Н	4.507870708	6.205445483	-1.532257109
С	5.464025664	3.831156805	-0.796986557
Н	6.237530293	4.404675969	-1.332326832
Н	5.552387417	4.034338040	0.280210010
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Ν	-1.630853202	-0.601594161	1.777471724
Ν	-2.442511284	-0.594975265	0.577996570
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С	-2.437106976	-2.894813948	2.301268669
Н	-3.211019749	-2.840057565	1.543993440
С	-2.310021493	-4.043803205	3.080028562
Н	-2.995953977	-4.872579361	2.905702908
С	-1.331000333	-4.158393110	4.071744055
Н	-1.248338238	-5.056258795	4.678738184
С	-0.473381281	-3.066088859	4.275803301
Н	0.288385858	-3.112864355	5.054638809
С	-0.585246505	-1.908667019	3.511230051
Н	0.077990415	-1.066714091	3.691889032
С	-3.770724181	-0.335401316	0.743438016
С	-4.594434433	-0.099221973	-0.406576801
Н	-4.125090980	-0.037644280	-1.385006253
С	-5.959259791	0.126350063	-0.293594793
Н	-6.532776590	0.310133269	-1.201166055
С	-6.600070368	0.149966103	0.958302008
Н	-7.671829931	0.313645991	1.036635106

С	-5.812411940	-0.042763808	2.097369520
Н	-6.277338287	-0.031258594	3.083276970
С	-4.436871161	-0.271650061	2.010966089
Н	-3.864217709	-0.468687474	2.910759519
С	-5.513158608	3.829132527	1.005259017
Н	-5.722817681	3.876614596	-0.073163303
Н	-6.200020040	4.510961881	1.532232497
С	-3.825681598	5.466774264	0.796830381
Н	-4.399223999	6.240505328	1.331818362
Н	-4.028812916	5.554681982	-0.280412914
Κ	-2.182109271	-2.311910884	-1.686265352
0	-4.165566965	-4.157949516	-1.269627795
Ν	0.606108360	-1.628758634	-1.777285384
Ν	0.599731716	-2.440184899	-0.577642122
С	1.781032298	-1.571476599	-2.485109428
С	2.899316929	-2.434933291	-2.301330392
Н	2.844770344	-3.208711711	-1.543905232
С	4.048153339	-2.307898064	-3.080325050
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Н	5.060227365	-1.246432109	-4.679420907
С	3.070074437	-0.471552334	-4.276253128
Н	3.116646591	0.290076268	-5.055236382
С	1.912805133	-0.583365560	-3.511441892
Н	1.070763615	0.079770874	-3.692064147
С	0.340220056	-3.768451624	-0.742763564
С	0.104373073	-4.591947421	0.407475272
Н	0.042952075	-4.122403971	1.385820217

С	-0.121076460	-5.956820919	0.294824195
Н	-0.304600301	-6.530169069	1.202554351
С	-0.144901076	-6.597891057	-0.956934958
Н	-0.308490856	-7.669682794	-1.035011431
С	0.047493939	-5.810447264	-2.096206807
Н	0.035814016	-6.275576973	-3.082015909
С	0.276251459	-4.434863822	-2.010138884
Н	0.473048197	-3.862382543	-2.910094555
С	-3.823943595	-5.510609614	-1.002127341
Н	-3.870474637	-5.719262033	0.076529003
Н	-4.506145722	-6.198032186	-1.527884237
С	-5.461713107	-3.823216357	-0.794122248
Н	-6.235685211	-4.397426400	-1.328043666
Н	-5.548861509	-4.025319769	0.283375787
Н	2.802674807	5.682487019	-1.348400856
Н	5.612461206	2.762137051	-0.963031371
Н	-5.610543467	-2.754393717	-0.961061832
Н	-2.800762710	-5.674720708	-1.346903617
Н	-5.677053798	2.805672204	1.349308739
Н	-2.756669354	5.615279551	0.962851477
Н	5.680152289	-2.797744738	1.346008355
Н	2.759863531	-5.607717608	0.961311614

Lowest Energy Frequencies (cm⁻¹) 15.11, 16.31, 17.61, 17.61, 20.16, 26.73 Sum of Electronic and Thermal Free Energies (Hartrees) –5785.43

Synthetic Details and Characterization

Synthesis of Li₄(Et₂O)₄[Ce(PhNNPh)₄] (4.1.1). Hydrazobenzene (0.10 g, 0.56 mmol) was dissolved in 2 mL of diethyl ether in a 20 mL scintillation vial. Ce[N(SiMe₃)₂]₃ (0.10 g, 0.14 mmol) was added to the mixture, resulting in a brown-orange suspension. After stirring for 1 h, the diethyl ether was removed under reduced pressure. Diethyl ether was added to the green-yellow solid, resulting in an orange suspension. In a separate 20 mL scintillation vial, LiN(SiMe₃)₂ (0.094 g, 0.56 mmol) was weighed and dissolved in hexanes to form a colorless solution. The colorless hexanes solution was layered over the orange suspension. Product formation was concentration-dependent, but not stoichiometry dependent. The product could also be formed using bulk reactions but crystalline yield was lower. After 1d, dark purple crystals formed. The crystals were collected by filtration over a medium frit, washed with hexane, and dried under reduced pressure. Yield: 0.119 g, 0.100 mmol, 71 %. ¹H NMR (400 MHz, C_6D_6) δ 7.29 (t, J = 7.4 Hz, 4 H), 6.50 (t, J = 7.4 Hz, 2 H), 6.10 (br, 4 H), 3.11 (s, 4 H), 0.76 (s, 6 H).⁷Li NMR (400 MHz, C₆D₆) δ 0.61. ¹³C NMR (360 MHz, C₆D₆) δ 161.11, 129.62, 128.6, 118.80, 66.29, 15.19. Elemental Analysis calculated for C₆₇H₆₅CeLi₄N₁₁O: C, 64.42; H, 6.76; N, 9.39. Found: C, 64.15; H, 7.08; N, 9.30.



Figure 4.4.5. ¹H NMR spectrum of $Li_4(Et_2O)_4[Ce(PhNNPh)_4]$ (4.1.1) collected in C_6D_6 .



Figure 4.4.6. ⁷Li NMR spectrum of $Li_4(Et_2O)_4[Ce(PhNNPh)_4]$ (4.1.1) collected in C_6D_6 .



Figure 4.4.7. ¹³C NMR spectrum of $Li_4(Et_2O)_4[Ce(PhNNPh)_4]$ (4.1.1) collected in C₆D₆.

Synthesis of Li₄(py)₄[Ce(PhNNPh)₄] (4.1.2). Hydrazobenzene (0.083 g, 0.45 mmol, 4 equiv.) was dissolved in 3 mL of diethyl ether in a 20 mL scintillation vial. Ce[N(SiMe₃)₂]₃•toluene (0.082 g, 0.12 mmol, 1 equiv.) was added to the mixture, resulting in a brown-orange suspension. After stirring for 1 h, the diethyl ether was removed under reduced pressure. Diethyl ether (or toluene) (5 mL) with pyridine (43 μL, 4.5 equiv.) was added to the green-yellow solid, resulting in an orange suspension. In a separate 20 mL scintillation vial, LiN(SiMe₃)₂ (0.076 g, 0.45 mmol, 4 equiv.) was weighed and dissolved in hexanes to form a colorless solution. The colorless hexanes solution was layered over the orange suspension. Product formation was concentration-dependent, but not stoichiometry dependent. The product could also be formed using bulk reactions but crystalline yield was lower. After 1d, dark purple crystals formed. The crystals were collected by filtration over a medium frit, washed with hexane, and dried 288 under reduced pressure. Yield: 0.103 g, 0.085 mmol, 74 %. ¹H NMR (360 MHz, C₆D₆) δ 7.93 (s, 2 H), 7.26 (s, 4 H), 6.69 (t, *J* = 7.2 Hz, 1 H), 6.49 (t, *J* = 7.2 Hz, 2 H), 6.36 (s, 2 H), 6.23 (s, 4 H) 3.13 (q, *J* = 7.0 Hz, 2 H) 0.88 (t, *J* = 7.0 Hz, 3 H). ⁷Li NMR (400 MHz, C₆D₆) δ 1.93 (0.2 Li), 1.47 (1 Li). ¹³C NMR (360 MHz, C₆D₆) δ 160.86, 149.31, 136.76, 129.36, 124.14, 118.49, 117.07. FTIR (C₆D₆) 3055.63, 2976.81, 2828.47, 2867.82, 1584.84 (vs), 1556.91, 1471.46 (vs), 1442.30 (s), 1416.36, 1296.71, 1286.64, 1254.62 (vs), 1164.28, 1118.78, 1071.37, 1026.25, 1019.52, 987.41, 869.14, 775.61, 751.14 (s), 702.66 (s), 693.13 (s), 618.17. Elemental Analysis calculated for Li₄(py)₃(Et₂O)[Ce(PhNNPh)₄] C₆₇H₆₅CeLi₄N₁₁O: C, 66.61; H, 5.42; N, 12.75. Found: C, 66.36; H, 5.39; N, 12.61.



Figure 4.4.8. ¹H NMR spectrum of $Li_4(py)_4[Ce(PhNNPh)_4]$ (**4.1.2**) collected in C₆D₆. Reproduced by permission of The Royal Society of Chemistry.



Figure 4.4.9. ⁷Li NMR spectrum of $Li_4(py)_4[Ce(PhNNPh)_4]$ (4.1.2) collected in C_6D_6 .

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Figure 4.4.10. ¹³C NMR spectrum of $Li_4(py)_4[Ce(PhNNPh)_4]$ (**4.1.2**) collected in C₆D₆. Reproduced by permission of The Royal Society of Chemistry.



Figure 4.4.11. Experimental (black) FTIR spectrum of $Li_4(py)_4[Ce(PhNNPh)_4]$ (**4.1.2**) collected in C₆D₆ and its calculated spectrum (red) of $Li_4(OMe_2)_4[Ce(PhNNPh)_4]$ (**4.1.3**), where the calculated energies are scaled by 0.9594.^[33] Reproduced by permission of The Royal Society of Chemistry.



Figure 4.4.12. UV-Vis spectra of 4.1.2 in fluorobenzene (red) and toluene (blue).

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Synthesis of Na₄(py)₈[Ce(PhNNPh)₄] (4.2). Hydrazobenzene (0.095 g, 0.52 mmol, 4 equiv.) was dissolved in 4 mL of diethyl ether in a 20 mL scintillation vial.

 $Ce[N(SiMe_3)_2]_3$ (0.082 g, 0.13 mmol, 1 equiv.) was added to the mixture, resulting in a brown-orange suspension. After stirring for 1 h, the diethyl ether was removed under reduced pressure. Diethyl ether (2 mL) was added to the green-yellow solid, and then pyridine (105 μ L, 10 equiv.) was added to form an orange suspension. NaN(SiMe₃)₂ (0.095 g, 0.52 mmol, 4 equiv.) was weighed in a separate 20 mL scintillation vial and dissolved in 1.5 mL diethyl ether. The dissolved NaN(SiMe₃)₂ was layered over the orange suspension. Finally, hexanes (1 mL) were layered over the two diethyl ether layers. 0.132 g (0.083 mmol) of purple needles were collected by filtration in a medium frit, washed with hexanes, and dried under reduced pressure. Product formation was concentration-sensitive but not stoichiometry sensitive. The product could also be formed using bulk reactions but crystalline yield was lower. Yield: 64 %. ¹H NMR (360 MHz, $C_{6}D_{6}$ δ 8.04 (s, 2 H), 7.05 (s, 2 H), 6.88 (t, J = 7.2 Hz, 1 H), 6.76-6.52 (m, 2H), 6.51-6.14 (m, 2H), 5.89 (s, 1 H), 3.21 (q, J = 7.0 Hz, 0.6 H), 1.06 (t, J = 7.0 Hz, 1 H). ¹³C NMR (360 MHz, C₆D₆) 161.23, 150.53, 136.39, 129.07, 124.04, 113.48. FTIR (C₆D₆) 3052.20, 2997.57, 2976.29, 22868.66, 1582.74 (vs), 1547.75 (s), 1468.83 (vs), 1440.44 (s), 1296.41 (s), 1289.19 (s), 1256.80 (vs), 1162.99 (s), 1148.41, 1118.74, 1069.80, 1033.85, 1018.29, 987.09 (vs), 860.03 (s), 793.83, 746.86 (s), 702.93 (vs), 613.74, 599.51. Elemental Analysis calculated for Na₄(py)₅(Et₂O)[Ce(PhNNPh)₄] C₇₇H₇₅CeNa₄N₁₃O: C, 64.65; H, 5.28; N, 12.73. Found: C, 64.58; H, 5.08; N, 12.70.



Figure 4.4.13. ¹H NMR spectrum of $Na_4(py)_8[Ce(PhNNPh)_4]$ (**4.2**) collected in C_6D_6 . Reproduced by permission of The Royal Society of Chemistry.



Figure 4.4.14. ¹³C NMR spectrum of $Na_4(py)_8[Ce(PhNNPh)_4]$ (**4.2**) collected in C_6D_6 . Reproduced by permission of The Royal Society of Chemistry.



Figure 4.4.15. Experimental (black) FTIR spectrum of $Na_4(py)_8[Ce(PhNNPh)_4]$ (**4.2**) collected in C_6D_6 and its calculated spectrum (red) of $Na_4(OMe_2)_4[Ce(PhNNPh)_4]$ (**4.2.2**), where the calculated energies are scaled by 0.9594.^[33] Reproduced by permission of The Royal Society of Chemistry.



Figure 4.4.16. UV-Vis spectra of 4.2 in fluorobenzene (red) and toluene (blue).

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Synthesis of K₅(py)₇[Ce(PhNNPh)₄] (4.3). Hydrazobenzene (0.095 g, 0.52 mmol, 4 equiv.) was dissolved in 4 mL of diethyl ether in a 20 mL scintillation vial. $Ce[N(SiMe_3)_2]_3$ (0.081 g, 0.13 mmol, 1 equiv.) was added to the mixture, resulting in a brown-orange suspension. After stirring for 1 h, the diethyl ether was removed under reduced pressure. Pyridine was added to the green-yellow solid, resulting in a dark red solution, which over time formed a red suspension. KN(SiMe₃)₂ (0.124 g, 0.64 mmol, 5 equiv.) was weighed and added to the pyridine solution. A dark brown solution immediately formed. The solution was stirred for 1 d and then the pyridine was removed under reduced pressure. The resulting solid was redissolved in pyridine (1.5 mL) and then layered with hexanes (3 mL). Dark brown needles formed. The solid was collected by filtration on a medium frit, washed with hexanes, and dried under reduced pressure. While this reported synthesis reports the method that yielded the product most consistently, it is important to note that the formation of product was extremely conditions and concentration sensitive although not stoichiometry sensitive. Yield: 0.131 g, 0.081 mmol, 63 %. ¹H NMR (360 MHz, pyridine-*d*₅) δ 7.003–6.89 (br d, 3 H), 6.23(br s, 1 H), 5.84 (br, 1 H). ¹³C NMR (360 MHz, pyridine-*d*₅) 159.95, 150.77, 136.60, 129.21, 128.14, 124.56, 118.98, 111.08. FTIR (nujol) 3049.33, 2922.30, 2853.02, 1582.33 (vs), 1544.48 (s), 1465.91 (vs), 1439.18, 1377.00, 1298.18 (vs), 1265.63 (vs), 1163.72 (vs), 1149.11, 1071.64, 1030.39, 1018.91, 995.23, 986.20, 862.36, 818.34, 783.64, 746.92 (vs), 702.19 (vs), 608.58, 591.44, 524.12. Elemental Analysis calculated for C₈₃H₇₅CeK₅N₁₅: C, 61.61; H, 4.67; N, 12.98. Found: C, 61.25; H, 4.32; N, 12.98.



Figure 4.4.17. ¹H NMR spectrum of K₅(py)₇[Ce(PhNNPh)₄] (4.3) collected in pyridine-

 d_5 . Reproduced by permission of The Royal Society of Chemistry.



Figure 4.4.18. ¹³C NMR spectrum of K₅(py)₇[Ce(PhNNPh)₄] (4.3) collected in pyridine-

 d_5 . Reproduced by permission of The Royal Society of Chemistry.



Figure 4.4.19. Experimental (black) FTIR spectrum of $K_5(py)_7[Ce(PhNNPh)_4]$ (**4.3**) collected in nujol and its calculated spectrum (red) of $K_4(OMe_2)_4[Ce(PhNNPh)_4]^-$ (**4.3.2**), where the calculated energies are scaled by 0.9594.^[33] Reproduced by permission of The Royal Society of Chemistry.

Metathesis of LiI with complex 4.3 K₅(py)₇[Ce(PhNNPh)₄]



Figure 4.4.20. Gas chromatogram of the metathesis reaction of complex **4.3** with LiI. Complex **4.3** was reacted with LiI first in diethyl ether. The reaction was then acidified with HNEt₃Cl, filtered over celite, and run on the GC/MS. At 2.233 min, m/Z = 86, corresponds to pyridine with Li⁺; the next trace at 9.352 min, m/Z = 182, corresponds to azobenzene; the final trace that can be integrated at 10.54 min, m/Z = 184, corresponds to 1,2-diphenylhydrazine. Reproduced by permission of The Royal Society of Chemistry.



12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 ppm

Figure 4.4.21. ¹H NMR spectrum in pyridine- d_5 of the following crude reaction mix: Ce{N(SiHMe₂)₂}₄ was prepared in situ by reacting K[Ce{N(SiHMe₂)₂}₄] with FcOTf.^[36] In a diethyl ether solution, KH or KN(SiMe₃)₂ and 1,2-diphenylhydrazine were added to Ce{N(SiHMe₂)₂}₄. The reaction resulted in complex **4.3** and ferrocene. Reproduced by permission of The Royal Society of Chemistry.



Figure 4.4.22. Atomic orbitals 87 and 101 of the calculated Li₄(Me₂O)₄[Ce(PhNNPh)₄] complex showing one set of the Ce–N bonding and antibonding orbitals. Reproduced by permission of The Royal Society of Chemistry.



Figure 4.4.23. ¹H NMR spectrum in pyridine- d_5 of the reaction of complex **4.3** with Ph₃CCl. The resonances originating from complex **4.3** were labeled "s.m.".



Figure 4.4.24. ¹H NMR spectrum in pyridine- d_5 of the reaction of complex **4.3** with FcPF₆. The resonances originating from complex **4.3** were labeled "s.m.". Ferrocene did appear in the ¹H NMR spectrum indicating that an oxidation may have taken place, but the oxidized product reverted to the original Ce(III) starting material, complex **4.3**.



Figure 4.4.25. ¹H NMR spectrum in pyridine- d_5 of the reaction of complex **4.3** with CuCl₂. The resonances originating from azobenzene were labeled "azo".



Figure 4.4.26. ¹H NMR spectrum in pyridine- d_5 of the reaction of complex **4.3** with I₂.



Figure 4.4.27. ¹H NMR spectrum in pyridine- d_5 of the reaction of complex **4.3** with 18crown-6. 18-crown-6 was labeled as "18-c-6", excess KN(SiMe₃)₂ was labeled as KN*, and the resonances belonging to either the starting material or the desired product were labeled with asterisks.



Figure 4.4.28. 30 % thermal ellipsoid plots of $Li_4(DME)_4[Ce(PhNNPh)_4]$ (left) and $Na_4(Et_2O)_4[Ce(PhNNPh)_4]$ (right).

Table 4.4.13. Crystallographic parameters for compounds $Li_4(DME)_4[Ce(PhNNPh)_4]$ and $Na_4(Et_2O)_4[Ce(PhNNPh)_4]$.

	Li ₄ (DME) ₄ [Ce(PhNNPh) ₄]	Na ₄ (Et ₂ O) ₄ [Ce(PhNNPh) ₄]
	(Penn4362)	(Penn4359)
Empirical formula	C ₆₄ H ₈₀ CeLi ₄ N ₈ O ₈	$C_{64}H_{80}N_8O_4Na_4Ce$
Formula weight	1257.24	1257.44
Temperature (K)	143(1)	143(1)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Tetragonal
Space group	C2/c	I4
Cell constants		
a (Å)	24.2064(17)	16.1012(8)
b (Å)	11.7485(7)	16.1012(8)
c (Å)	22.7377(13)	12.4081(7)

α (°)	90.00	90.00
β (°)	98.059(5)	90.00
γ (°)	90.00	90.00
$V(Å^3)$	6402.5(7)	3216.8(3)
Ζ	4	2
$\rho_{calc} (mg/cm^3)$	1.304	1.298
μ (Mo K α) (mm ⁻¹)	0.769	0.786
F(000)	2616	1308
Crystal size (mm ³)	0.38 x 0.12 x 0.10	0.45 x 0.03 x 0.02
Theta range for data collection	1.70 to 27.75°	1.79 to 27.50°
In day non and	$-31 \le h \le 31, -15 \le k \le 15, -$	-20 \leq h \leq 20, -20 \leq k \leq 20, -
index ranges	$29 \leq l \leq 29$	$16 \le l \le 16$
Reflections collected	72479	32163
Independent collections	7516 [R(int) = 0.0286]	3695 [R(int) = 0.0380]
Completeness to theta = 27.75°	99.5%	100.0%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max and min. transmission	0.7456 and 0.6635	0.7456 and 0.6883
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F^2
Data / restraints / parameters	7516 / 0 / 389	3695 / 0 / 187
Goodness-of-fit on F ²	1.047	1.064
Final R indices [I>2sigma(I)]	R1 = 0.0175, wR2 = 0.0454	R1 = 0.0198, wR2 = 0.0426

R indices (all data)	R1 = 0.0197, wR2 = 0.0466	R1 = 0.0201, wR2 = 0.0428
Largest diff. peak and	0.222 and 0.202	0.554 and 0.201
hole (e.Å $^{-3}$)	0.555 and -0.205	0.334 and -0.291

4.5 BIBLIOGRAPHY

- S. Cotton, *Lanthanide and Actinide Chemistry*, John Wiley and Sons Inc., Hoboken, NJ, **2006**.
- [2] A. W. G. Platt, *The Rare Earth Elements: Fundamentals and Applications*, John Wiley & Sons Ltd., Chichester, United Kingdom, 2012.
- [3] N. G. Connelly, W. E. Geiger, *Chem. Rev.* **1996**, *96*, 877-910.
- [4] A. K. Das, *Coord. Chem. Rev.* 2001, 213, 307-325; G. A. Molander, *Chem. Rev.* 1992, 92, 29-68.
- [5] T. Imamoto, Y. Koide, S. Hiyama, *Chem. Lett.* 1990, *19*, 1445-1446; T. Kreuzer,
 E. S. Lox, D. Lindner, J. Leyrer, *Catal. Today* 1996, *29*, 17-27; T. D. Beeson, A.
 Mastracchio, J.-B. Hong, K. Ashton, D. W. C. MacMillan, *Science* 2007, *316*,
 582-585; V. Sridharan, J. C. Menendez, *Chem. Rev.* 2010, *110*, 3805-3849; S. W.
 Gersten, G. J. Samuels, T. J. Meyer, *J. Am. Chem. Soc.* 1982, *104*, 4029-4030; T.L. Ho, *Synthesis* 1973, 347-354; S. V. More, M. N. V. Sastry, C.-F. Yao, *Green Chem.* 2006, *8*, 91-95; W. Ruttinger, G. C. Dismukes, *Chem. Rev.* 1997, *97*, 1-24.
- [6] V. Nair, L. Balagopal, R. Rajan, J. Matthew, Acc. Chem. Res. 2004, 37, 21-30; V.
 Nair, A. Deepthi, Chem. Rev. 2007, 107, 1862-1891.
- [7] K. Eguchi, T. Setoguchi, T. Inoue, H. Arai, *Solid State Ionics* 1992, *52*, 165-172.

- [8] S. Park, J. M. Vohs, R. J. Gorte, *Nature* 2000, 404, 265-267; G. A. Deluga, J. R. Salge, L. D. Schmidt, X. E. Verykios, *Science* 2004, *303*, 993-997; E. P. Murray, T. Tsai, S. A. Barnett, *Nature* 1999, 400, 649-651; S. B. Adler, *Chem. Rev.* 2004, *104*, 4791-4844; M. Mogensen, N. M. Sammes, G. A. Tompsett, *Solid State Ionics* 2000, *129*, 63-94.
- [9] J. Kaspar, P. Fornasiero, N. Hickey, *Catal. Today* 2003, 77, 419-449; J. Kaspar,
 P. Fornasiero, *J. Solid State Chem.* 2003, *171*, 19-29; R. Burch, *Catal. Rev.* 2004, 46, 271-333.
- [10] T. Bunluesin, R. J. Gorte, G. W. Graham, *Appl. Catal. B* 1998, *15*, 107-114; Q.
 Fu, H. Saltsburg, M. Flytzani-Stephanopoulos, *Science* 2003, *301*, 935-938; Y. Li,
 Q. Fu, M. Flytzani-Stephanopoulos, *Appl. Catal. B* 2000, *27*, 179-191; J. A.
 Rodriguez, S. Ma, P. Liu, J. Hrbek, J. Evans, M. Perez, *Science* 2007, *318*, 1757-1760.
- [11] L. Vivier, D. Duprez, *ChemSusChem* 2010, *3*, 654-678; L. Xu, J. Wang, *Environ. Sci. Technol.* 2012, *46*, 10145-10153; A. Kawashima, K. Matsubara, K. Honda, *Bioresource Technol.* 2008, *99*, 3439-3443; M. Dejhosseini, T. Aida, M.
 Watanabe, S. Takami, D. Hojo, N. Aoki, T. Arita, A. Kishita, T. Adschiri, *Energy Fuels* 2013, *27*, 4624-4631.
- [12] J. A. Bogart, A. J. Lewis, S. A. Medling, N. A. Piro, P. J. Carroll, C. H. Booth, E. J. Schelter, *Inorg. Chem.* 2013, 52, 11600-11607; N. A. Piro, J. R. Robinson, P. J. Walsh, E. J. Schelter, *Coord. Chem. Rev.* 2014, 260, 21-36.

- [13] J. R. Robinson, C. H. Booth, P. J. Carroll, P. J. Walsh, E. J. Schelter, *Chem. Eur. J.* 2013, *19*, 5996-6004; D. Werner, G. B. Deacon, P. C. Junk, R. Anwander, *Chem. Eur. J.* 2014, *20*, 4426-4438; A. Sen, H. A. Stecher, A. L. Rheingold, *Inorg. Chem.* 1992, *31*, 473-479.
- [14] J. Robinson, P. J. Carroll, P. J. Walsh, E. J. Schelter, *Angew. Chem. Int. Ed.* 2012, 51, 10159-10163.
- [15] J. R. Robinson, Z. Gordon, C. H. Booth, P. J. Carroll, P. J. Walsh, E. J. Schelter, J. Am. Chem. Soc. 2013, 135, 19016-19024.
- [16] P. Comba, *Coord. Chem. Rev.* 2000, 200-202, 217-245; J. H. Timmons, J. W. L. Martin, A. E. Martell, P. R. Rudolf, A. Clearfield, *Inorg. Chem.* 1988, 27, 1638-1640; Q. Yu, C. A. Salhi, E. A. Ambundo, M. J. Heeg, L. A. Ochrymowycz, D. B. Rorabacher, *J. Am. Chem. Soc.* 2001, *123*, 5720-5729; E. I. Solomon, R. G. Hadt, *Coord. Chem. Rev.* 2011, 255, 774-789; B. L. Vallee, R. J. P. Williams, *Proc. Natl. Acad. Sci. U.S.A.* 1968, 59, 498-505; R. Lumry, H. Eyring, *J. Phys. Chem.* 1954, 58, 110-120; B. G. Malmstrom, *Eur. J. Biochem.* 1994, 223, 711-718; J. J. Warren, K. M. Lancaster, J. H. Richards, H. B. Gray, *J. Inorg. Biochem.* 2012, *115*, 119-126; S. M. Berry, M. H. Baker, N. J. Reardon, *J. Inorg. Biochem.* 2010, *104*, 1071-1078.
- [17] C. R. Hamilton, R. A. Baglia, A. D. Gordon, M. J. Zdilla, J. Am. Chem. Soc. **2011**, 133, 4208-4211.

- [18] S. K. Kondaveeti, S. Vaddypally, J. D. McCall, M. J. Zdilla, *Dalton Trans*. 2012, 41, 8093-8097.
- [19] S. Vaddypally, S. K. Kondaveeti, M. J. Zdilla, *Chem. Commun.* 2011, 47, 9696-9698.
- [20] P. B. Hitchcock, A. G. Hulkes, M. F. Lappert, Z. Li, *Dalton Trans.* 2004, 129-136.
- [21] W. J. Evans, D. J. Drummond, L. R. Chamberlain, R. J. Doedens, S. G. Bott, H. Zhang, J. L. Atwood, J. Am. Chem. Soc. 1988, 110, 4983-4994; A. A. Trifonov, M. N. Bochkarev, H. Schumann, J. Loebel, Angew. Chem. Int. Ed. Engl. 1991, 30, 1149-1151; K. L. Miller, B. N. Williams, D. Benitez, C. T. Carver, K. R. Ogilby, E. Tkatchouk, W. A. Goddard III, P. L. Diaconescu, J. Am. Chem. Soc. 2010, 132, 342-355; R. Allmann, in *The chemistry of the hydrazo, azo and azoxy groups, Vol. I* (Ed.: S. Patai), John Wiley & Sons, New York, 1975, pp. 23-52.
- [22] E. L. Muetterties, C. M. Wright, Q. Rev. Chem. Soc. 1967, 21, 109-194; E. L.
 Muetterties, L. J. Guggenberger, J. Am. Chem. Soc. 1974, 96, 1748-1756; J. L.
 Hoard, J. V. Silverton, Inorg. Chem. 1963, 2, 235-242.
- [23] L. Yang, D. R. Powell, R. P. Houser, *Dalton Trans.* 2007, 955-964.
- [24] M. H. Reineke, M. D. Sampson, A. L. Rheingold, C. P. Kubiak, *Inorg. Chem.* **2015**, *54*, 3211-3217.
- [25] T. S. Calderwood, C. L. Johlman, J. L. Roberts Jr., C. L. Wilkins, D. T. Sawyer, *J. Am. Chem. Soc.* **1984**, *106*, 4683-4687.

- M. J. Zdilla, A. K. Verma, S. C. Lee, *Inorg. Chem.* 2008, 47, 11382-11390; M. J. Zdilla, A. K. Verma, S. C. Lee, *Inorg. Chem.* 2011, 50, 1551-1562; D. S. J. Arney, C. J. Burns, *J. Am. Chem. Soc.* 1995, *117*, 9448-9460; W. J. Evans, G. Kociok-Kohn, V. S. Leong, J. W. Ziller, *Inorg. Chem.* 1992, *31*, 3592-3600; B. Gemund, H. Noth, H. Sachdev, M. Schmidt, *Chem. Ber.* 1996, *129*, 1335-1344; Y. Ohki, Y. Takikawa, T. Hatanaka, K. Tatsumi, *Organometallics* 2006, *25*, 3111-3113; F. Alonso, G. Radivoy, M. Yus, *Tetrahedron* 2000, *56*, 8673-8678; J. M. Hoover, A. DiPasquale, J. M. Mayer, F. E. Michael, *Organometallics* 2007, *26*, 3297-3305; Y. Nakajima, H. Suzuki, *Organometallics* 2003, *22*, 959-969; A. F. Heyduk, R. A. Zarkesh, A. I. Nguyen, *Inorg. Chem.* 2011, *50*, 9849-9863; R. A. Zarkesh, A. F. Heyduk, *Organometallics* 2011, *30*, 4890-4898.
- [27] D. H. Kim, U. S. Shin, C. E. Song, J. Molec. Catal. A: Chem. 2007, 271, 70-74;
 S. Fukuzumi, K. Ohkubu, Chem. Eur. J. 2000, 6, 4532-4535; S. Fukuzumi, N.
 Satoh, T. Okamoto, K. Yasui, T. Suenobu, Y. Seko, M. Fujitsuka, O. Ito, J. Am.
 Chem. Soc. 2001, 123, 7756-7766; S. Fukuzumi, Y. Fujii, T. Suenobu, J. Am.
 Chem. Soc. 2001, 123, 10191-10199; S. Fukuzumi, J. Synth. Org. Chem., Jpn.
 2003, 61, 1046-1055; S. Fukuzumi, Org. Biomol. Chem. 2003, 1, 609-620; K.
 Ohkubo, T. Suenobu, H. Imahori, A. Orita, J. Otera, S. Fukuzumi, Chem. Lett.
 2001, 978-979; J. Park, Y. Morimoto, Y.-M. Lee, W. Nam, S. Fukuzumi, Inorg.
 Chem. 2014, 53, 3618-3628.

- [28] K. Ohkubo, S. C. Menon, A. Orita, J. Otera, S. Fukuzumi, J. Org. Chem. 2003, 68, 4720-4726.
- [29] D. F. Evans, J. Chem. Soc. 1959, 2003-2005; E. M. Schubert, J. Chem. Educ.
 1992, 69, 62.
- [30] M. D. Walter, R. Fandos, R. A. Andersen, New J. Chem. 2006, 30, 1065-1070.
- [31] A. Panagiotopoulos, T. F. Zafiropoulos, S. P. Perlepes, E. Bakalbassis, I. Masson-Ramade, O. Kahn, A. Terzis, C. P. Raptopoulou, *Inorg. Chem.* 1995, *34*, 4918-4920; C. Benelli, D. Gatteschi, *Chem. Rev.* 2002, *102*, 2369-2388; H. An, H. Zhang, Z. Chen, Y. Li, X. Liu, H. Chen, *Dalton Trans.* 2012, *41*, 8390-8400.
- [32] C. A. Smith, E. W. Ainscough, H. M. Baker, A. M. Brodie, E. N. Baker, J. Am. Chem. Soc. 1994, 116, 7889-7890.
- [33] M. P. Andersson, P. Uvdal, J. Phys. Chem. A 2005, 109, 2937-2941; K. K.
 Irikura, R. D. Johnson III, R. N. Kacker, J. Phys. Chem. A 2005, 109, 8430-8437.
- [34] H.-G. Cho, L. Andrews, *Organometallics* 2012, *31*, 535-544; X. Wang, L.
 Andrews, B. Vlaisavljevich, L. Gagliardi, *Inorg. Chem.* 2011, *50*, 3826-3831; X.
 Wang, H.-G. Cho, L. Andrews, M. Chen, D. A. Dixon, H.-S. Hu, J. Li, *J. Phys. Chem. A* 2011, *115*, 1913-1921.
- [35] D. D. Weis, G. E. Ewing, Anal. Chem. 1998, 70, 3175-3183.
- [36] U. J. Williams, D. Schneider, W. L. Dorfner, C. Maichle-Mossmer, P. J. Carroll,
 R. Anwander, E. J. Schelter, *Dalton Trans*. 2014, 43, 16197-16206.

- [37] A. R. Crozier, A. M. Bienfait, C. Maichle-Mossmer, K. W. Tornroos, R. Anwander, *Chem. Commun.* 2013, 49, 87-89.
- [38] S. Vaddypally, S. K. Kondaveeti, J. H. Roudebush, R. J. Cava, M. J. Zdilla, *Chem. Commun.* 2014, 50, 1061-1063.
- [39] D. Quane, J. Chem. Ed. 1970, 47, 396-398.
- [40] D. C. Bradley, J. S. Ghotra, F. A. Hart, J. Chem. Soc., Dalton Trans. 1973, 1021 1023.
- [41] G. A. Bain, J. F. Berry, J. Chem. Educ. 2008, 85, 532-536.
- [42] Bruker, Bruker AXS Inc., Madison, Wisconsin, USA, 2009.
- [43] Bruker, Bruker AXS Inc., Madison, Wisconsin, USA, 2009.
- [44] G. M. Sheldrick, University of Gottingen, Germany, 2008.
- [45] G. M. Sheldrick, University of Gottingen, Germany, 2007.
- [46] G. M. Sheldrick, Acta Cryst. 2008, A64, 112-122.
- [47] S. R. Sofen, S. R. Cooper, K. N. Raymond, *Inorg. Chem.* 1979, *18*, 1611-1616;
 W. L. Smith, K. N. Raymond, *J. Am. Chem. Soc.* 1981, *103*, 3341-3349; D. G.
 Blight, D. L. Kepert, *Inorg. Chem.* 1972, *11*, 1556-1561; S. J. Lippard, B. J. Russ, *Inorg. Chem.* 1968, *7*, 1686-1688.
- [48] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R.
 Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji,
 M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L.
 Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida,

T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J.
E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N.
Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C.
Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E.
Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E.
Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L.
Martin, K. Morokuma, V. G. Zakrzewski, V. Voth, J. Cioslowski, D. J. Fox, *Revision D.01*, Gaussian, Inc., Wallingford, CT, **2009**.

- [49] Institute for Theoretical Chemistry, University of Cologne, http://www.tc.uni-koeln.de/PP/clickpse.en.html; X. Cao, M. Dolg, *J. Molec. Struct. (Theochem)*2002, 581, 139-147; M. Dolg, H. Stoll, H. Preuss, *J. Chem. Phys.* 1989, 90, 1730-1734.
- [50] Chemcraft, www.chemcraftprog.com.

CHAPTER 5

Accessing Electron Poor Cerium(IV) Complexes by Alkali Metal Promoted Ligand Reduction

Abstract:

A series of substituted 1,2-diarylhydrazines (ArNHNHAr) were reacted with Ce(III) and Li^+ to explore the use of Ce(III) as a reductant and to measure the impact of the ligand substitution on the electronic structure at the cerium metal center. The 1,2-diarylhydrazido ligands were coordinated by the Li^+ cation and then reduced by a Ce(III) cation to form $Li_4(Et_2O)_4[Ce^{IV}(ArNNAr)_4]$ complexes. Stabilization of the resulting Ce(IV) product depended on the substituents on the 1,2-diarylhydrazido ligands. Isolable cerium products formed only with electron withdrawing substituents on the 1,2-diarylhydrazido rings, whereas electron donating substituents resulted in intractable mixtures of Ce(III) products and 1,2-bis(aryl)diazene (ArN=NAr). The presence of electron withdrawing substituents at the 1,2-diarylhydrazido ligands formed relatively electron poor Ce(IV) complexes, which were probed by UV-Vis spectroscopy, cyclic voltammetry, and DFT calculations. The Lewis acid promoted reduction of
hydrazobenzene derivatives by Ce(III) proved to be a successful method to access very electron poor cerium(IV) complexes.

Adapted from work to be submitted to Inorg. Chem.

5.1 Introduction

Alkali metals and alkali metal cations have been used to promote important heterogeneous and homogeneous reactions.^[1-3] For example, the addition of alkali metals to iron-based heterogeneous catalysts in both the Fischer-Tropsch and nitrogen fixation reactions increased selectivity and activity of those catalysts.^[1] The alkali metal was thought both to impact the electronics of the active catalytic metal center as well as those of the substrate at the surface.^[1] In homogeneous reactions, bifunctional Lewis acid-Lewis acid catalysts such as the rare earth metal BINOLate (REMB) framework, $M_3(THF)_n[(BINOLate)_3RE] M = Li, RE = Y, La, Pr, Sm, Dy, Er, Tm, Yb, Lu, BINOLate$ = 1,1'-bi-2-naphtholate, have been used to achieve enantioselective aza-Michael additions(Scheme 5.1.1).^[3] Both the rare earth and the alkali metal cations activate the twosubstrates and place them in close proximity to each other. The choice of alkali metalcation in the REMB system modulates the sterics and electronics at the lanthanide metalcenter, impacting the reactivity of that system.^[4]



Scheme 5.1.1. Proposed cooperation of the rare earth (RE) Lewis acid with the alkali metal (M) Lewis acid in the rare earth metal BINOLate (REMB) catalysts which were used for the enantioselective 1,4-addition of alkoxylamine. Adapted with permission of Noriyuki Yamagiwa, Hongbo Qin, Shigeki Matsunaga, Masakatsu Shibasaki. *J. Am. Chem. Soc.* 2005, *127*, 13419-13427 (Ref. 3). Copyright 2005 American Chemical Society.

Reduction of a substrate also can occur when the rare earth in the REMB complex is Ce(III). Two equiv Li₃(THF)₄[(BINOLate)₃Ce(THF)] cooperatively reduce 1 equiv 1,4-benzoquinone.^[5] Typically, cerium is considered to be a potent oxidant, ($E^{\circ}(Ce^{IV/III}) =$ 1.40 V versus Fc/Fc⁺),^[6, 7] but the use of two cerium Lewis acids stabilizes the twoelectron reduction of *p*-benzoquinone by approximately 1.6 V.^[5] Previously, we used Ce(III) cations with alkali metal cations, M = Li⁺ and Na⁺, to activate and reduce 1,2diphenylhydrazine to aniline while simultaneously forming M₄(py)_x[Ce^{IV}(PhNNPh)₄] complexes, where x = 4 (Li) or 8 (Na) (Scheme 5.1.2).^[8] In this system, the 1,2diphenylhydrazine behaved both as the supporting ligand to a high-valent cerium cation and the oxidant. Intrigued by this reaction, we expanded this system by substituting the 1,2-diphenylhydrazine phenyl ring to observe how the sterics and the electronics of the substrate impacted its reduction by Ce(III) and the stabilization of the resulting oxidized $Li_4(Et_2O)_4[Ce^{IV}(ArNNAr)_4]$.



Scheme 5.1.2. Syntheses of Li₄(py)₄[Ce(PhNNPh)₄] and Na₄(py)₈[Ce(PhNNPh)₄].^[8]

We synthesized 1,2-bis(3,5-dimethylphenyl)hydrazine (^{Me2}ArNHNHAr^{Me2}), *N,N'*bis-(4-chlorophenyl)hydrazine (^{Cl}ArNHNHAr^{Cl}), *N,N'*-bis-(3,5-dichlorophenyl)hydrazine (^{Cl2}ArNHNHAr^{Cl2}), and 3,3',5,5'-tetrakis(trifluoromethyl)hydrazobenzene (Ar^FNHNHAr^F) to test the electronic limitations of the Ce(III) cation as the reducing agent and the effect of varying the steric bulk of the ligands on the resulting Ce(IV) coordination geometries in this system (Schemes 5.2.1 and 5.2.3). A more electron donating substituent was expected to stabilize the Ce(IV) cation but disfavor the reduction of the arylhydrazine, whereas an electron withdrawing substitution would poorly stabilize the Ce(IV) cation but be easier to reduce. As hypothesized with this system, the more electron donating ligand, 1,2-bis(3,5-dimethylphenyl)hydrazine, formed the least stable cerium(IV) complex where the ^{Me2}ArN=NAr^{Me2} diazene compound was the only isolable product in that system, while an electron poor Ar^FNNAr^F cerium(IV) complex could be isolated. Finally, the isolation of a series of electron withdrawing

substitutions on the diphenylhydrazido ligand allowed us to measure the ligands' effects on the electronic structure of the cerium metal center.

5.2 Results and Discussion

Based on previous results where cerium(III) reduced the PhNHNHPh ligand in the presence of Li^+ cations to form a cerium(IV) diphenylhydrazido complex, $Li_4(py)_4[Ce^{IV}(PhNNPh)_4]$, we set out to synthesize a series of Li^+ Ce(IV)-diarylhydrazido complexes. The complexes $Li_4(Et_2O)_4[Ce(PhNNPh)_4]$ (**5.1**), $Li_4(Et_2O)_4[Ce(^{Cl}ArNNAr^{Cl})_4]$ (**5.2**) $Li_4(Et_2O)_4[Ce(^{Cl}ArNNAr^{Cl})_4]$ (**5.3**), and $Li_4(Et_2O)_4[Ce(Ar^FNNAr^F)_4]$ (**5.4**) were synthesized in poor to moderate yield (31–71%) and characterized by X-ray diffraction, NMR spectroscopy, UV-Vis spectroscopy, FTIR spectroscopy, magnetic susceptibility measurements, electrochemistry and DFT calculations. The electronic structures of each complex then were compared. Syntheses and experimental results and procedures will be described in detail in section 5.4.

5.2.1 Synthesis of ligands and complexes 5.1–5.4.

The initial goal of this project was to synthesize a series of four 1,2diarylhydrazine ligands, 2 with similar steric profiles but different electronic properties (PhNHNHPh and bis(pentafluorophenyl)-hydrazine [^{F5}ArNHNHAr^{F5}]; 1,2-bis(3,5dimethylphenyl)hydrazine [^{Me2}ArNHNHAr^{Me2}] and Ar^FNHNHAr^F) and two with different steric profiles but similar electronic properties (PhNHNHPh and ^{Me2}ArNHNHAr^{Me2}; ^{F5}ArNHNHAr^{F5} and Ar^FNHNHAr^F). We hypothesized that this set of ligands would allow us to isolate the electronic and steric effects of the ligand on Ce(IV) 317 product formation, ligand reduction, and structural and electronic properties of the resulting cerium complexes (Scheme 5.2.1). 1,2-bis(3,5-dimethylphenyl)hydrazine (Me2 ArNHNHAr Me2),^[9, 10] *N,N'*-bis(pentafluorophenyl)-hydrazine (F5 ArNHNHAr F5),^[11, 12] and 3,3',5,5'-tetrakis(trifluoromethyl)hydrazobenzene (Ar F NHNHAr F)^[11-14] (Scheme 5.2.1) were synthesized first by oxidation of the parent aniline to the substituted azobenzene, and then by subsequent reduction of the azobenzene to the desired hydrazines. Then the electronic effects of the substituents on the phenyl rings were tested by electrochemistry, showing the electron withdrawing substituents –CF₃ and –F caused over a 600 mV shift in the reduction potential compared to the parent azobenzene in acetonitrile (Figure 5.2.1).



Scheme 5.2.1. Series of 1,2-diarylhydrazine compounds that were reacted with Ce[N(SiMe₃)₂]₃ and LiN(SiMe₃)₂. (A) 1,2-bis(3,5-dimethylphenyl)hydrazine (^{Me2}ArNHNHAr^{Me2}), (B) 1,2-diphenylhydrazine (PhNHNHPh), (C) 3,3',5,5'-tetrakis(trifluoromethyl)hydrazobenzene (Ar^FNHNHAr^F), and (D) bis(pentafluorophenyl)-hydrazine (^{F5}ArNHNHAr^{F5}).

We then attempted to synthesize $Li_4(Et_2O)_4[Ce(ArNNAr)_4]$ complexes with the new ligand set in a similar manner to the syntheses of $Li_4(py)_4[Ce(PhNNPh)_4]$ and $Li_4(Et_2O)_4[Ce(PhNNPh)_4]$ (**5.1**) described in the previous chapter and shown in the introduction (Scheme 5.1.1). In general, all of the cerium complexes were synthesized first by adding 4 equiv ArNHNHAr ligand to 1 equiv $Ce^{III}[N(SiMe_3)_2]_3$ in diethyl ether to form a yellow-orange suspension (Scheme 5.2.2). 4 equiv $LiN(SiMe_3)_2$ were subsequently added to the reaction mix. The resulting dark purple products $Li_4(Et_2O)_4[Ce^{IV}(ArNNAr)_4]$ were extracted and crystallized from Et_2O , fluorobenzene, or toluene. However, syntheses of $Li_4(Et_2O)_4[Ce(^{F5}ArNNAr^{F5})_4]$ and $Li_4(Et_2O)_4[Ce(^{Me2}ArNNAr^{Me2})_4]$ complexes yielded intractable mixtures of products.

Scheme 5.2.2. Syntheses of Li₄(Et₂O)₄[Ce(ArNNAr)₄] complexes. Yields of successfully synthesized complexes **5.1–5.4** were also included.

The Lewis acidic Ce^{3+} and Li^{+} cations, together with the SiMe₃ group in $[N(SiMe_3)_2]^-$, evidently abstracted fluoride from the ^{F5}ArNHNHAr^{F5} ligand based on the ¹⁹F NMR spectra of the reaction mixtures, causing ligand decomposition and a wide variety of products observed in solution (Figure 5.4.10). The issues with synthesizing the $Li_4(Et_2O)_4[Ce(^{Me2}ArNNAr^{Me2})_4]$ complex were different than those for the

^{F5}ArNHNHAr^{F5} complex. Reaction of ^{Me2}ArNHNHAr^{Me2} with Ce[N(SiMe₃)₂]₃ and $LiN(SiMe_3)_2$ in Et₂O appeared to form the $Li_4(Et_2O)_4[Ce(^{Me2}ArNNAr^{Me2})_4]$. However, upon addition of the 4 equiv LiN(SiMe₃)₂, the solution turned dark purple which was characteristic of the formation of the desired oxidized product. Within hours, the reaction mixture became brown and bright orange crystals formed. The orange crystals were collected and isolated, and were confirmed to be 1,2-bis(3,5-dimethylphenyl)diazene, (^{Me2}ArN=NAr^{Me2}) by ¹H NMR spectroscopy and X-ray crystallography (Figures 5.4.11– 5.4.12 in section 5.4). We hypothesized that the $Li_4(Et_2O)_4[Ce(^{Me2}ArNNAr^{Me2})_4]$ complex likely formed but decomposed upon electron transfer from the ligand to the metal, resulting in the formation of a significant quantity of the 1,2-bis(3,5dimethylphenyl)diazene as well as brown, intractable Ce(III) products. The more electron donating substitution on the phenyl ring stabilized the formation of ^{Me2}ArN=NAr^{Me2} over the reduced hydrazide compound, and also lowered the energy of the ligand to metal charge transfer, leading to the degradation of the $Li_4(Et_2O)_4[Ce(^{Me2}ArNNAr^{Me2})_4]$ complex (see Figure 5.2.1 and Figures 5.4.11–5.4.12).

Reaction of the electron poor $Ar^FNHNHAr^F$ with $Ce[N(SiMe_3)_2]_3$ and LiN(SiMe_3)_2 in Et_2O did successfully form Li_4(Et_2O)_4[Ce(Ar^FNNAr^F)_4] (**5.4**) with no apparent ligand degradation, isolated in 49% yield (Scheme 5.2.2, Figure 5.2.2). Unlike $^{Me2}ArNHNHAr^{Me2}$, the Ar^FNHNHAr^F was more difficult to oxidize by over 600 mV (see Figure 5.2.1), evidently making the ligand to metal charge transfer pathway to form the free diazene less favorable and facilitating the isolation of complex **5.4**.

Once it was evident that $Li_4(Et_2O)_4[Ce(^{Me2}ArNNAr^{Me2})_4]$ and

Li₄(Et₂O)₄[Ce(^{F5}ArNNAr^{F5})₄] complexes could not be isolated, a series of Li₄(Et₂O)₄[Ce(ArNNAr)₄] complexes were synthesized, where the electron density of the ArNNAr unit was varied in order to measure the ligands' impact on the electronic properties of the resulting cerium metal center. To avoid the degradation observed in previously tested reactions, fluoride-containing substituents and electron rich ArNHNHAr ligands were avoided.

Using Hammett parameters as a guide for the electronic effects of the substitutions,^[15] *N*,*N'*-bis-(4-chlorophenyl)hydrazine (^{Cl}ArNHNHAr^{Cl})^[13, 16] and *N*,*N'*-bis-(3,5-dichlorophenyl)hydrazine (^{Cl2}ArNHNHAr^{Cl2}),^[13, 17, 18] (Scheme 5.2.3) were synthesized first by over-oxidation of the parent aniline to the substituted azobenzene, and then reduction of the azobenzene to the desired hydrazines. Both the ^{Cl}ArNHNHAr^{Cl2} and ^{Cl2}ArNHNHAr^{Cl2} ligands were easier to reduce than the unsubstituted PhNHNHPh and harder to reduce than Ar^FNHNHAr^F (Figure 5.2.1). Once the hydrazine ligands were isolated, the rest of the Li₄(Et₂O)₄[Ce(ArNNAr)₄] (**5.2–5.3**) complexes were synthesized as described previously (Scheme 5.2.2, Figure 5.2.2).

The reactions to form the $Li_4(Et_2O)_4[Ce(ArNNAr)_4]$ (**5.1–5.4**) complexes had similar side products to those of $Li_4(py)_4[Ce(PhNNPh)_4]$ discerned in Chapter 4. The formation of Li-ArNNAr clusters lowered the yields of complexes **5.1–5.4**, where the characteristically bright orange, insoluble material crashed out of the solution. A particularly large amount of bright orange Li cluster and presumably intractable Ce^{III}

products formed with complex **5.3**, lowering the yield significantly. Changing the solvent, temperature, and/or concentration of the reaction mixture did not prevent or minimize the Li cluster formation, as was the case for complex **5.1** and Li₄(py)₄[Ce(PhNNPh)₄], described in Chapter 4. We were unable to crystallographically characterize any of the clusters with the substituted 1,2-diarylhydrazine ligands.



Scheme 5.2.3. 1,2-diarylhydrazine ligands synthesized. (A) N,N'-bis-(4-chlorophenyl)hydrazine (^{Cl}ArNHNHAr^{Cl}) and (B) N,N'-bis-(3,5-dichlorophenyl)hydrazine (^{Cl2}ArNHNHAr^{Cl2}).



Figure 5.2.1. Cyclic voltammetry of 1,2-bis(3,5-dimethylphenyl)diazene

^{Me2}ArN=NAr^{Me2} (green), azobenzene PhN=NPh (black), 1,2-bis(4-chlorophenyl)diazene ^{Cl}ArN=NAr^{Cl} (red), 1,2-bis(3,5-dichlorophenyl)diazene ^{Cl2}ArN=NAr^{Cl2} (purple), 3,3'5,5'tetrakis(trifluoromethyl)azobenzene Ar^FN=NAr^F (blue), and decafluoroazobenzene ^{F5}ArN=NAr^{F5} (orange) in 0.1 M [*n*NBu₄][PF₆] in acetonitrile. Scan rate was 100 mV/s for all compounds.

To expand the scope of hydrazine-based ligands with cerium, we also attempted to synthesize cerium complexes with BocNHNHBoc, where Boc was the protecting group COO'Bu. BocNHNHBoc was prepared according to a literature procedure,^[19] and then crystallized in dry toluene at -25° C for further purification. Because Boc could be removed with *n*-BuLi, BocNHNHBoc could be used as an "N–N^{2–}" or N atom transfer reagent with the goal of forming either a Ce(N₂) or Ce-imido complex. Use of N-atom transfer reagents had been used to synthesize transition metal and uranium imido and nitrido complexes previously.^[20, 21] N-atom transfer reagents also formed interesting coordination compounds with uranium. For example, instead of forming a uranium imido complex and anthracene with the N-atom transfer reagent 2,3:5,6-dibenzo-7-aza bicycle[2.2.1]hepta-2,5-diene or its lithium salt, uranium coordinated the N-atom transfer reagent.^[21, 22]

To see if BocNHNHBoc could be used as a transfer reagent or as a ligand for cerium, several reactions were attempted. First, the deprotonated compound {[Li(THF)]₂[BocNNBoc]}_n was collected and analyzed by X-ray crystallography (see Figure 5.4.38 and Table 5.4.7). Then further reactions with cerium were attempted. Protonolysis reactions of 4 equiv BocNHNHBoc with Ce[N(SiMe₃)₂]₃ and 4 equiv LDA in Et₂O resulted in insoluble white powders. Metathesis reaction of Ce(OTf)₃ with 3

equiv $\{[Li(THF)]_2[BocNNBoc]\}_n$ in THF formed a white solid and a yellow solution, and subsequent reaction with 1 equiv *n*-BuLi resulted in an orange solution. The reaction mixture was insoluble in C₆D₆ and efforts to grow single crystals of the product yielded multicrystalline material.

5.2.2 Structural Characterization of Complexes 5.1–5.4

Similar to the Li₄(py)₄[Ce(PhNNPh)₄] complex that was previously reported,^[8] the cerium cations in complexes **5.1–5.4** were also coordinated to four ArNNAr^{2–} dianionic ligands resulting in eight coordinate complexes (Figure 5.2.2). The four lithium cations bridged two ArNNAr^{2–} units and bound one molecule of diethyl ether. By charge balance and Evans' method studies,^[23] complexes **5.1–5.4** all contained diamagnetic Ce(IV) metal centers (see Figures 5.2.2 and Figures 5.4.13–5.4.15 and Table 5.4.3 in section 5.4). The synergistic effect of the Ce(III) metal center and the Lewis acidic Li⁺ successfully reduced the ArNHNHAr ligand to form ArNH₂ and Li₄(Et₂O)₄[Ce^{IV}(ArNNAr)₄] (Scheme 5.2.2).^[8]

The N–N bond distances for complexes **5.1–5.4**, ranging from 1.436(7)–1.464(6) Å, were consistent with a single bond and did not vary much with ligand substitution (Table 5.2.1).^[24] The average Ce–N bond distances ranged from 2.407(5)–2.486(5). The lengthening of the Ce–N bonds could be attributed to the addition of sterically bulky substituents at the 3,5 positions. The solution structure was also affected by the ligands' steric bulk. In the ¹H NMR spectra of complexes **5.1–5.4**, the *o*-Ar protons in complexes **5.1** and **5.2** were inequivalent but in fast exchange showing two broad, coalesced signals

at room temperature. However, two sharp, separated *o*-Ar resonances were observed for complexes **5.3** and **5.4** at room temperature (Figures 5.4.1, 5.4.2, 5.4.4, and 5.4.6 in section 5.4), illustrating the higher barrier to rotation compared to complexes **5.1** and **5.2**.



Figure 5.2.2. 30% thermal ellipsoid plots for complexes $Li_4(Et_2O)_4[Ce(PhNNPh)_4]$ (**5.1**) at the top left, $Li_4(Et_2O)_4[Ce(^{Cl}ArNNAr^{Cl})_4]$ (**5.2**) at the top right,

Li₄(Et₂O)₄[Ce(^{Cl2}ArNNAr^{Cl2})₄] (**5.3**) at the bottom left, and Li₄(Et₂O)₄[Ce(Ar^FNNAr^F)₄] (**5.4**) at the bottom right. Hydrogen atoms are omitted for clarity in all structures. In complex **5.4**, the diethyl ether bound to each lithium cation was also removed for clarity. Selected bond distances for complex **5.1** (Å): Ce(1)–N(1) 2.4665(10), Ce(1)–N(2) 2.3915(10), N(1)–N(2) 1.4578(13), Li(1)–N(1) 1.984(2), Li(2)–N(1) 2.639(2), Li(2)–N(2) 2.018(2). Selected bond distances for complex **5.2** (Å): Ce(1)–N(1) 2.407(5), Ce(1)–N(2) 2.422(5), N(1)–N(2) 1.464(6), Li(4)–N(1) 2.032(12), Li(4)–N(2) 2.712(12), Li(1)–N(2) 2.038(11). Selected bond distances for complex **5.3** (Å): Ce(1)–N(1) 2.391(2), Ce(1)–N(2) 2.436(2), N(1)–N(2) 1.449(3), Li(4)–N(1) 2.071(6), Li(3)–N(2) 2.059(6). Selected bond distances for complex **5.4** (Å): Ce(1)–N(1) 2.466(6), Ce(1)–N(2) 2.511(6), N(1)–N(2) 1.453(9), Li(1)–N(1) 2.052(14), Li(1)–N(2) 2.717(13), Li(3)–N(2) 2.117(15).

The geometry of complexes **5.1–5.4** also varied with the ligands' steric bulk. To describe the effect that the ligand sterics had on the geometry of complexes **5.1–5.4**, the parameter τ_4 was used.^[25] τ_4 typically describes 4-coordinate complexes, where a value of 0 indicates a square planar complex and a value of 1 indicates a tetrahedral complex.^[25] Since complexes **5.1–5.4** were eight-coordinate, we instead used the four centroids between the N–N bonds in order to apply the τ_4 parameter. This method had proven a convenient metric to describe the eight-coordinate alkali metal cerium 1,2-diphenylhydrazido complexes previously, as described in Chapter 4.^[8] The unsubstituted

1,2-diphenylhydrazido ligands in complex **5.1** had the most planar arrangement of N–N centroids about the cerium metal center with a τ_4 value of 0.199 (Table 5.2.1). Upon substitution, the arrangement of the N–N centroids became less planar, and the τ_4 parameter generally increased as the steric bulk of the substituted ligand increased, from 0.337–0.386 (Table 5.2.1).

Complex	Ce–N	Ce–N	N–N	N–N	$ au_4$	$ au_4$
	(Å, avg)	(Å, avg)	(Å, avg)	(Å, avg),	(exp.)	(calc.)
	exp.	calc	exp.	calc.		
5.1	2.429(10)	2.465	1.4578(13)	1.440	0.199	0.000
5.2 ^{<i>a</i>}	2.407(5)	2.444	1.451(7)	1.443	0.349,	0.366
					0.360	
5.3	2.412(2)	2.448	1.453(3)	1.441	0.337	0.295
5.4	2.486(6)	2.439	1.455(9)	1.443	0.386	0.331

Table 5.2.1. Average Ce(1)–N and N–N bonds and the tabulation of τ_4 parameters for complexes **5.1**, **5.2**, **5.3**, and **5.4** measured by X-ray crystallography or DFT calculations. ^{*a*} Two molecules of complex **5.2** were in the asymmetric unit.

5.2.3 Spectroscopic and Electrochemical Characterization of Complexes 5.1–5.4

To observe the effect of the ligands on the electronics of the cerium metal center, UV-Vis spectroscopy, FTIR spectroscopy, and cyclic voltammetry were measured. As anticipated from the Hammett parameters of the ligands bound to cerium,^[15] the electron withdrawing groups installed on the phenyl ring increased the energy of the main ligandto-metal charge transfer band that caused the dark purple color of complexes **5.1–5.4** by 1065 cm⁻¹ (Figure 5.2.3, Table 5.2.2, and Figures 5.4.19–5.4.24 in section 5.4).



Figure 5.2.3. UV-Vis spectra of Li₄(py)₄[Ce(PhNNPh)₄] (black),

 $Li_4(Et_2O)_4[Ce(^{Cl}ArNNAr^{Cl})_4]$ (5.2) (red), $Li_4(Et_2O)_4[Ce(^{Cl2}ArNNAr^{Cl2})_4]$ (5.3) (purple), and $Li_4(Et_2O)_4[Ce(Ar^FNNAr^F)_4]$ (5.4) (blue) in toluene.

Complex	<i>E</i> (cm ⁻¹)	N–N stretch (expt, cm ⁻¹)	N–N stretch (calc, cm ⁻¹)	E _{1/2} (V vs. Fc/Fc ⁺)	Δ E (V)
Li ₄ (py) ₄ [Ce(PhNNPh) ₄]	18,523	987.41	1011	-1.93	0.13
$Li_4(Et_2O)_4[Ce(^{Cl}ArNNAr^{Cl})_4]$ (5.2)	18,577	960.37	1004	-1.66	0.22
$Li_{4}(Et_{2}O)_{4}[Ce(^{Cl2}ArNNAr^{Cl2})_{4}]$ (5.3)	18,706	1003.25	1033	-1.41	0.35
$Li_4(Et_2O)_4[Ce(Ar^FNNAr^F)_4]$ (5.4)	19,588	1007.75	1036	-1.48^{a}	0.11 ^{<i>a</i>}

Table 5.2.2. Energy of the ligand to metal charge transfer transition, energy of the N–N stretching mode, potential of the Ce^{IV/III} redox couple, and $E_{pc}-E_{pa}$ (ΔE) of complexes **5.1**, **5.2**, **5.3**, and **5.4** measured by UV-Vis spectroscopy, FTIR spectroscopy, and cyclic voltammetry respectively. ^{*a*} Decomposition was evident in the cyclic voltammetry of complex **5.4**.

We attempted to measure the electron withdrawing effect by FTIR spectroscopy. The FTIR spectra were assigned using DFT calculations (see the experimental section 5.4 for computational details and Figures 5.4.16–5.4.18, Table 5.2.2).^[8] While we were able to locate two sets of N–N stretches, the Ce–N stretches and bends were of low intensity and could not be assigned. The energy of the N–N stretches did not follow a particular trend (Table 5.2.2). The Ce(IV) cation was expected to withdraw electron density from the N–N unit which should affect the N–N stretching mode. However, the electronic structure of those Ce–N bonds were impacted by the geometry changes observed in the complexes, making the Ce(IV) PhNNPh^{2–} bonding orbitals distinct from those of the Ce(IV) substituted ArNNAr bonding orbitals (see section 5.4 Figure 5.4.37). Electron withdrawing substituents also removed electron density away from the Ce(IV) center, making it unclear how the Ce(IV) bonds would impact the N–N stretching mode. The combination of the geometry changes and the effect of the electron withdrawing substituents likely contributed to the lack of a clear trend observed for the N–N stretching modes in complexes **5.1–5.4**.

The electrochemical potentials at which the Ce^{IV/III} reduction occurred were expected to be indicative of the electronic environment at the cerium cation, where a more electron poor cerium center was expected to be easier to reduce. The (^{CI2}ArNNAr^{CI2})^{2–} cerium complexes' redox potentials were easier to reduce by 450 mV compared to the unsubstituted PhNNPh^{2–} cerium complex (Table 5.2.2, Figure 5.2.4), demonstrating that the electron withdrawing ligands strongly impacted the electron density at the Ce(IV) metal center.

In addition to the Ce^{IV/III} potential, we also observed that the difference between E_{pa} and E_{pc} (ΔE) for the Ce^{IV/III} couple increased, becoming more irreversible with increasing steric bulk of the ligand (Figure 5.2.4, Table 5.2.2). To better understand the cause of the increasing ΔE , we examined the Ce^{IV/III} redox couple by differential pulse voltammetry (DPV). The DPV of complexes **5.2** and **5.3** both showed two cerium oxidation features, one of which was due to decomposition upon reduction of Ce(IV) (see

Figures 5.4.30 and 5.4.32 in section 5.4). Compound **5.4** had even more complex features that formed upon reduction to Ce(III). After the initial reduction of Ce(IV), new reduction and oxidation features appeared in the CV, and also could be found in the DPV (see Figures 5.4.33–5.4.36 in section 5.4). Furthermore, the solution changed color from dark purple at the beginning of the experiment, to brown as time progressed, which strongly suggested that the reduction of the complex **5.4** had triggered decomposition. Because of the quasi-reversible to irreversible redox waves of complexes **5.2–5.4**, unlike $Li_4(py)_4[Ce(PhNNPh)_4]$ which had reversible $Ce^{IV/III}$ electrochemistry, we do not expect to be able to isolate a $M_5(Et_2O)_4[Ce^{III}(ArNNAr)_4]$ (M = Li, Na, or K) complex for any of the substituted ligands.



Figure 5.2.4. Cyclic voltammetry of $Li_4(py)_4[Ce(PhNNPh)_4]$ (black), $Li_4(Et_2O)_4[Ce(^{Cl}ArNNAr^{Cl})_4]$ (**5.2**) (red), and $Li_4(Et_2O)_4[Ce(^{Cl2}ArNNAr^{Cl2})_4]$ (**5.3**) (purple) in 0.1 M [*n*NBu₄][BAr^F₄] in fluorobenzene. Scan rate was 100 mV/s for all compounds. $Li_4(Et_2O)_4[Ce(Ar^FNNAr^F)_4]$ (**5.4**) decomposed during the course of the cyclic voltammetry experiment (see Figures 5.4.33–5.4.36 in section 5.4).

5.3 Conclusions

We explored the use of Ce(III) and Li⁺ for alkali metal promoted reduction of 1,2diarylhydrazine substrates with varying substituents. While Ce(III) and Li⁺ could reduce the electron donating 1,2-bis(3,5-dimethylphenyl)hydrazine, the resulting product was unstable and was subject to decomposition. Electron poor 1,2-diarylhydrazines resulted in the isolable high valent products, Li₄(Et₂O)₄[Ce^{IV}(ArNNAr)₄], demonstrating that electron transfer did occur between the metal and ligand. The electron poor ligands used strongly impacted the electronics at the cerium metal center, where the most electron withdrawing ligand led to the complex Li₄(Et₂O)₄[Ce^{IV}(Ar^FNNAr^F)₄], which had the highest energy LMCT band and the Ce^{IV/III} potential was easiest to reduce of the series. Thus using Lewis acid promoted reduction could be a method to isolate electron poor Ce(IV) species. Furthermore, we illustrated that steric bulk of the substituted 1,2diarylhydrazine impacted the Ce(IV) solid state and solution structures.

5.4 Experimental Section

Experimental Procedures

General Methods. Unless otherwise indicated all reactions and manipulations were performed under an inert atmosphere (N₂) using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. Nexus II drybox equipped with a molecular sieves 13X / Q5 Cu-0226S catalyst purifier system. Glassware was oven-dried overnight at 150 °C prior to use. ¹H, ¹³C, and ⁷Li NMR spectra were obtained on a Bruker DMX-300, on a Bruker DMX-360, or on a Bruker DRX-400 Fourier transform NMR spectrometer at 300, 360,

and 400 MHz respectively. VT ¹H NMR spectroscopy of complex **5.1** was recorded on a Bruker BioDRX-600 Fourier transform NMR spectrometer at 600 MHz. Chemical shifts were recorded in units of parts per million downfield from residual proteo solvent peaks (^{1}H) , or characteristic solvent peaks (^{13}C) . The ⁷Li spectra were referenced to external solution standards of LiCl in H₂O. Evans' method^[23] was performed on a Bruker BioDRX-500 Fourier transform NMR spectrometer at 500 MHz. Hexamethyldisiloxane was used as the internal standard for Evans's method experiments. Evans' method on complex $Li_4(py)_4[Ce(PhNNPh)_4]$, the pyridine solvated analogue of complex 5.1, was reported previously, see Chapter 4.^[8] UV–vis-NIR absorption measurements of complexes were performed in toluene using a PerkinElmer 950 UV-vis/NIR Spectrophotometer. One mm path length screw cap quartz cells were used with a toluene blank. The spectra were fit using the Fitvk program.^[26] UV-Vis spectra of complex $Li_4(py)_4[Ce(PhNNPh)_4]$, the pyridine solvated analogue of complex 5.1, was reported previously, see Chapter 4, although we fit the spectra in this chapter only.^[8] The infrared spectra were obtained from 400–4000 cm⁻¹ using a PerkinElmer 1600 series infrared spectrometer. Solution spectra were first collected with a background of air, and then the solvent spectrum was subtracted using PerkinElmer software. FTIR spectra of complex $Li_4(py)_4[Ce(PhNNPh)_4]$, the pyridine solvated analogue of complex 5.1, was reported previously, see Chapter 4.^[8] Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility using a Perkin-Elmer Series II 2400 CHNS

analyzer (Li₄(Et₂O)₄[Ce(PhNNPh)₄]) and the remaining at Complete Analysis Laboratories Inc. in Parsippany, NJ using a Carlo Erba EA 1108 analyzer.

Materials. Tetrahydrofuran, diethyl ether, hexane, fluorobenzene and pentane were purchased from Fisher Scientific. The solvents were sparged for 20 min with dry N2 and dried using a commercial two-column solvent purification system comprising columns packed with Q5 reactant and neutral alumina respectively (for hexane and pentane), or two columns of neutral alumina (for THF, diethyl ether, and fluorobenzene). Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. Methylene chloride d_2 was stored over 4 Å molecular sieves for three days before use, benzene- d_6 was stored over potassium mirror for three days before use, and CDCl₃ was stirred over calcium hydride for three days, distilled, and freeze-pump-thawed for three cycles before use. Ce[N(SiMe₃)₂]₃ was prepared following a published procedure.^[27] Li[N(SiMe₃)₂] (Acros) was recrystallized from hot pentane prior to use. Hydrazobenzene (Sigma Aldrich) was sublimed under reduced pressure first at 60° C to remove azobenzene, and then at 90° C prior to use. Alternatively, hydrazobenzene was recrystallized in dry toluene and pentane at -25° C. 2-bis(3,5-dimethylphenyl)hydrazine,^[10, 16] N,N'-bis-(4chlorophenyl)hydrazine,^[12, 13, 16] N,N'-bis-(3,5-dichlorophenyl)hydrazine,^[12, 13, 18] and

3,3',5,5'-tetrakis(trifluoromethyl)hydrazobenzene ^[11-13] were prepared according to literature procedures by first oxidizing the parent aniline to the substituted azobenzene, and then reducing the azobenzene using Zn and saturated NH₄Cl. All of the substituted hydrazines were recrystallized in dry toluene and pentane at -25° C.

Electrochemistry. Voltammetry experiments (CV and DPV) were performed using a CH Instruments 620D Electrochemical Analyzer/Workstation and the data were processed using CHI software v 9.24. Voltammetry experiments on $Li_4(py)_4[Ce(PhNNPh)_4]$, the pyridine-solvated analogue of complex 5.1, were reported previously, see Chapter 4.^[8] Voltammetry experiments on complexes 5.2–5.4 and hydrazobenzene, and substituted hydrazobenzene ligands were performed in fluorobenzene in an N2 atmosphere drybox using electrochemical cells that consisted of a 4 mL vial, glassy carbon (3 mm diameter) working electrode, a platinum wire counter electrode, and a silver wire plated with AgCl as a quasi-reference electrode. Voltammetry experiments on azobenzene and the substituted azobenzenes were performed on the Schlenk line in acetonitrile that was purged with N2. Electrochemical cells that consisted of a 10 mL vial, glassy carbon (3 mm diameter) working electrode, a platinum wire counter electrode, and a silver wire plated with AgCl as a quasi-reference electrode were used. The working electrode surfaces were polished prior to each set of experiments, and were periodically replaced to prevent the buildup of oxidized product on the electrode surfaces. Potentials were reported versus ferrocene (Fc). For complexes 5.2-5.4, hydrazobenzene, and substituted hydrazobenzene ligands, the potentials were converted from cobaltocene for calibration at the end of each run.^[7] Solutions employed during CV studies were ~3 mM in analyte. For electrochemistry collected in fluorobenzene, the solution was 100 mM in $[nBu_4N][B(3,5-(CF_3)_2-C_6H_3)_4]$ ($[nBu_4N][BAr^F_4]$), and electrochemistry collected in acetonitrile had 100 mM in [*n*Bu₄N][PF₆] as the electrolyte.

All data were collected in a positive-feedback IR compensation mode. Scan rate dependences of 25–1000 mV/s were performed to determine electrochemical reversibility.

Computational Details. All calculations were performed with Gaussian '09 Revision D.01,^[28] with the B3LYP hybrid DFT method. A 28-electron small core effective core potential was applied to cerium with published segmented natural orbital basis set incorporating quasi-relativistic effects,^[29] while the 6-31 G* basis set was applied to all other atoms. The computations for complex **5.1** was reported previously, see Chapter 4.^[8] Geometry optimizations of **5.2–5.4** were based on their crystal structures with diethyl ether truncated to dimethyl ether to reduce the calculation time. No other restrictions were placed on the systems besides the spin. Frequency calculations of complexes **5.2–5.4** found no negative frequencies indicating that the optimized structures found were at an energy minimum. Molecular orbitals were rendered using Chemcraft v. 1.6.^[30] TD-DFT calculations were performed in the gas phase. Bonding orbitals were identified using the AO Mix program.^[31] The atomic orbital contributions were found through fragment molecular orbital analysis where fragment 1 was Ce, and fragment 2 was Li₄(OMe₂)₄[ArNNAr]₄.

X-Ray Crystallography. X-ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-K α radiation (λ = 0.71073 Å) at a temperature of 143(1) or 100 (1) K. In all cases, rotation frames were integrated using SAINT,^[32] producing a listing of unaveraged F² and σ (F²) values which

were then passed to the SHELXTL^[33] program package for further processing and structure solution on a Dell Pentium 4 computer. The intensity data were corrected for Lorentz and polarization effects and for absorption using TWINABS^[34] or SADABS.^[35] The structures were solved by direct methods (SHELXS-97).^[36] Refinement was by fullmatrix least squares based on F² using SHELXL-97.^[36] All reflections were used during refinements. The weighting scheme used was w=1/[$\sigma^2(F_o^2)$ + (0.0907P)² + 0.3133P] where P = ($F_o^2 + 2F_c^2$)/3. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model.

Synthetic Details and Characterization

Synthesis of Li₄(Et₂O)₄[Ce(PhNNPh)₄] (5.1). Synthesis of this complex was described in Chapter 4, section 4.4.



Figure 5.4.1. ¹H NMR spectrum of $Li_4(Et_2O)_4[Ce(PhNNPh)_4]$ (**5.1**) collected in C_6D_6 from 280–300 K.

Synthesis of Li₄(Et₂O)₄[Ce(^{CI}ArNNAr^{CI})₄] (5.2). *p*-Dichlorohydrazobenzene (0.119 g, 0.469 mmol) was dissolved in 4 mL of diethyl ether in a 20 mL scintillation vial. Ce(N(SiMe₃)₂)₃ (0.080 g, 0.117 mmol) was added to the mixture, resulting in a yellow solution. After stirring for 30 min, the diethyl ether was removed under reduced pressure. Diethyl ether was added to the green-yellow solid, resulting in an orange suspension. LiN(SiMe₃)₂ (0.079 g, 0.469 mmol) was weighed and dissolved in hexanes to form a colorless solution. The colorless hexanes solution was layered over the orange suspension. After two days, dark purple crystals form. The crystals were collected over a medium frit, washed 3 times with hexanes, and dried under reduced pressure. Yield 0.086 g, 0.0586 mmol, 50 %. ¹H NMR (400 MHz, C₆D₆) δ 7.22 (d, *J* = 8.5 Hz, 4 H, *m*-Ar), 5.95 and 5.53 (broad singlets, 4 H, *o*-Ar), 2.904 (s, 4 H, Et₂O), 0.590 (s, 6 H, Et₂O). ⁷Li NMR (400 MHz, C₆D₆) δ 0.421 (2), and 0.300 (3). ¹³C NMR (91 MHz, C₆D₆) δ 158.79, 124.85, 124.62, 123.38, 65.86, 14.23. Elemental Analysis calculated for C₆₄H₇₂N₈O₄Cl₈Li₄Ce: C, 52.34: H, 4.94; N, 7.63. Found: C, 52.19; H, 4.86; N, 7.54.



Figure 5.4.2. ¹H NMR spectrum of Li₄(Et₂O)₄[Ce(^{Cl}ArNNAr^{Cl})₄] (5.2) collected in C₆D₆.



Figure 5.4.3. ⁷Li NMR (left) and ¹³C NMR (right) spectra of $Li_4(Et_2O)_4[Ce(^{Cl}ArNNAr^{Cl})_4]$ (**5.2**) collected in C_6D_6 .

Synthesis of Li₄(Et₂O)₄[Ce(^{Cl2}ArNNAr^{Cl2})₄] (5.3). 3,3',5,5'-tetrachlorohydrazobenzene (0.30 g, 0.94 mmol) was dissolved in 4 mL of diethyl ether in a 20 mL scintillation vial. $Ce(N(SiMe_3)_2)_3$ (0.16 g, 0.23 mmol) was added to the mixture, resulting in a vellow suspension. After stirring for 30 min, the diethyl ether was removed under reduced pressure. Diethyl ether was added to the yellow solid, resulting in a yellow-orange suspension. The suspension was then cooled to -25 °C. LiN(SiMe₃)₂ (0.16 g, 0.94 mmol) was weighed and added to the cold diethyl ether suspension and stirred for 4 h. The solution was then dried under reduced pressure. The dark purple product was extracted in toluene and filtered over celite to remove a bright orange solid. The only products that remained in solution were free ligand and the desired complex. To remove the free ligand, another 0.1 equiv lithium diisopropylamide solution was added to the complex and stirred. The solution was then dried under vacuum. The product was extracted in diethyl ether and filtered over celite to remove an orange solid. The solution was then dried under vacuum, and the residual amine and lithium diisopropylamide was washed away with pentane. Complex 5.3 was also somewhat soluble in pentane, and some product was washed away in pentane. The product was then crystallized in the freezer from a concentrated solution of diethyl ether. The crystals were collected over a medium frit, washed once with pentane, and dried under reduced pressure. Yield 0.13 g, 0.73 mmol, 31 %. ¹H NMR (400 MHz, C6D6) δ 6.619 (s, 2 H), 6.512 s, 2 H), 5.805 (s, 2 H), 3.420 (br s, 4 H, Et₂O), 1.107 (br s, 6 H, Et₂O). ⁷Li NMR (400 MHz, C6D6) δ 0.799. ¹³C NMR (91 MHz, C6D6) δ 161.05, 136.92, 135.43, 120.90, 115.83, 107.25, 66.59, 34.79.

Elemental Analysis calculated for C₆₄H₆₄CeLi₄N₈O₄Cl₁₆: C, 44.07; H, 3.70; N, 6.42. Found: C, 43.78; H, 3.45; N, 6.34.



Figure 5.4.4. ¹H NMR spectrum of $Li_4(Et_2O)_4[Ce(^{Cl2}ArNNAr^{Cl2})_4]$ (5.3) collected in





Figure 5.4.5. ⁷Li NMR (left) and ¹³C NMR (right) spectra of

 $Li_4(Et_2O)_4[Ce(^{Cl2}ArNNAr^{Cl2})_4]$ (5.3) collected in C_6D_6 .

Synthesis of Li₄(Et₂O)₄[Ce(Ar^FNNAr^F)₄] (5.4). Di-3,3',5,5'-

bis(trifluoromethyl)hydrazobenzene Ar^FNHNHAr^F (0.21 g, 0.47 mmol) was dissolved in 4 mL of diethyl ether in a 20 mL scintillation vial. Ce(N(SiMe₃)₂)₃ (0.080 g, 0.12 mmol) was added to the mixture, resulting in a yellow solution. After stirring for 30 min, the diethyl ether was removed under reduced pressure. Diethyl ether was added to the greenyellow solid, resulting in an orange suspension. LiN(SiMe₃)₂ (0.079 g, 0.47 mmol) was added to the solution forming a dark brown-purple oil. The resulting oily solution was stirred overnight. The solution was then dried under reduced pressure. The product was extracted in toluene, filtered over celite and concentrated. The concentrated purple solution was then placed in a freezer at -25° C to crystallize. After two days, dark purple crystals formed. The crystals were collected over a medium frit, washed 3 times with hexanes, and dried under reduced pressure. Yield 0.13 g, 0.058 mmol, 49 %, crystalline yield. ¹H NMR (400 MHz, CDCl₃) δ 6.93 (d, J = 15.9 Hz, 2 H, o-Ar), 5.753 (s, 1 H, p-Ar), 3.431 (s, 4 H, Et₂O), 1.01 (m, 6 H, Et₂O). ⁷Li NMR (400 MHz, CDCl₃) δ 0.538. ¹⁹F NMR (282 MHz, CDCl₃) δ –62.860 (3 F), –63.538 (3 F). ¹H NMR (300 MHz, CD₂Cl₂) δ 6.916 (broad singlet, 2 H, o-Ar), 5.792 (broad singlet, 1 H, p-Ar), 3.495 (s, 4 H, Et₂O), 0.882 (m, 6 H, Et₂O). ⁷Li NMR (400 MHz, CD₂Cl₂) δ 0.682. ¹⁹F NMR (282 MHz, CD_2Cl_2) δ -63.234 and -63.367 (2 F), -63.541 (1 F), -63.774 (3 F). ¹³C NMR spectra only showed the $CDCl_3$ resonances or the CD_2Cl_2 resonances because of the poor solubility of complex 5.4 in non-coordinating solvents. Elemental Analysis calculated for C₈₀H₆₄N₈O₄F₄₈Li₄Ce: C, 42.12; H, 2.83; N, 4.91. Found: C, 41.96; H, 2.64; N, 4.94.



Figure 5.4.6. ¹H NMR spectrum of $Li_4(Et_2O)_4[Ce(Ar^FNNAr^F)_4]$ (**5.4**) collected in CDCl₃. The complex decomposes slightly in CDCl₃.



Figure 5.4.7. ⁷Li NMR (left) and ¹⁹F NMR (right) spectra of Li₄(Et₂O)₄[Ce(Ar^FNNAr^F)₄] (**5.4**) collected in CDCl₃. The sample was not soluble enough to observe any resonances by ¹³C NMR spectroscopy in CDCl₃.



Figure 5.4.8. ¹H NMR spectrum of $Li_4(Et_2O)_4[Ce(Ar^FNNAr^F)_4]$ (**5.4**) collected in CD_2Cl_2 .



Figure 5.4.9. ⁷Li NMR (left) and ¹⁹F NMR (right) spectra of $Li_4(Et_2O)_4[Ce(Ar^FNNAr^F)_4]$ (5.4) collected in CD₂Cl₂. The sample was not soluble enough to observe any resonances by ¹³C NMR spectroscopy in CD₂Cl₂.

Attempts to synthesize $Li_4(Et_2O)_4[Ce(^{F5}ArNNAr^{F5})_4]$ and $Li_4(Et_2O)_4[Ce(^{Me2}ArNNAr^{Me2})_4]$ NMR Spectroscopy



Figure 5.4.10. ¹⁹F NMR spectra of the following reaction mixes: at top, Ce[N(SiMe₃)₂]₃ with 4 equiv ^{F5}ArNHNHAr^{F5} and 4 equiv LiN(SiMe₃)₂; in the middle, Ce[N(SiMe₃)₂]₃ with 4 equiv ^{F5}ArNHNHAr^{F5}; and at the bottom, LiN(SiMe₃)₂ with 4 equiv ^{F5}ArNHNHAr^{F5}. The ¹⁹F NMR resonances for the free ligand was labeled as "s. m.", and the resonances for Me₃SiF were labeled as Si-F.^[37]



Figure 5.4.11. ¹H NMR spectra of the following reaction mixes: at top, Ce[N(SiMe₃)₂]₃ with 4 equiv ^{Me2}ArNHNHAr^{Me2} and at bottom, Ce[N(SiMe₃)₂]₃ with 4 equiv ^{Me2}ArNHNHAr^{Me2} and 4 equiv LiN(SiMe₃)₂. The ¹H NMR resonances for the free ligand were labeled as "s. m.", and ^{Me2}ArN=NAr^{Me2} resonances were labeled as "azo?".



Figure 5.4.12. Thermal ellipsoid plot of the soluble orange crystals isolated from the reaction mixture of $Ce[N(SiMe_3)_2]_3$ with 4 equiv $^{Me2}ArNHNHAr^{Me2}$ and 4 equiv $LiN(SiMe_3)_2$. Hydrogen atoms were omitted for clarity. Selected bond distance (Å): N(1)-N(2), 1.2565(14).

X-ray structural parameters for ^{Me2}ArN=NAr^{Me2} and complexes 5.2–5.4

	Me ² ArN=NAr ^{Me2}		
	(Penn4492)	Complex 5.2 (Femi4364)	
Empirical formula	$C_{16}H_{18}N_2$	C ₆₄ H ₇₂ N ₈ O ₄ Cl ₈ Li ₄ Ce	
Formula weight	238.32	1468.78	
Temperature (K)	100(1)	100(1)	
Wavelength (Å)	0.71073	0.71073	
Crystal system	Monoclinic	Triclinic	
Space group	P2 ₁ /c	P1	
Cell constants			
a (Å)	8.1508(3)	14.7988(5)	
b (Å)	13.3908(4)	20.7565(7)	
c (Å)	12.4176(4)	22.4945(8)	
α (°)	90.00	90.464(2)	
β (°)	104.064(2)	92.957(2)	
γ (°)	90.00	90.456(2)	
$V(Å^3)$	1314.70(8)	6900.0(4)	
Z	4	4	
$\rho_{calc} (mg/cm^3)$	1.204	1.414	
μ (Mo K α) (mm ⁻¹)	0.071	1.020	
F(000)	512	3000	
Crystal size (mm ³)	0.50 x 0.10 x 0.08	0.50 x 0.25 x 0.10	
Theta range for data	2.27 to 27.58°	1 29 to 27 509	
collection		1.38 10 27.30	
Index ranges	$-10 \le h \le 10, -17 \le k \le 15,$	$-18 \le h \le 18, \ -26 \le k \le 26,$	
much langes	$-16 \le l \le 15$	$0 \leq l \leq 29$	

Table 5.4.1. Crystallographic parameters for ^{Me2}ArN=NAr^{Me2} and complex **5.2**.

Reflections collected	21395	212076	
Independent collections	3035 [R(int) = 0.0219]	30906 [R(int) = 0.0477]	
Completeness to theta =	99.6	07 50/	
27.58, 27.49°		91.570	
Absorption correction	Semi-empirical from	Semi-empirical from	
Absorption correction	equivalents	equivalents	
Max and min. transmission	0.7456 and 0.7089	0.7456 and 0.5993	
Refinement method	Full-matrix least-squares	Full-matrix least-squares	
Kermement method	on F ²	on F ²	
		30006 / 402 / 1720	
Data / restraints /	3035 / 0 / 165	30006 / 402 / 1720	
Data / restraints / parameters	3035 / 0 / 165	30906 / 492 / 1720	
Data / restraints / parameters Goodness–of–fit on F ²	3035 / 0 / 165 1.056	30906 / 492 / 1720 1.154	
Data / restraints / parameters Goodness–of–fit on F ² Final R indices	3035 / 0 / 165 1.056 R1 = 0.0444, wR2 =	30906 / 492 / 1720 1.154 R1 = 0.0497, wR2 =	
Data / restraints / parameters Goodness–of–fit on F ² Final R indices [I>2sigma(I)]	3035 / 0 / 165 1.056 R1 = 0.0444, wR2 = 0.1386	30906 / 492 / 1720 1.154 R1 = 0.0497, wR2 = 0.1375	
Data / restraints / parameters Goodness-of-fit on F ² Final R indices [I>2sigma(I)] P indices (all data)	3035 / 0 / 165 1.056 R1 = 0.0444, wR2 = 0.1386 R1 = 0.0554, wR2 =	30906 / 492 / 1720 1.154 R1 = 0.0497, wR2 = 0.1375 R1 = 0.0635, wR2 =	
Data / restraints / parameters Goodness–of–fit on F ² Final R indices [I>2sigma(I)] R indices (all data)	3035 / 0 / 165 1.056 R1 = 0.0444, wR2 = 0.1386 R1 = 0.0554, wR2 = 0.1485	30906 / 492 / 1720 1.154 R1 = 0.0497, wR2 = 0.1375 R1 = 0.0635, wR2 = 0.1488	
Data / restraints / parameters Goodness-of-fit on F ² Final R indices [I>2sigma(I)] R indices (all data) Largest diff. peak and hole	3035 / 0 / 165 1.056 R1 = 0.0444, wR2 = 0.1386 R1 = 0.0554, wR2 = 0.1485 0.346 and -0.245	30906 / 492 / 1720 1.154 R1 = 0.0497, wR2 = 0.1375 R1 = 0.0635, wR2 = 0.1488 1.652 and -1.542	

Table 5.4.2. Crystallographic parameters for complexes **5.3** and **5.4**.

	Complex 5.3 (Penn4693)	Complex 5.4 (Penn4453)
Empirical formula	C71H72CeLi4N8O4Cl16	C ₈₀ H ₆₄ N ₈ O ₄ F ₄₈ Li ₄ Ce
Formula weight	1836.45	2281.27
Temperature (K)	100(1)	100(1)
Wavelength (Å)	0.71073	0.71073
Crystal system	Tetragonal	Monoclinic
Space group	P4 ₁	$P2_1/n$

Cell constants			
a (Å)	13.0287(5)	16.1545(12)	
b (Å)	13.0287(5)	16.2394(11)	
c (Å)	47.9343(18)	41.225(3)	
α (°)	90.00	90.00	
β (°)	90.00	95.418(4)	
γ (°)	90.00	90.00	
V (Å ³)	8136.7(5)	10766.6(13)	
Ζ	4	4	
$\rho_{calc} (mg/cm^3)$	1.499	1.407	
μ (Mo K α) (mm ⁻¹)	1.136	0.551	
F(000)	3712	4536	
Crystal size (mm ³)	0.45 x 0.18 x 0.10	0.42 x 0.30 x 0.15	
Theta range for data collection	1.70 to 25.36°	1.35 to 27.59°	
T 1	$-15 \le h \le 15, -15 \le k \le 15,$	$-21 \le h \le 21, -21 \le k \le 21,$	
Index ranges	$-57 \le l \le 57$	$-53 \le l \le 53$	
Reflections collected	130992	167870	
Independent collections	14881 [R(int) = 0.0334]	24734 [R(int) = 0.0627]	
Completeness to theta = 27.49°	99.9%	99.2%	
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	
Max and min. transmission	0.7452 and 0.6383	0.7456 and 0.6043	
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	
Data / restraints / parameters	14881 / 1 / 947	24734 / 430 / 1403	
Goodness-of-fit on F ²	1.198	1.066	
--	--------------------	--------------------	
Final R indices	R1 = 0.0233, wR2 =	R1 = 0.1148, wR2 =	
[I>2sigma(I)]	0.0540	0.2643	
R indices (all data)	R1 = 0.0240, wR2 =	R1 = 0.1322, wR2 =	
	0.0542	0.2720	
Largest diff. peak and hole $(e.Å^{-3})$	0.313 and -0.723	2.402 and -3.994	

Calculating τ₄:

The centroids between the four N–N bonds were calculated using Mercury software.^[25] $\tau = \frac{360^{\circ} - (\alpha + \beta)}{141^{\circ}}$ α and β represent the two largest angles θ between one N–N centroid, Ce, and another N–

N centroid calculated using Mercury. 0 indicates a square planar structure while 1 implicates a tetrahedral structure.

Evans' Method^[23]

A A		
(M)		
.0191	0.000	0.00
0.054	0.000	0.00
0.017	0.000	0.00
	.0191).054).017	.0191 0.000 0.054 0.000 0.017 0.000

Table 5.4.3. Table of Evans' method results for complexes 5.2–5.4, with

hexamethyldisiloxane as the internal standard. Evans' method of the pyridine-solvated version of complex **5.1** was reported previously, see Chapter 4.^[8]



Figure 5.4.13. Evans' method results for complex $Li_4(Et_2O)_4[Ce(^{Cl}ArNNAr^{Cl})_4]$ (**5.2**), with hexamethyldisiloxane as the internal standard. At left is the benzene- d_6 resonance, and at right is the hexamethyldisiloxane resonance used as a standard.



Figure 5.4.14. Evans' method results for complex $\text{Li}_4(\text{Et}_2\text{O})_4[\text{Ce}(^{\text{Cl}2}\text{ArNNAr}^{\text{Cl}2})_4]$ (**5.3**), with hexamethyldisiloxane as the internal standard. At left is the hexamethyldisiloxane resonance used as a standard and at right is the benzene- d_6 resonance.



Figure 5.4.15. Evans' method results for complex $Li_4(Et_2O)_4[Ce(Ar^FNNAr^F)_4]$ (**5.4**), with hexamethyldisiloxane as the internal standard. At left is the methylene chloride resonance, and at right is the hexamethyldisiloxane resonance used as a standard.

FTIR Spectra of complexes 5.2–5.4:

The Li₄(py)₄[Ce(PhNNPh)₄] calculated and experimental FTIR spectra were previously reported, see Chapter 4.^[8]



Figure 5.4.16. Experimental FTIR spectrum (black) of $Li_4(Et_2O)_4[Ce(^{Cl}ArNNAr^{Cl})_4]$ (5.2) in C₆D₆ overlayed with the calculated FTIR spectrum (red). The calculated spectrum's energies were scaled by 0.9594.^[38]



Figure 5.4.17. Experimental FTIR spectrum (black) of $Li_4(Et_2O)_4[Ce(^{Cl2}ArNNAr^{Cl2})_4]$ (5.3) in C₆D₆ overlayed with the calculated FTIR spectrum (red). The calculated spectrum's energies were scaled by 0.9594.^[38]



Figure 5.4.18. Experimental FTIR spectrum (black) of $Li_4(Et_2O)_4[Ce(Ar^FNNAr^F)_4]$ (**5.4**) in dichloromethane overlayed with the calculated FTIR spectrum (red). The calculated spectrum's energies were scaled by 0.9594.^[38]

UV-Vis Absorption Spectra of complexes 5.1–5.4:



Figure 5.4.19. UV-Vis spectrum of complex $Li_4(py)_4[Ce(PhNNPh)_4]$ in toluene (black).^[8] The blue, purple and green traces show the Gaussian curves used to fit the spectrum with maxima at 18,523, 22,788, and 46,867 cm⁻¹. The sum of those traces formed the fit curve, represented by the red dashed line.



Figure 5.4.20. UV-Vis spectrum of complex $Li_4(Et_2O)_4[Ce(^{Cl}ArNNAr^{Cl})_4]$ (**5.2**) in toluene (black). The blue, purple and green traces show the Gaussian curves used to fit the spectrum with maxima at 18,577, 23,677, and 28,065 cm⁻¹. The sum of those traces formed the fit curve, represented by the red dashed line.

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Figure 5.4.21. UV-Vis spectrum of complex $Li_4(Et_2O)_4[Ce(^{Cl2}ArNNAr^{Cl2})_4]$ (**5.3**) in toluene (black). The blue, purple and green traces show the Gaussian curves used to fit the spectrum with maxima at 18,706, 22,653, and 32,178 cm⁻¹. The sum of those traces formed the fit curve, represented by the red dashed line.



Figure 5.4.22. UV-Vis spectrum of complex $Li_4(Et_2O)_4[Ce(Ar^FNNAr^F)_4]$ (**5.4**) in toluene (black). The blue, purple and green traces show the Gaussian curves used to fit the spectrum with maxima at 19,588, 21,874, and 29,872 cm⁻¹. The sum of those traces formed the fit curve, represented by the red dashed line.



Figure 5.4.23. Depiction of the ligand to metal charge transfer transition calculated at $18,800 \text{ cm}^{-1}$ (532 nm) for complex **5.1** Li₄(Me₂O)₄[Ce(PhNNPh)₄].



Figure 5.4.24. Depiction of the ligand to metal charge transfer transition calculated at 21,000 cm⁻¹ (475 nm) for complex **5.1** Li₄(Me₂O)₄[Ce(PhNNPh)₄].

Electrochemistry:



Figure 5.4.25. Cyclic voltammetry of 1,2-diphenylhydrazine in 0.1 M $[nNBu_4][BAr^F_4]$ in

fluorobenzene. Scan rate was 100 mV/s.



Figure 5.4.26. Cyclic voltammetry of *N*,*N*'-bis-(4-chlorophenyl)hydrazine in 0.1 M $[nNBu_4][BAr^F_4]$ in fluorobenzene. Scan rate was 100 mV/s.



Figure 5.4.27. Cyclic voltammetry of bis-(3,5-dichlorophenyl)hydrazine in 0.1 M

 $[nNBu_4][BAr^{F_4}]$ in fluorobenzene. Scan rate was 100 mV/s.



Figure 5.4.28. Cyclic voltammetry of 3,3',5,5'-tetrakis(trifluoromethyl)hydrazobenzene in 0.1 M [*n*NBu₄][BAr^F₄] in fluorobenzene. Scan rate was 100 mV/s.



Figure 5.4.29. Scan rate dependence plot of $Li_4(Et_2O)_4[Ce(^{Cl}ArNNAr^{Cl})_4]$ (5.2) in 0.1 M





Figure 5.4.30. Differential pulse voltammetry of $Li_4(Et_2O)_4[Ce(^{Cl}ArNNAr^{Cl})_4]$ (**5.2**) in 0.1 M [*n*NBu₄][BAr^F₄] in fluorobenzene.



Figure 5.4.31. Scan rate dependence plot of $Li_4(Et_2O)_4[Ce(^{Cl2}ArNNAr^{Cl2})_4]$ (5.3) in 0.1

M $[nNBu_4][BAr^F_4]$ in fluorobenzene. Scan rate ranged from 25–1000 mV/s.



Figure 5.4.32. Differential pulse voltammetry of $Li_4(Et_2O)_4[Ce(^{Cl2}ArNNAr^{Cl2})_4]$ (**5.3**) in 0.1 M [*n*NBu₄][BAr^F₄] in fluorobenzene.



Figure 5.4.33. Scan rate dependence plot of $Li_4(Et_2O)_4[Ce(Ar^FNNAr^F)_4]$ (**5.4**) in 0.1 M [*n*NBu₄][BAr^F₄] in fluorobenzene. Scan rate ranged from 25–1000 mV/s. The complex appeared to decompose with repeated electrochemical reduction.



Figure 5.4.34. Cyclic voltammetry of $Li_4(Et_2O)_4[Ce(Ar^FNNAr^F)_4]$ (5.4) in 0.1 M

 $[nNBu_4][BAr^F_4]$ in fluorobenzene. Scan rate was 100 mV/s. This scan was taken before isolating the metal wave and testing the scan rate dependence of the complex. The complex appeared to decompose with repeated electrochemical reduction.



Figure 5.4.35. Cyclic voltammetry of $Li_4(Et_2O)_4[Ce(Ar^FNNAr^F)_4]$ (5.4) in 0.1 M

 $[nNBu_4][BAr^F_4]$ in fluorobenzene. Scan rate was 100 mV/s. This scan was taken after isolating the metal wave and testing the scan rate dependence of the complex. The complex appeared to decompose with repeated electrochemical reduction, as was apparent by the solution color change and the growth of new waves.



Figure 5.4.36. Differential pulse voltammetry of $Li_4(Et_2O)_4[Ce(Ar^FNNAr^F)_4]$ (**5.4**) in 0.1 M [*n*NBu₄][BAr^F₄] in fluorobenzene. The complex appeared to decompose with repeated electrochemical reduction, as was apparent by the solution color change and the growth of new waves.

 Table 5.4.4. Li₄(OMe₂)₄[Ce(^{Cl}ArNNAr^{Cl})₄]

Ce	0.000049942	0.000034017	-0.000608956
Cl	4.935807454	-0.027040863	-5.932986405
Cl	4.176419226	6.217363878	2.772943253
Cl	-0.024815778	-4.934234728	5.934648498
Cl	6.218344020	-4.174018370	-2.772181169
Cl	-4.934890908	0.023921809	-5.934356392
Cl	-4.175897351	-6.217406900	2.773804256
Cl	-6.216865022	4.175109258	-2.774727168
Cl	0.021522834	4.935904124	5.933848488
0	4.556554930	-0.284075323	2.130654208
0	-0.284363515	-4.557566939	-2.128960121
0	-4.557169009	0.284490433	2.129066206
0	0.284971338	4.557056918	-2.129870121
N	1.588881414	1.387029207	-1.188233047
N	2.122768658	1.248662094	0.145043055
N	1.386668181	-1.588311410	1.188410136
N	1.248420011	-2.122760672	-0.144664967
N	-1.588479567	-1.387335204	-1.188414047
N	-2.122566771	-1.248561074	0.144738055
N	-1.248293125	2.122844700	-0.145466968
N	-1.386987270	1.588665488	1.187683137
С	2.412694559	1.023100069	-2.251412128
С	1.828924776	0.904018493	-3.537195229
Н	0.757898732	1.063391054	-3.646242234

С	2.592402724	0.585051815	-4.655525311
Н	2.125728441	0.498644717	-5.632000388
С	3.966475391	0.375190839	-4.516976303
С	4.571559693	0.489748135	-3.266980206
Н	5.640761869	0.331520772	-3.167360197
С	3.804427247	0.813444208	-2.148409121
Н	4.284839743	0.920568834	-1.181804046
С	2.567994958	2.438619577	0.724787100
С	2.998619585	3.556808612	-0.027841958
Н	3.005093386	3.498867915	-1.110898042
С	3.483655863	4.709105835	0.597028091
Н	3.827371642	5.548304126	-0.000149956
С	3.556680186	4.768193026	1.985270194
С	3.140364728	3.679619464	2.758393255
Н	3.173846164	3.739770889	3.841318336
С	2.649919655	2.538568824	2.135959205
Н	2.286704716	1.716591601	2.747037254
С	1.023166074	-2.411870603	2.251919218
С	0.904124540	-1.827725824	3.537538315
Н	1.063001108	-0.756588727	3.646187321
С	0.585780884	-2.590966838	4.656205399
Н	0.499378819	-2.123992560	5.632537450
С	0.376597893	-3.965200582	4.518194390
С	0.491197148	-4.570663886	3.268392295
Н	0.333528772	-5.639987101	3.169185287
С	0.814217193	-3.803755372	2.149471206
Н	0.921395795	-4.284462874	1.183021133
С	2.438504507	-2.567849984	-0.724259013

С	3.556828599	-2.997995627	0.028442046
Н	3.498792888	-3.004553419	1.111488127
С	4.709426882	-3.482413937	-0.596347003
Н	5.548720218	-3.825794726	0.000888044
С	4.768751107	-3.555155287	-1.984596107
С	3.680111509	-3.139167824	-2.757794168
Н	3.740458962	-3.172381280	-3.840719249
С	2.538700790	-2.649462711	-2.135434118
Н	1.716699553	-2.286384765	-2.746571165
С	-2.412135758	-1.023818084	-2.251853129
С	-1.828197035	-0.905310527	-3.537614226
Н	-0.757139987	-1.064622089	-3.646443237
С	-2.591566058	-0.587031859	-4.656213310
Н	-2.124766826	-0.501071776	-5.632667363
С	-3.965701745	-0.377373879	-4.517980301
С	-4.570956992	-0.491426156	-3.268026204
Н	-5.640208191	-0.333389787	-3.168650199
С	-3.803923470	-0.814372215	-2.149176121
Н	-4.284461932	-0.921187834	-1.182602046
С	-2.567921058	-2.438395539	0.724701099
С	-2.649676736	-2.538162802	2.135886205
Н	-2.286355792	-1.716156596	2.746863255
С	-3.139902804	-3.679159467	2.758460254
Н	-3.173197218	-3.739114915	3.841432337
С	-3.556344301	-4.768089022	1.985740193
С	-3.483383961	-4.708896816	0.597413089
Н	-3.827078753	-5.548203106	0.000317044
С	-2.998526699	-3.556728579	-0.027690958

Н	-3.005059524	-3.499018874	-1.110758043
С	-2.438150614	2.567997990	-0.725495013
С	-2.537731866	2.649859646	-2.136690120
Н	-1.715475624	2.286849679	-2.747521165
С	-3.678790556	3.139876726	-2.759453165
Н	-3.738672989	3.173279129	-3.842396249
С	-4.767695150	3.555886219	-1.986641107
С	-4.708951945	3.482957926	-0.598379001
Н	-5.548427266	3.826424738	-0.001446956
С	-3.556680688	2.998289654	0.026816046
Н	-3.499055990	3.004759491	1.109884127
С	-1.023937127	2.412498731	2.251129214
С	-0.815189249	3.804399518	2.148466209
Н	-0.922039867	4.284887983	1.181868135
С	-0.492947168	4.571629116	3.267391292
Н	-0.335445790	5.640961369	3.168030284
С	-0.378909880	3.966468872	4.517393390
С	-0.587892873	2.592226111	4.655603401
Н	-0.501961781	2.125498879	5.632095481
С	-0.905483562	1.828666013	3.536941313
Н	-1.064301133	0.757536912	3.645746321
С	5.677679126	0.558618840	1.863106186
Н	5.917588194	1.166718235	2.743936254
Н	5.399052752	1.218958698	1.040813124
С	4.773059525	-1.157617550	3.238537289
Н	5.603028939	-1.846174372	3.032523273
Н	3.852379929	-1.723485129	3.392717303
С	-1.157890770	-4.774329535	-3.236801201

Н	-1.723504339	-3.853564969	-3.391410214
Η	-1.846677561	-5.604028925	-3.030474188
С	0.558048641	-5.678773147	-1.860866100
Η	1.166105972	-5.919255155	-2.741569165
Η	-0.044524779	-6.551815753	-1.578433079
С	-4.773920603	1.158003686	3.236921293
Η	-3.853253013	1.723818268	3.391363303
Η	-5.000910776	0.576887912	4.140200361
С	1.158776565	4.773581485	-3.237538202
Η	0.577887755	5.000196625	-4.141058274
Н	1.724778153	3.852952875	-3.391515214
С	-0.557877833	5.678127128	-1.862591096
Н	-1.165787238	5.917942214	-2.743577165
Н	0.044330625	6.551520842	-1.580463077
Li	2.979251761	-0.368615638	1.020234119
Li	-0.368970790	-2.979893759	-1.019087033
Li	-2.979483848	0.368926707	1.019169124
Li	0.369452655	2.979778753	-1.019388034
С	-5.678269212	-0.558135733	1.861200185
Н	-6.551515868	0.044279708	1.579059164
Н	-5.918381272	-1.166326104	2.741911251
Н	-5.603803019	1.846606498	3.030712275
Н	-5.399515835	-1.218395600	1.038888126
Н	1.218445517	-5.399929758	-1.038694034
Н	-0.576795026	-5.001595701	-4.140024272
Н	6.551008810	-0.043722610	1.581067164
Н	4.999786692	-0.576518753	4.141893358
Н	-1.218393685	5.399500754	-1.040440038

Lowest Energy Frequencies (cm⁻¹) 3.17, 7.12, 7.24, 8.87, 14.81

Sum of Electronic and Thermal Free Energies (Hartrees) -7092.776253

Table 5.4.5. $Li_4(OMe_2)_4[Ce(^{Cl2}ArNNAr^{Cl2})_4]$

Ce	-0.000012443	0.000033957	-0.000181714
Ν	1.094103945	1.853816946	-1.097003218
Ν	0.872359839	2.307454603	0.253082661
N	-2.307454449	0.872383219	-0.252721418
Ν	-1.853494147	1.094073227	1.097282861
N	-1.094370042	-1.853573392	-1.097220974
Ν	-0.872413244	-2.307383963	0.252789175
N	2.307453528	-0.872244145	-0.253316146
Ν	1.853682169	-1.094269700	1.096687685
0	-1.134962329	4.406515749	2.229502486
0	-4.407105284	-1.134843698	-2.228604943
0	1.135318730	-4.406993728	2.228227063
0	4.406686679	1.135435372	-2.229119388
С	0.623529410	2.670410457	-2.122911308
С	0.227409770	4.010928450	-1.936555634
Η	0.273036236	4.457119720	-0.951979864
С	-0.185301571	4.765548590	-3.030800399
С	-0.220216134	4.259757091	-4.328364530
Η	-0.544245529	4.863251903	-5.165739826
С	0.183951418	2.933051793	-4.496653738
С	0.597924274	2.138519227	-3.435326296

Н	0.903374156	1.111218474	-3.610634304
С	1.976891588	2.897790110	0.863096713
С	1.987150477	3.039941200	2.273052229
Н	1.172384432	2.639652823	2.866009942
С	3.048134711	3.676227825	2.898537218
С	4.152523052	4.173909645	2.197685752
Н	4.978100220	4.653214357	2.706857212
С	4.129921707	4.022937048	0.815871158
С	3.074137968	3.416546028	0.136437963
Н	3.065241509	3.407148930	-0.945709675
С	-2.897882102	1.976952480	-0.862608648
С	-3.416463259	3.074205406	-0.135842133
Н	-3.406914250	3.065264179	0.946300850
С	-4.022862365	4.130060071	-0.815156668
С	-4.173992604	4.152737951	-2.196952979
Н	-4.653274720	4.978386124	-2.706029674
С	-3.676474082	3.048349949	-2.897916499
С	-3.040207572	1.987277803	-2.272549378
Н	-2.640021765	1.172520018	-2.865589807
С	-2.669889138	0.623486229	2.123346726
С	-2.137692890	0.597754514	3.435648300
Н	-1.110311893	0.903061529	3.610724947
С	-2.932028836	0.183838228	4.497152223
С	-4.258832555	-0.220162923	4.329163318
Н	-4.862172784	-0.544151166	5.166672469
С	-4.764924288	-0.185127746	3.031715029
С	-4.010508876	0.227537411	1.937299387
Н	-4.456935678	0.273280420	0.952838629

С	-0.624109271	-2.670147863	-2.123307852
С	-0.228158012	-4.010748059	-1.937153911
Н	-0.273478320	-4.456957681	-0.952578475
С	0.183877345	-4.765450496	-3.031600520
С	0.218227131	-4.259677455	-4.329186337
Н	0.541712241	-4.863239986	-5.166725657
С	-0.185813778	-2.932905079	-4.497284914
С	-0.599087707	-2.138279414	-3.435747780
Н	-0.904522169	-1.110952108	-3.610927675
С	-1.976865494	-2.897805191	0.862874438
С	-1.986854736	-3.040141684	2.272806050
Н	-1.171955899	-2.639953999	2.865654387
С	-3.047754889	-3.676417217	2.898421990
С	-4.152315186	-4.173949640	2.197732420
Н	-4.977827599	-4.653250864	2.707014811
С	-4.129974185	-4.022828493	0.815925488
С	-3.074286714	-3.416421401	0.136356892
Н	-3.065595544	-3.406901164	-0.945781505
С	2.897908466	-1.976632619	-0.863485421
С	3.416542297	-3.074034334	-0.136972095
Н	3.406692737	-3.065485734	0.945171242
С	4.023380133	-4.129496381	-0.816505504
С	4.175003221	-4.151572221	-2.198259777
Н	4.654707240	-4.976875334	-2.707499802
С	3.677511016	-3.046993837	-2.898942864
С	3.040724346	-1.986356420	-2.273377339
Н	2.640682173	-1.171380011	-2.866217644
С	2.670277104	-0.624015025	2.122743374

С	2.138318700	-0.598673325	3.435142094
Н	1.110952764	-0.903991203	3.610306183
С	2.932871360	-0.185147820	4.496629486
С	4.259663585	0.218833322	4.328526077
Н	4.863176998	0.542509849	5.166026339
С	4.765520787	0.184176917	3.030981446
С	4.010885899	-0.228093804	1.936575383
Н	4.457142126	-0.273573982	0.952023347
С	-2.128957634	4.467900548	3.257290648
Н	-1.691722218	4.870757737	4.179294235
Н	-2.474089920	3.448049045	3.437356706
С	-0.561141211	5.686145645	1.948413882
Н	-0.117889126	6.109617675	2.857870253
Н	-1.322955357	6.368554951	1.552353991
С	-5.686704562	-0.561167030	-1.947071630
Н	-6.368930190	-1.323087921	-1.550899425
Н	-6.110484308	-0.117845721	-2.856350589
С	-4.468705490	-2.128748773	-3.256470529
Н	-5.096873440	-2.970188310	-2.939632504
Н	-3.448877430	-2.473798201	-3.436847061
С	0.561453727	-5.686537077	1.946816534
Н	0.118375346	-6.110318834	2.856212463
Н	1.323198863	-6.368804881	1.550378911
С	2.129530294	-4.468726371	3.255785853
Н	2.474715307	-3.448935142	3.436110536
Н	2.970820047	-5.096948424	2.938658268
С	5.686351336	0.561667266	-1.948079437
Н	6.368745243	1.323507760	-1.552040887

Η	6.109813364	0.118438022	-2.857551572
С	4.468000959	2.129451923	-3.256887934
Η	5.096346263	2.970803669	-2.940166857
Η	3.448138052	2.474605714	-3.436864762
Cl	-0.660914597	6.440261431	-2.768652731
Cl	0.168768397	2.247169783	-6.115333741
Cl	3.015426339	3.865284885	4.646837194
Cl	5.480665272	4.657518107	-0.123193506
Cl	-4.657229060	5.480812701	0.124039356
Cl	-3.865704856	3.015766706	-4.646201774
Cl	-2.245764278	0.168514438	6.115672785
Cl	-6.439763687	-0.660509369	2.769939590
Cl	0.659250202	-6.440268628	-2.769682209
Cl	-0.171443635	-2.247083136	-6.115997753
Cl	-3.014709209	-3.865653774	4.646694962
Cl	-5.480946689	-4.657218440	-0.122943577
Cl	4.657792258	-5.480452543	0.122370103
Cl	3.867623790	-3.013507760	-4.647111974
Cl	2.246903120	-0.170305009	6.115277702
Cl	6.440354408	0.659506409	2.769063447
Li	-2.888843093	-0.899098854	-1.068149029
Li	0.899169245	-2.888688145	1.067942740
Li	-0.899016699	2.888498128	1.068789249
Li	2.888626268	0.899387287	-1.068437764
Н	-5.536092938	0.224437572	-1.205122485
Η	-4.871846085	-1.691455184	-4.178322047
Н	1.692484466	-4.871880635	4.177748588
Н	-0.224366797	-5.535835493	1.205117098

Н	-2.970321408	5.096215980	2.940542229
Н	0.224538501	5.535683725	1.206513285
Η	4.870782693	1.692237361	-4.178934045
Н	5.535949425	-0.224018844	-1.206173458

Lowest Energy Frequencies (cm⁻¹) 8.90, 14.53, 16.65, 16.98, 17.59

Sum of Electronic and Thermal Free Energies (Hartrees) -10769.608802

Table 5.4.6. $Li_4(OMe_2)_4[Ce(Ar^FNNAr^F)_4]$

Ce	0.020530911	-0.006932557	-0.028172573
F	0.264497105	-1.929438967	-6.332459718
F	1.641346967	-0.420588286	-5.590607032
F	2.408570040	-2.202081490	-6.583039062
F	-2.599578124	-6.434017351	-1.549495375
F	-3.434582161	-7.399444303	0.216373729
F	-4.305778864	-5.553874087	-0.534632500
F	-0.214794931	-6.041716825	4.338770779
F	-2.302171223	-5.565898053	4.724148133
F	-0.779411332	-4.012681879	4.867496989
F	0.135326582	1.430288394	5.625314603
F	1.863070896	2.144525330	6.744827280
F	1.594636724	0.014248227	6.392761741
F	5.297189677	3.568783089	1.678025798
F	4.836899701	4.451187559	3.616162804
F	6.221966503	2.783052105	3.481458793
F	6.313244128	-0.175812889	-4.043986174
F	5.767296616	-2.224732879	-4.531122942

F	4.292196826	-0.628419468	-4.697537618
F	-5.493714730	4.358463042	0.278839876
F	-6.423618913	2.674813830	1.285299898
F	-7.323400738	3.497815138	-0.520572954
F	-5.456729157	2.148442464	-4.952743856
F	-5.985230435	0.094574319	-4.466204366
F	-3.940896180	0.583066543	-5.010893742
F	-2.329708787	-0.007026717	6.272236013
F	-2.578729689	-2.148823043	6.567602115
F	-0.747956147	-1.370996634	5.677728869
F	-6.313336628	-3.224523252	3.499703190
F	-6.118967602	-2.756414370	1.379341781
F	-4.999497158	-4.407302445	2.240106669
F	0.086102482	6.176292050	4.240008593
F	2.103759224	5.564928018	4.779071873
F	0.469235631	4.123960620	4.837924130
F	0.173620872	1.874242436	-6.371670005
F	-1.237154071	0.365379867	-5.697736743
F	-1.953618981	2.135269248	-6.747264459
0	2.610266525	-3.555392338	2.483167120
0	-3.504822858	-2.711146415	-2.438403540
0	-2.721024049	3.556506928	2.277460455
Ν	-0.220581065	-2.114111334	-1.149632689
Ν	0.092500976	-2.469638105	0.213050015
Ν	2.060842791	-0.266283172	1.216791119
Ν	2.494185066	0.088518972	-0.112826372
Ν	-2.435323517	-0.083953654	-0.312296926
N	-2.107334319	0.257056062	1.052413197

Ν	-0.068557791	2.465906834	0.176402528
Ν	0.327310258	2.086581348	-1.158638815
С	0.656737891	-2.597230895	-2.118774856
С	0.629245662	-2.026643769	-3.408299801
Н	-0.077703418	-1.230708824	-3.628732447
С	1.513964637	-2.454597533	-4.397301651
С	2.438008467	-3.469888613	-4.152176759
Н	3.141192430	-3.775804912	-4.916000794
С	2.447758155	-4.060186073	-2.885256092
С	1.572712657	-3.645004901	-1.885869222
Н	1.585863087	-4.128277945	-0.917801518
С	1.464130396	-1.760237389	-5.732996829
С	3.401297230	-5.194768802	-2.613171841
F	3.636712789	-5.354977844	-1.287375738
F	4.595737516	-4.994415041	-3.210000829
F	2.922236612	-6.372131871	-3.070555131
С	-0.688344685	-3.492043333	0.738210147
С	-1.474488765	-4.361497397	-0.047224946
Н	-1.477022270	-4.260775815	-1.126029738
С	-2.210856148	-5.392472275	0.545189174
С	-2.152131449	-5.634140274	1.913249488
Н	-2.714976457	-6.441766306	2.363239590
С	-1.351894833	-4.790351038	2.694941817
С	-0.660383075	-3.726800151	2.134211433
Н	-0.090182883	-3.062686059	2.773636094
С	-3.130869256	-6.205329117	-0.326250182
С	-1.174989053	-5.095293740	4.157718345
С	2.494058207	0.571672013	2.241134771

С	1.852880921	0.498782294	3.495170194
Н	1.038617854	-0.206864084	3.639819107
С	2.232471663	1.337014464	4.542086420
С	3.265883354	2.261445906	4.390580793
Н	3.533642359	2.930955267	5.197742212
С	3.922234326	2.319484606	3.157883236
С	3.557910094	1.488344420	2.102497200
Н	4.091679057	1.538452817	1.162452336
С	1.464814855	1.238515390	5.834074129
С	5.069243053	3.281099608	2.983313144
С	3.539595460	-0.683714230	-0.604856438
С	4.355243575	-1.506499364	0.200954016
Н	4.200165637	-1.536599860	1.272806330
С	5.404644621	-2.243442857	-0.358135480
С	5.713983914	-2.156240664	-1.711414988
Н	6.534256223	-2.720361815	-2.136504824
С	4.929929961	-1.311458473	-2.509677953
С	3.855266491	-0.610974447	-1.983377840
Н	3.243707859	-0.000916590	-2.637904141
С	6.176032012	-3.179888395	0.534603787
F	6.355137450	-2.663599400	1.772462198
F	7.391235335	-3.479529249	0.038060976
F	5.515610762	-4.355493992	0.701650191
С	5.318087099	-1.096969906	-3.947826476
С	-3.446264892	0.683091802	-0.877430977
С	-4.311768356	1.514740966	-0.135330495
Н	-4.227527339	1.557108966	0.944105627
С	-5.323579059	2.243938182	-0.769084306

С	-5.547922166	2.137575048	-2.137437843
Н	-6.340669268	2.694465240	-2.620147482
С	-4.716050467	1.281712521	-2.873422752
С	-3.675123474	0.590963096	-2.271833036
Н	-3.021438661	-0.025890700	-2.877708648
С	-6.150304685	3.188487514	0.063550960
С	-5.017262612	1.039497076	-4.327953084
С	-2.671222511	-0.562384127	2.027526982
С	-2.161634806	-0.516526605	3.341355243
Н	-1.336494209	0.151363078	3.573847976
С	-2.698222499	-1.321636658	4.344678456
С	-3.765618091	-2.183790848	4.089601385
Н	-4.176645798	-2.805116584	4.875173933
С	-4.291733902	-2.214113356	2.795126924
С	-3.762406308	-1.422061953	1.779784334
Н	-4.210457250	-1.435941299	0.795234944
С	-2.095373411	-1.220723583	5.721558610
С	-5.432966029	-3.147664082	2.481464815
С	0.683651369	3.494968249	0.729098313
С	1.534483770	4.335547899	-0.020449129
Η	1.599618362	4.218089368	-1.095471541
С	2.254550372	5.362987841	0.598509713
С	2.120761255	5.627449622	1.957075122
Н	2.672710086	6.430351264	2.428794655
С	1.245584801	4.821112312	2.698835932
С	0.561757009	3.766558751	2.113839935
Н	-0.070944931	3.134727900	2.726047872
С	3.226482557	6.157728618	-0.233646445

F	2.763594421	6.368399320	-1.487496355
F	4.409268069	5.502136639	-0.366806684
F	3.503126877	7.359825702	0.306227517
С	0.987093114	5.163761688	4.141343527
С	-0.480452432	2.565829268	-2.187991251
С	-0.373424209	1.983757959	-3.468128559
Н	0.339532488	1.180406664	-3.635798095
С	-1.188704475	2.409598052	-4.516051233
С	-2.119005779	3.433702584	-4.340053590
Н	-2.768556892	3.738278233	-5.150620539
С	-2.206788532	4.034915102	-3.081386659
С	-1.401557568	3.622262429	-2.024097553
Н	-1.473939183	4.113617735	-1.062744478
С	-1.057878286	1.704483427	-5.840612960
С	-3.167236047	5.178332943	-2.880034012
F	-3.482330317	5.353892607	-1.572953618
F	-2.652616723	6.347691079	-3.319066176
F	-4.324355329	4.979795090	-3.547011599
С	2.709451175	-4.963382282	2.228548200
Η	1.907441768	-5.499763226	2.748694473
Η	3.686250209	-5.333312851	2.558985805
С	2.767183794	-3.247828821	3.873773793
Н	2.736772580	-2.161415557	3.975626252
Н	3.734029448	-3.618167216	4.234898958
0	3.679839412	2.666871409	-2.243644838
С	3.425265414	2.882031883	-3.637100131
Η	2.342669846	2.877390883	-3.777562204
Н	3.826536177	3.854043742	-3.947685979

С	5.077787848	2.738201676	-1.932198113
Н	5.470397011	3.722607358	-2.209309082
Н	5.626126838	1.950664055	-2.462183331
С	-3.165389113	-2.930158596	-3.812998484
Н	-2.076546946	-2.908311778	-3.889995959
Н	-3.598218033	-2.144413272	-4.444573177
С	-4.918237118	-2.799477872	-2.211565330
Н	-5.091811140	-2.664659829	-1.142933194
Н	-5.280950736	-3.790265082	-2.506737415
С	-2.975228003	3.256237178	3.655527400
Н	-2.969081636	2.170014703	3.762605919
Н	-3.958036416	3.643306808	3.949717745
С	-2.794185349	4.963541919	2.009926605
Н	-2.027037847	5.499740101	2.580979433
Н	-3.789358327	5.340143894	2.270585951
Li	-2.261596584	-1.947455696	-1.182818352
Li	-1.936333655	2.297083665	1.046789901
Li	1.895823163	-2.300453508	1.207055580
Li	2.364913171	1.929388262	-1.043860270
Η	-2.632981194	5.102959296	0.940132353
Η	-2.198292311	3.696342143	4.292674874
Η	-3.531158454	-3.910713614	-4.140181644
Η	-5.442170908	-2.021756103	-2.779616247
Η	1.956535573	-3.698530307	4.459535928
Η	2.623998082	-5.108934548	1.150893539
Η	5.180027268	2.607442010	-0.853975455
Н	3.880739554	2.084723920	-4.237481380

Lowest Energy Frequencies (cm⁻¹) 13.98, 14.64, 15.81, 16.52, 17.58 Sum of Electronic and Thermal Free Energies (Hartrees) –8808.531432



Figure 5.4.37. Molecular orbital of a Ce–N bonding interaction in Li₄(Me₂O)₄[Ce(PhNNPh)₄] (**5.1**) (at left) and Li₄(Me₂O)₄[Ce(^{Cl}ArNNAr^{Cl})₄] (**5.2**) (right). The remaining substituted Li₄(Me₂O)₄[Ce(ArNNAr)₄] had a similar orbital set as that shown for complex **5.2**.



Figure 5.4.38. Thermal ellipsoid plot of {[Li(THF)]₂[BocNNBoc]}_n.

	{[Li(THF)] ₂ [BocNNBoc]} _n (Penn4714)	
Empirical formula	C ₉ H ₁₇ NO ₃ Li	
Formula weight	194.18	
Temperature (K)	100(1)	
Wavelength (Å)	0.71073	
Crystal system	Triclinic	
Space group	PT	
Cell constants		
a (Å)	5.7936(2)	
b (Å)	9.3599(4)	
c (Å)	10.2623(4)	
α (°)	96.524(2)	
β (°)	91.822(2)	
γ (°)	102.132(2)	
V (Å ³)	539.66(4)	
Z	2	
$\rho_{calc} (mg/cm^3)$	1.195	
μ (Mo K α) (mm ⁻¹)	0.087	
F(000)	210	
Crystal size (mm ³)	0.30 x 0.10 x 0.08	
Theta range for data collection	2.00 to 27.59°	
Index ranges	$-7 \le h \le 7, -12 \le k \le 12, -13 \le l \le 13$	
Reflections collected	12917	
Independent collections	2476 [R(int) = 0.0223]	
Completeness to theta = $27.58, 27.49^{\circ}$	99.0	
Absorption correction	Semi-empirical from equivalents	

Table 5.4.7. Crystallographic parameters for ${[Li(THF)]_2[BocNNBoc]}_n$.

0.7456 and 0.6797
Full-matrix least-squares on F ²
2476 / 0 / 131
1.052
R1 = 0.0356, wR2 = 0.0863
R1 = 0.0429, wR2 = 0.0904
0.311 and -0.195

5.5 BIBLIOGRAPHY

- [1] G. Ertl, S. B. Lee, M. Weiss, *Surf. Sci.* 1982, *114*, 527-545; T. S. Rahman, S. Stolbov, F. Mehmood, *Appl. Phys. A* 2007, *87*, 367-374; C.-F. Huo, B.-S. Wu, P. Gao, Y. Yang, Y.-W. Li, H. Jiao, *Angew. Chem. Int. Ed.* 2011, *50*, 7403-7406; F. Solymosi, *J. Mol. Catal.* 1991, *65*, 337-358; S. J. Jenkins, D. A. King, *J. Am. Chem. Soc.* 2000, *122*, 10610-10614; Z.-P. Liu, P. Hu, *J. Am. Chem. Soc.* 2001, *123*, 12596-12604; K. Herzog, J. Gaube, *J. Catal.* 1989, *115*, 337-346; F. Xu, Z. Huang, P. Hu, Y. Chen, L. Zheng, J. Gao, X. Tang, *Chem. Commun.* 2015, Just accepted.
- [2] R. Grabowski, B. Grzybowska, K. Samson, J. Sloczynski, J. Stoch, K. Wcislo, *Appl. Catal. A-Gen.* 1995, *125*, 129-144; M. Akimoto, E. Echigoya, *J. Catal.*1974, *35*, 278-288; J. J. Mortensen, B. Hammer, J. K. Norskov, *Phys. Rev. Lett.*1998, *80*, 4333-4336; Y. Zhai, D. Pierre, R. Si, W. Deng, P. Ferrin, A. U. Nilekar, G. Peng, J. A. Herron, D. C. Bell, H. Saltsburg, M. Mavrikakis, M. Flytzani-

Stephanopoulos, *Science* **2010**, *329*, 1633-1636; M. Shibasaki, M. Kanai, S. Matsunaga, N. Kumagai, Acc. Chem. Res. 2009, 42, 1117-1127; Y. Horiuchi, V. Gnanadesikan, T. Ohshima, H. Masu, K. Katagiri, Y. Sei, K. Yamaguchi, M. Shibasaki, Chem. Eur. J. 2005, 11, 5195-5204; N. Yoshikawa, Y. M. A. Yamada, J. Das, H. Sasai, M. Shibasaki, J. Am. Chem. Soc. 1999, 121, 4168-4178; T. Yukawa, B. Seelig, Y. Xu, H. Morimoto, S. Matsunaga, A. Berkessel, M. Shibasaki, J. Am. Chem. Soc. 2010, 132, 11988-11992; S. Handa, V. Gnanadesikan, S. Matsunaga, M. Shibasaki, J. Am. Chem. Soc. 2010, 132, 4925-4934; M. Shibasaki, N. Kumagai, Angew. Chem. Int. Ed. 2013, 52, 223-234; J. M. Smith, A. R. Sadique, T. R. Cundari, K. R. Rodgers, G. Lukat-Rodgers, R. J. Lachicotte, C. J. Flaschenriem, J. Vela, P. L. Holland, J. Am. Chem. Soc. 2006, 128, 756-769; M. M. Rodriguez, E. Bill, W. W. Brennessel, P. L. Holland, Science 2011, 334, 780-783; K. P. Chiang, S. M. Bellows, W. W. Brennessel, P. L. Holland, Chem. Sci. 2014, 5, 267-274; A. R. Sadique, E. A. Gregory, W. W. Brennessel, P. L. Holland, J. Am. Chem. Soc. 2007, 129, 8112-8121; K. Jonas, D. J. Brauer, C. Kruger, P. J. Roberts, Y.-H. Tsay, J. Am. Chem. Soc. 1976, 98, 74-81; J. Jubb, S. Gambarotta, J. Am. Chem. Soc. 1994, 116, 4477-4478; G. Henrici-Olive, S. Olive, J. Mol. Catal. 1982, 16, 187-193; R. L. Miller, P. T. Wolczanski, A. L. Rheingold, J. Am. Chem. Soc. 1993, 115, 10422-104234; R. Whyman, A. P. Wright, J. A. Iggo, B. T. Heaton, J. Chem. Soc., Dalton Trans. 2002, 771-777; N. M. West, A. J. M. Miller, J. A. Labinger, J. E. Bercaw, Coordin. Chem. Rev.

2011, *255*, 881-898; J. P. Collman, J. I. Brauman, G. Tustin, G. S. Wann III, J. Am. Chem. Soc. **1983**, *105*, 3913-3922; G. C. Demitras, E. L. Muetterties, *J. Am. Chem. Soc.* **1977**, *99*, 2796-2797.

- [3] N. Yamagiwa, H. Qin, S. Matsunaga, M. Shibasaki, J. Am. Chem. Soc. 2005, 127, 13419-13427.
- [4] J. R. Robinson, Z. Gordon, C. H. Booth, P. J. Carroll, P. J. Walsh, E. J. Schelter, J. Am. Chem. Soc. 2013, 135, 19016-19024; J. Robinson, P. J. Carroll, P. J.
 Walsh, E. J. Schelter, Angew. Chem. Int. Ed. 2012, 51, 10159-10163.
- [5] J. R. Robinson, C. H. Booth, P. J. Carroll, P. J. Walsh, E. J. Schelter, *Chem. Eur.* J. 2013, 19, 5996-6004.
- [6] S. Cotton, *Lanthanide and Actinide Chemistry*, John Wiley and Sons Inc.,
 Hoboken, NJ, 2006; A. W. G. Platt, *The Rare Earth Elements: Fundamentals and Applications*, John Wiley & Sons Ltd., Chichester, United Kingdom, 2012.
- [7] N. G. Connelly, W. E. Geiger, *Chem. Rev.* **1996**, *96*, 877-910.
- [8] J. R. Levin, W. L. Dorfner, P. J. Carroll, E. J. Schelter, *Chem. Sci.* 2015, 6, Just Accepted.
- [9] H. Song, D. Chen, C. Pi, X. Cui, Y. Wu, J. Org. Chem. 2014, 79, 2955-2962.
- [10] L. K. Sydnes, S. Elmi, P. Heggen, B. Holmelid, D. Malte-Sorensen, Synlett 2007, 1695-1698.
- [11] Y. Takeda, S. Okumura, S. Minakata, *Angew. Chem. Int. Ed.* 2012, *51*, 7804-7808.
- [12] J. M. Birchall, R. N. Haszeldine, J. E. G. Kemp, J. Chem. Soc. C, 1970, 449-455.
- [13] E. S. Rhee, H. J. Shine, J. Am. Chem. Soc. 1986, 108, 1000-1006.
- [14] I. M. Zalesskaya, A. N. Blakitnyi, E. P. Saenko, Y. A. Fialkov, L. M.Yagupol'skii, *Zh. Org. Khim.* **1980**, *16*, 1194-1202.
- [15] C. Hansch, A. Leo, R. W. Taft, Chem. Rev. 1991, 91, 165-195.
- [16] C. Zhang, N. Jiao, Angew. Chem. Int. Ed. 2010, 49, 6174-6177.
- [17] R. B. Carlin, W. O. J. Forshey, J. Am. Chem. Soc. 1950, 72, 793-801; A. Hadasch,
 B. Meunier, Eur. J. Inorg. Chem. 1999, 2319-2325.
- [18] B. Priewisch, K. Ruck-Braun, J. Org. Chem. 2005, 70, 2350-2352.
- [19] K. B. Ling, A. D. Smith, *Chem. Commun.* **2011**, *47*, 373-375.
- [20] D. Adhikari, F. Basuli, H. Fan, J. C. Huffman, M. Pink, D. J. Mindiola, *Inorg. Chem.* 2008, 47, 4439-4441; B. L. Tran, J. Krzystek, A. Ozarowski, C.-H. Chen, M. Pink, J. A. Karty, J. Telser, K. Meyer, D. J. Mindiola, *Eur. J. Inorg. Chem.* 2013, 3916-3929; D. J. Mindiola, C. C. Cummins, *Angew. Chem. Int. Ed.* 1998, 37, 945-947; T. A. Betley, J. C. Peters, *J. Am. Chem. Soc.* 2004, *126*, 6252-6254; J. M. Smith, D. Subedi, *Dalton Trans.* 2012, 41, 1423-1429.
- [21] T. W. Hayton, *Dalton Trans.* **2010**, *39*, 1145-1158.
- [22] K. Meyer, D. J. Mindiola, T. A. Baker, W. M. Davis, C. C. Cummins, *Angew*.
 Chem. Int. Ed. 2000, *39*, 3063-3066; S. C. Bart, F. W. Heinemann, C. Anthon, C.
 Hauser, K. Meyer, *Inorg. Chem.* 2009, *48*, 9419-9426.

- [23] E. M. Schubert, J. Chem. Educ. 1992, 69, 62; D. F. Evans, J. Chem. Soc. 1959, 2003-2005.
- S. Vaddypally, S. K. Kondaveeti, M. J. Zdilla, *Chem. Commun.* 2011, 47, 9696-9698; S. K. Kondaveeti, S. Vaddypally, J. D. McCall, M. J. Zdilla, *Dalton Trans.* 2012, 41, 8093-8097; R. Allmann, in *The chemistry of the hydrazo, azo and azoxy groups, Vol. 1* (Ed.: S. Patai), John Wiley & Sons, New York, 1975, pp. 23-52; W. J. Evans, D. J. Drummond, L. R. Chamberlain, R. J. Doedens, S. G. Bott, H. Zhang, J. L. Atwood, *J. Am. Chem. Soc.* 1988, *110*, 4983-4994; P. B. Hitchcock, A. G. Hulkes, M. F. Lappert, Z. Li, *Dalton Trans.* 2004, 129-136; A. A. Trifonov, M. N. Bochkarev, H. Schumann, J. Loebel, *Angew. Chem. Int. Ed. Engl.* 1991, *30*, 1149-1151; K. L. Miller, B. N. Williams, D. Benitez, C. T. Carver, K. R. Ogilby, E. Tkatchouk, W. A. Goddard III, P. L. Diaconescu, *J. Am. Chem. Soc.* 2010, *132*, 342-355.
- [25] L. Yang, D. R. Powell, R. P. Houser, *Dalton Trans.* 2007, 955-964.
- [26] M. Wojdyr, J. Appl. Cryst. 2010, 43, 1126-1128.
- [27] D. C. Bradley, J. S. Ghotra, F. A. Hart, J. Chem. Soc., Dalton Trans. 1973, 1021-1023.
- [28] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R.
 Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji,
 M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L.
 Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida,

T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J.
E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N.
Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C.
Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E.
Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E.
Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L.
Martin, K. Morokuma, V. G. Zakrzewski, V. Voth, J. Cioslowski, D. J. Fox, *Vol. Revision D.01*, Gaussian, Inc., Wallingford, CT, **2009**.

- [29] Institute for Theoretical Chemistry, University of Cologne, http://www.tc.uni-koeln.de/PP/clickpse.en.html; X. Cao, M. Dolg, J. Molec. Struct. (Theochem)
 2002, 581, 139-147; M. Dolg, H. Stoll, H. Preuss, J. Chem. Phys. 1989, 90, 1730-1734.
- [30] Chemcraft, http://www.chemcraftprog.com/
- [31] S. I. Gorelsky, AOMix: Program for Molecular Orbital Analysis, version 6.5, University of Ottawa, http://www.sg-chem.net/, 2011.
- [32] Bruker, Bruker AXS Inc., Madison, Wisconsin, USA, 2009.
- [33] Bruker, Bruker AXS Inc., Madison, Wisconsin, USA, 2009.
- [34] G. M. Sheldrick, University of Gottingen, Germany, 2008.
- [35] G. M. Sheldrick, University of Gottingen, Germany, 2007.
- [36] G. M. Sheldrick, Acta Cryst. 2008, A64, 112-122.

- [37] M. Lehmann, A. Schulz, A. Villinger, *Angew. Chem. Int. Ed.* 2009, *48*, 7444-7447.
- [38] M. P. Andersson, P. Uvdal, J. Phys. Chem. A 2005, 109, 2937-2941.

CHAPTER 6

Density Functional Theory as a Predictive Tool for Cerium Redox Properties in Non-Aqueous Solvents

Abstract:

Two methods to correlate and predict cerium redox potentials were tested. Eight previously reported cerium complexes in a tetrahedral ligand field were calculated in a dichloromethane solvent continuum using the B3LYP basis set. Then, the computed $E_{1/2}$ values were correlated with the experimental $E_{1/2}$ measured in dichloromethane, and the energies of the Ce^{IV} LUMO orbitals were correlated with the experimental ground state E_{pc} . The predictive capabilities of these two correlations were tested using a new cerium nitroxide complex, Ce(O-DiNOx)₂, and we found that the computed versus experimental $E_{1/2}$ correlation resulted in a more accurate prediction than the calculated –LUMO energy *versus* experimental E_{pc} correlation. Two different non-aqueous solvent correlations were combined- using solvent continua for dichloromethane and acetonitrile- to develop one correlation to predict the redox potential of cerium complexes regardless of the nonaqueous solvent.

Adapted from work to be submitted to Inorg. Chem.

6.1 Introduction

Cerium, the only lanthanide with an accessible Ln^{IV/III} reduction potential in molecular chemistry, is an important platform for one-electron redox reactions.^[1] Many industrial applications including solid oxide fuel cell electrodes,^[2] de-pollutant catalysts such as automotive catalytic converters,^[3] and heterogeneous catalysts^[4, 5] take advantage of the reversible Ce^{IV/III} couple and the stability of the solid state material, cerium dioxide (ceria).^[2, 3, 5] In molecular chemistry, ceric ammonium nitrate (CAN) is used as a potent oxidant, particularly in the oxidation of alcohols to carbonyls and water oxidation catalyst systems.^[6]

To further develop molecular cerium's utility in redox reactions and catalysis, we surveyed the literature for reported cerium electrochemical potentials.^[7] We observed that the ligand environment, despite the isolated nature of the 4*f* orbitals, greatly impacted the cerium reduction potential over a range of 2 V measured under either aqueous or non-aqueous conditions.^[7] Thus ligand design was paramount to explore new redox chemistry with cerium complexes.

Computational chemistry has become a powerful tool in predicting reduction potentials of new compounds, including organic molecules, transition metal and f-block metal complexes.^[8-13] Previously, our group developed a correlation between DFT calculated and experimental electrochemical data for a series of cerium complexes in

acetonitrile.^[13] We used a similar method to the one described by Batista and coworkers for transition metal complexes,^[11] where first the ΔG was calculated by determining the free energies of Ce^{IV} and Ce^{III} of each complex in an acetonitrile solvent continuum. The E_{1/2} values were obtained by applying the Nernst equation to the calculated ΔG and referencing the values to the E_{1/2} of ferrocene computed in the same solvent continuum.

Recently, Gillmore and coworkers used DFT calculations to determine the reduction potentials for a wide range of organic molecules.^[9] Instead of calculating both the oxidized and reduced forms of the molecules of interest, Gillmore and coworkers calculated only the LUMO of the species that was to be reduced in a solvent continuum. The experimental reduction potential correlated well with the energy of the LUMO in over 74 different organic molecules, indicating that this method may be applied to other systems. Compared to calculating the $E_{1/2}$ to develop a semi-empirical correlation, use of the LUMO energy in such correlations would at least halve the computation time needed to predict the reduction potentials of new complexes.

In this chapter, we compare the accuracy of using the LUMO versus experimental E_{pc} method to the computed versus experimental $E_{1/2}$ approach to correlate and predict cerium redox potentials in a dichloromethane solvent continuum. We focused on correlating calculated and experimental reduction potentials of previously reported 4-coordinate cerium complexes with an approximately tetrahedral ligand field. To test the semi-empirical correlations, we designed a new 4-coordinate cerium nitroxide complex in an approximately tetrahedral crystal field, Ce(O-DiNOx)₂ and predicted its potential in dichloromethane. Subsequently, Ce(O-DiNOx)₂ was synthesized and studied by

electrochemistry. The reduction potential predicted by correlating the computed versus experimental $E_{1/2}$ gave a percent error of 1.1 %, while the correlation of the LUMO versus the experimental E_{pc} lead to a percent error of 5.7 %, indicating that the $E_{1/2}$ correlations provide more accurate predictions of cerium redox chemistry. Finally, considering that ligand field electrostatics is the most important indicator of cerium redox chemistry, we developed a combined acetonitrile and dichloromethane calculated versus experimental correlation.

6.2 Results

6.2.1. Pseudo 4-coordinate semi-empirical models in dichloromethane.

Previously, our group had synthesized a series of 8-coordinate cerium pyridyl nitroxide complexes with an approximate D_{2d} geometry and recorded their electrochemistry in acetonitrile.^[13] Based on these complexes and several other previously reported D_{2d} complexes, a correlation of calculated versus experimental cerium redox potentials in acetonitrile was generated, revealing a link between the crystal field of the ligand and the cerium reduction potential.^[13] To expand on efforts dedicated to predicting cerium redox potentials based on semi-empirical methods, previously reported cerium complexes in an approximately tetrahedral crystal field environment were calculated in a different non-aqueous solvent, dichloromethane. We also calculated one complex that was in an approximately octahedral crystal field, where 4 of the coordination sites were anionic oxygens and the remaining 2 sites were donor solvents, THF molecules, to test if this pseudo-4 coordinate complex also fit the tetrahedral ligand environment correlation.

To achieve a wide range of ligand fields, we combed the literature for 4coordinate cerium complexes with various types of donors. We chose previously characterized homoleptic anionic N and O donors, $Ce[N(SiHMe_2)_2]_4$,^[14, 15] $Ce(N^iPr_2)_4$,^[16] and $Ce(OAr)_4$ where OAr = 2,6-diphenylphenol;^[14] a homoleptic nitroxide complex, $Ce(arene-DiNOx)_2$;^[17] heteroleptic complexes, $Ce[N(SiMe_3)_2]_3X$, where X = F, Cl, and Br;^[18-22] and two heterobimetallic complexes, $Li(THF)[Ce(N^iPr_2)_4]^{[16]}$ and the 8coordinate $Li(THF)_2[Ce(MBP)_2(THF)_2]$ where MBP = methylene bis-phenolate^[23] to include in our correlation.

The Ce(III) and Ce(IV) calculated geometry optimizations for all of the complexes included in the correlation were calculated using the B3LYP basis set in a dichloromethane solvent continuum starting from their previously reported crystal structure geometries (see Tables 6.4.3–6.4.22 in section 6.4). The experimental cerium reduction potentials of complexes Ce[N(SiHMe₂)₂]₄, Ce(OAr)₄, and Ce(arene-DiNOx)₂ were reported in dichloromethane previously.^[14, 17] Electrochemistry of Ce[N(SiMe₃)₂]₃X, where X = F, Cl, and Br and Li(THF)₂[Ce(MBP)₂(THF)₂] only had been reported in THF,^[19, 21-23] and no electrochemistry had been reported for Ce(NⁱPr₂)₄ or Li(THF)[Ce(NⁱPr₂)₄].^[16] Thus complexes Ce[N(SiMe₃)₂]₃X, where X = F, Cl, and Br and Li(THF)[Ce(NⁱPr₂)₄] were synthesized and their electrochemistry recorded in dichloromethane (Figures 6.4.6–6.4.15 in section 6.4). Because of the high basicity of the NⁱPr₂⁻ ligand, the electrochemistry of Ce(NⁱPr₂)₄ could not be performed in dichloromethane, and was recorded in THF instead (Figures 6.4.14–6.4.15 in section 6.4). To correct for the influence of solvent on the electron transfer between the working

electrode and the analyte, either the Ce(N^{*i*}Pr₂)₄ or Li(THF)₂[Ce(MBP)₂(THF)₂] complexes, the experimental data was normalized by using the difference in reduction potential of cobaltocene versus ferrocene measured in dichloromethane and glyme (-0.02 V).^[24] The difference in the E_{1/2} of Ce[N(SiMe₃)₂]₃Br between dichloromethane and THF was only -0.03 V,^[22] supporting the use of the -0.02 V normalization for the electrochemistry of both Ce(N^{*i*}Pr₂)₄ and Li(THF)₂[Ce(MBP)₂(THF)₂].

Once all of the experimental and calculated data for the 4-coordinate complexes were attained, two correlation plots were made: one comparing calculated versus experimental $E_{1/2}$ values, and the other comparing the Ce^{IV} –LUMO energies versus the experimental reduction potentials for the series of complexes (Figures 6.2.1-6.2.2). The calculated $E_{1/2}$ values were corrected by 0.506 V, the systematic error attributed to referencing the calculated cerium potentials to ferrocene (Table 6.2.2).^[11, 13] No corrections were made to the LUMO energy versus the experimental reduction potential plot. By the metrics of the mean absolute deviation (MAD) and the goodness of fit parameter r^2 , the calculated versus experimental $E_{1/2}$ correlation was a better method for predicting the cerium reduction potentials in dichloromethane (Table 6.2.2), where the MAD at 0.058 V was approximately half and r^2 at 0.977 better by 0.1 compared to the LUMO energy versus E_{pc} (Figures 6.2.1–6.2.2, Table 6.2.2). One complex, Ce[N(SiHMe₂)₂]₄ showed the largest error in the LUMO energy versus the reduction potential correlation (Figure 6.2.2). To clarify the reasoning behind this anomaly, the LUMO orbitals of Ce[N(SiHMe₂)₂]₄, Li(THF)[Ce(N^{*i*}Pr₂)₄]⁺, and Ce[N(SiMe₃)₂]₃F were depicted (see section 6.4, Figure 6.4.17). The LUMO orbital of Ce[N(SiHMe₂)₂]₄ was

similar to the other complexes in the series, thus it remains unclear why the redox potential for this compound could not effectively be predicted.



Figure 6.2.1. Correlation of calculated versus experimental $E_{1/2}$ of a series of 4coordinate tetrahedral complexes. The green square showing the data point for Li(THF)₂[Ce(MBP)₂(THF)₂] was not included in the correlation.



Figure 6.2.2. Correlation of calculated –LUMO energy versus the experimental reduction potential of a series of 4-coordinate tetrahedral complexes. The green square showing the data point for $Li(THF)_2[Ce(MBP)_2(THF)_2]$ was not included in the correlation.

The Li(THF)₂[Ce(MBP)₂(THF)₂] calculated $E_{1/2}$ and LUMO energy poorly correlated with the experimental data (green square data point in Figures 6.2.1 and 6.2.2). Both the calculated $E_{1/2}$ and the calculated LUMO energy underestimated the reduction potential of the cerium center in Li(THF)₂[Ce(MBP)₂(THF)₂]. Based on the systematically underestimated reduction potential of the Li(THF)₂[Ce(MBP)₂(THF)₂] complex, we postulated that the isolated solid state structure was not the same as the solution structure in THF, the solvent in which the experimental electrochemistry was performed. In the solid state, the Li⁺ was inner sphere and associated with the Ce(MBP)₂ complex. In a THF solution, however, the Li⁺ cation could be fully solvated by THF,

changing from an inner sphere cation in the crystal structure to an outer sphere cation in solution. If the Li⁺ cation was bound to the methylene bis-phenolate ligands, the Li⁺ would withdraw electron density from the methylene bis-phenolate ligands and away from the cerium metal center, causing a smaller (less negative) Ce^{IV} reduction potential. An outer sphere Li⁺ cation would make the cerium metal center more electron rich, resulting in a larger (more negative) Ce^{IV} reduction potential, which would better correlate with the experimental data. To examine whether this was the cause of the large error in the Li(THF)₂[Ce(MBP)₂(THF)₂] calculation, the complex Ce(MBP)₂(THF)₂ also was calculated using the B3LYP basis set in a dichloromethane solvent continuum based on its reported crystal structure (see Tables 6.4.11 and 6.4.21 in section 6.4). The calculated E_{1/2} and LUMO energy values of Ce(MBP)₂(THF)₂ were correlated with the experimental Li(THF)₂[Ce(MBP)₂(THF)₂] electrochemical data, and these correlations were added to the calculated versus experimental $E_{1/2}$ and the –LUMO energy versus experimental E_{pc} plots respectively (Figures 6.2.1 and 6.2.2). The calculated Ce(MBP)₂(THF)₂ correlated well with the experimental Li(THF)₂[Ce(MBP)₂(THF)₂] data, indicating that the Li⁺ cation was outer-sphere in THF.

Table 6.2.1. Experimental $E_{1/2}$ and E_{pc} values, and calculated $E_{1/2}$ and LUMO energies for 4-coordinate and one octahedral complexes. ^{*a*}The $E_{1/2}$ values reported here were not corrected. ^{*b*}Indicated the corrected $E_{1/2}$ value. ^{*c*}The E_{pc} was not reported and was estimated based on the reported experimental results. ^{*d*}Experimental electrochemistry measured in THF and not dichloromethane.

Complex	E _{1/2} Exp.	E _{1/2} Calc.	E _{pc} Exp	LUMO	Ref
	(V vs.	(V vs.	(V vs.	energy	
	Fc/Fc ⁺)	$Fc/Fc^{+})^{a}$	Fc/Fc ⁺)	(eV)	
Ce[N(SiHMe ₂) ₂] ₄	-1.04	-1.24	-1.14	-3.13	13
Li(THF)Ce[N ⁱ Pr ₂] ₄	-0.85	-1.25	-0.90	-2.78	
$Ce[N^{i}Pr_{2}]_{4}$	-1.86^{d}	-1.87	-1.93^{d}	-1.97	
Ce[N(SiMe ₃) ₂] ₃ Br	-0.34	-0.72	-0.38	-3.23	
Ce[N(SiMe ₃) ₂] ₃ Cl	-0.42	-0.87	-0.46	-3.23	
Ce[N(SiMe ₃) ₂] ₃ F	-0.61	-1.02	-0.68	-3.03	
Ce(OAr) ₄	-0.50	-0.83	-0.54	-3.30	13
Li(THF) ₂ [Ce(MBP) ₂ (THF) ₂]	-0.95^{d}	-0.59	$-1.09^{c, d}$	-3.47	29
Ce(MBP) ₂ (THF) ₂	-0.95^{d}	-2.21	$-1.09^{c, d}$	-2.14	13
Ce(O-DiNOx) ₂	-1.84	-1.91	-1.92	-2.02	
		$(-1.82)^{b}$			
Ce(arene-diNOX) ₂	-1.74	-1.93	-1.79	-2.18	25

Table 6.2.2. Correlations of the calculated $E_{1/2}$ and LUMO energies with experimental reduction potentials of pseudo-tetrahedral cerium complexes measured in dichloromethane.

	4-coordinate	4-coordinate	
	$E_{1/2}$ (calc) vs.	<i>–LUMO</i> vs. E _{pc}	
	E _{1/2} (exp)	(exp)	
MAD (V)	0.058	0.13	
R^2	0.977	0.873	
Slope	0.772	0.800	
Correction factor/y-intercept	0.506	3.65	
Predicted potential	-1.82	-2.03	
$Ce(ODiNOx)_2$ (V vs. Fc/Fc ⁺)			

6.2.2. Synthesis and characterization of Ce(O-DiNOx)₂

To test the DFT semi-empirical models, we designed a cerium nitroxide complex, Ce(O-DiNOx)₂ and calculated its Ce(IV) LUMO energy and E_{1/2} potential (Tables 6.2.1–6.2.2). O-DiNOx was prepared first by a lithium-halogen exchange of bis(2bromobenzyl)ether at -20 °C (Scheme 6.2.1). The lithiated benzylether was then reacted with 2.5 equiv 2-methyl-2-nitrosopropane at -20 °C to yield O-DiNOx, a tan solid, in 83 % yield. Once the ligand was prepared, the Ce(O-DiNOx)₂ complex was prepared by reacting 2 equiv Ce[N(SiMe₃)₂]₃ with 3 equiv O-DiNOx and 1 equiv DiNOx oxidized with PbO₂ at -78 °C (Scheme 6.2.1). The product, a brown solid, was obtained in 46 % yield.





Ce(**O-DiNOx**)₂ crystallized as a 7-coordinate complex with 3 nitroxides binding η_2 through the N–O⁻ and 1 nitroxide binding solely through the anionic O⁻ (Figure 6.2.5). Ce–O bond distances of Ce(O-DiNOx)₂, ranging from 2.1641(19)–2.2593(19), were comparable to previously reported cerium 1-hydroxypyridin-2-one,^[25] pyridylnitroxide,^[13, 26] hydroxylaminato,^[27] and hydroxamate^[28] complexes. Only two other previously reported cerium nitroxide, hydroxylamine or hydroxamate complexes had η_2 interactions with the N–O bond, the Ce[2-(t Buhydroxylaminato)-4- t Bu-anisole]₄ complex,^[27] and the Ce(arene-DiNOx)₂ complex,^[17] which could be used to compare the Ce-N and N-O bond distances in Ce(O-DiNOx)₂. In Ce(O-DiNOx)₂, the Ce-N and N-O bond distances ranged from 2.488(2)-2.653(2), and 1.414(3)-1.432(3) respectively. These bond distances were similar to the Ce[2-(t Buhydroxylaminato)-4- t Bu-anisole]₄ and the Ce(arene-DiNOx)₂ complexes, where the Ce–N bond distances were 2.557(4) and 2.5510(18)–2.5976(18) respectively, and the N–O bond distances were 1.461(9) and 1.422(2)–1.439(2) respectively.^[17, 27] Interestingly, Ce(arene-DiNOx)₂ had significantly shorter the Ce–O bond distances compared to Ce(O-DiNOx)₂, ranging from, 2.0940(15)– 2.2208(15).

The optimized structure of $Ce(O-DiNOx)_2$ calculated by DFT did not show any coordination through the nitroxide N, only the anionic O⁻ (Figure 6.2.5). The Ce–O bond distances of the experimental and computed $Ce(O-DiNOx)_2$ complex were very similar, for example Ce(1)-O(2) was 2.236(2) and 2.233 Å for the experimental and calculated bond distances respectively. The Ce(1)-N bond distances and the Ce(1)-O(1) bond distances were lengthened in the calculated structure compared to the experimental crystal structure of $Ce(O-DiNOx)_2$ which was attributed to crystal packing (Figure 6.2.5).^[27]



Figure 6.2.3. 30 % thermal ellipsoid plot of $Ce(O-DiNOx)_2$ (left) and the calculated structure of $Ce(O-DiNOx)_2$ (right). Hydrogen atoms were omitted for clarity in both structures. Selected experimental bond distances for $Ce(O-DiNOx)_2$ (Å): Ce(1)-N(1) 2.526(2), Ce(1)-N(2) 2.653(2), Ce(1)-N(4) 3.473, Ce(1)-O(1) 2.7171(19), Ce(1)-O(2) 2.236(2), Ce(1)-O(6) 2.1641(19), and N(1)-O(2) 1.432(3). Selected calculated bond distances for $Ce(O-DiNOx)_2$ (Å): Ce(1)-N(4) 3.481, Ce(1)-O(1) 2.804, Ce(1)-O(2) 2.233, Ce(1)-O(6) 2.202.

To compare the predicted $E_{1/2}$ and E_{pc} values to the experimental values of Ce(**O**-**DiNOx**)₂, the cyclic voltammetry of Ce(**O**-**DiNOx**)₂ was measured in dichloromethane (Figures 6.4.5–6.4.6 in the section 6.4). The experimental $E_{1/2}$ was measured at -1.84 V versus Fc/Fc⁺, whereas the computed versus experimental $E_{1/2}$ correlation predicted a value of -1.82 V versus Fc/Fc⁺ (Tables 6.2.1–6.2.2). The experimental E_{pc} was measured at -1.92 V versus Fc/Fc⁺, while the LUMO versus experimental E_{pc} correlation predicted the E_{pc} to be at a more reducing potential, -2.03 V versus Fc/Fc⁺ (Tables 6.2.1–6.2.2). The percent errors for the predictions were 1.1 % and 5.7 % for the $E_{1/2}$ and LUMO methods respectively, indicating that the $E_{1/2}$ correlation gave a more accurate prediction than the LUMO correlation. However, the percent error of LUMO correlation was still low, and considering that the time needed to complete the calculation was much smaller, this could still be a viable method to predict Ce^{IV/III} reduction potentials.

6.2.3 Non-aqueous correlations of the Ce^{IV/III} reduction potentials

Because the Ce^{IV/III} reduction potentials are mainly governed by ligand electrostatics,^[7] we considered that a more generalized non-aqueous solvent calculated versus experimental correlation could be achieved. We hypothesized that the Ce^{IV/III} potentials would not be extremely sensitive to the solvent so long as the anionic ligands saturated the coordination sphere about the cerium cation. To test this hypothesis, the tetrahedral complex computed versus experimental correlations in dichloromethane were combined with the previously reported computed versus experimental D_{2d} complex correlations in acetonitrile (Figures 6.2.6–6.2.7).^[13] For the combined dichloromethane and acetonitrile computed $E_{1/2}$ versus experimental $E_{1/2}$ correlation, the calculated $E_{1/2}$ values were corrected using their respective solvent-dependent correction factors, 0.51 for dichloromethane (DCM) and 0.30 for acetonitrile (MeCN).^[13] No correction factors were necessary for the combining the energy of the LUMO versus experimental E_{pc} correlations. Both the computed $E_{1/2}$ versus experimental $E_{1/2}$ DCM and MeCN correlation and energy of the LUMO versus experimental E_{pc} DCM and MeCN correlation were able to fit a line ($r^2 > 0.9$), however the linear fit was not as good as either the original dichloromethane or acetonitrile correlations (Tables 6.2.2–6.2.3).^[13] Based on the r^2 , MAD, and the slope, both methods had approximately the same accuracy when looking at two or more non-aqueous solvents. Thus, to predict a cerium complex's redox potential in any non-aqueous solvent, the best method would be to use the –LUMO energy versus measured E_{pc} plot provided in Figure 6.2.7 and Table 6.2.3 because the solvent-dependent correction factors do not need to be calculated first in order to obtain an accurate line for this method.



Figure 6.2.4. Correlation of calculated versus experimental $E_{1/2}$ of a series of tetrahedral complexes in dichloromethane (red circles) and D_{2d} complexes in acetonitrile (blue squares).



Figure 6.2.5. Correlation of calculated –LUMO energy versus the experimental reduction potential of a series of tetrahedral complexes in dichloromethane (red circles) and D_{2d} complexes in acetonitrile (blue squares).

Table 6.2.3. Correlations of the calculated $E_{1/2}$ and LUMO energies with experimentalreduction potentials of cerium complexes measured in dichloromethane and acetonitrile.

	MeCN and DCM	MeCN and DCM
	$E_{1/2}$ (calc) vs. $E_{1/2}$ (exp)	-LUMO (calc) vs. E_{pc}
		(exp)
MAD (V)	0.15	0.13
R^2	0.924	0.928
Slope	0.926	0.913
Correction factor/y-	0.30 (MeCN) and 0.51	3.71
intercept	(DCM)	

6.3 Conclusions

A series of 4-coordinate cerium(IV) and cerium(III) complexes were calculated using the B3LYP basis set and a dichloromethane solvent continuum. The two correlation lines generated by the calculated $E_{1/2}$ versus the experimental $E_{1/2}$ and the Ce^{IV} –LUMO energies versus the experimental E_{pc} were then used to predict the cerium redox potential for Ce(O-DiNOx)₂. Ce(O-DiNOx)₂ was synthesized and the electrochemistry of this complex was measured in dichloromethane. The computed $E_{1/2}$ versus experimental $E_{1/2}$ correlation yielded a more accurate prediction than the correlation of the LUMO energies with the experimental E_{pc} . Then, because the cerium redox potentials mainly were impacted by the electrostatics of the ligands, we were able to generate one unifying correlation of the computed $E_{1/2}$ versus experimental $E_{1/2}$ in both acetonitrile and dichloromethane, as well as another unifying correlation of the LUMO energies with the experimental E_{pc} in these two non-aqueous solvents. Based on the linearity of these fits, both of these correlations were equally accurate. Thus, to quickly predict cerium redox potentials in non-aqueous solvents, we recommend using the LUMO energies with the experimental E_{pc} correlation provided in Figure 6.2.7 and Table 6.2.3.

6.4 Experimental Section

General Methods. Unless otherwise indicated all reactions and manipulations were performed under an inert atmosphere (N₂) using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. Nexus II drybox equipped with a molecular sieves 13X / Q5 Cu-0226S catalyst purifier system. Glassware was oven-dried overnight at 150 °C prior to use. ¹H and ¹³C spectra were obtained on a Bruker DMX-300 or on a Bruker BioDRX-500 Fourier transform NMR spectrometer at 300 and 500 MHz respectively. Chemical shifts were recorded in units of parts per million downfield from residual proteo solvent peaks (¹H), or characteristic solvent peaks (¹³C). Elemental analyses were performed at Complete Analysis Laboratories Inc. in Parsippany, NJ using a Carlo Erba EA 1108 analyzer.

Materials. Tetrahydrofuran, dimethoxyethane, toluene, fluorobenzene, hexane, and pentane were purchased from Fisher Scientific. The solvents were sparged for 20 min with dry N_2 and dried using a commercial two-column solvent purification system comprising columns packed with Q5 reactant and neutral alumina respectively (for hexane and pentane), or two columns of neutral alumina (for THF, dichloromethane, diethyl ether, and toluene). Pyridine, also purchased from Fisher Scientific, was freeze-

pump-thawed for 4 cycles and stored over 4 Å molecular sieves for three days before use. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. Pyridine d_5 was stored over 4 Å molecular sieves for three days before use, and benzene- d_6 was dried and stored over potassium for 2 days before use. Ce[N(SiMe_3)_2]_3,^[29] Ce[N(SiMe_3)_2]_3X, where X = F, Cl, and Br,^[14, 20, 21] Li[Ce(n^i PrN)_4],^[16] and Ce(n^i PrN)_4^[16] were prepared following published procedures.

Electrochemistry. Voltammetry experiments (CV and DPV) were performed using a CH Instruments 620D Electrochemical Analyzer/Workstation and the data were processed using CHI software v 9.24. All experiments were performed in an N₂ atmosphere drybox using electrochemical cells that consisted of a 4 mL vial, glassy carbon (3 mm diameter) working electrode, a platinum wire counter electrode, and a silver wire plated with AgCl as a quasi-reference electrode. The working electrode surfaces were polished prior to each set of experiments, and were periodically replaced to prevent the buildup of oxidized product on the electrode surfaces. Potentials were reported versus ferrocene (Fc). Except for Ce(N^{*i*}Pr₂)₄, electrochemistry was collected in solutions of 100 mM [*n*Bu₄N][B(3,5-(CF₃)₂-C₆H₃)₄] ([*n*Bu₄N][BAr^F₄]) in methylene chloride. Electrochemistry of Ce(N^{*i*}Pr₂)₄ was collected in a solution of 100 mM [*n*Bu₄N][BAr^F₄] in THF. All data were collected in a positive-feedback IR compensation mode. Scan rate dependences of 25–1000 mV/s were performed to determine electrochemical reversibility.

Computational Details. All calculations were performed with Gaussian '09 Revision D.01,^[30] with the B3LYP hybrid DFT method. A 28-electron small core effective core potential was applied to cerium with published segmented natural orbital basis set

incorporating quasi-relativistic effects,^[31] while the 6-31 G* basis set was applied to all other atoms. Geometry optimizations of all calculated complexes were based on their crystal structures. No other restrictions were placed on the systems besides the spin. Frequency calculations of all calculated complexes found no negative frequencies, except for Ce[N(SiMe₃)₂]₃Cl which had one small negative frequency at -6.75, for Ce[NⁱPr₂]₄⁻ which had one negative frequency at -45.60, and for ferrocene which had one negative frequency at -37.77 (Fe²⁺) and -30.77 (Fe³⁺), indicating that the optimized structures found were at an energy minimum. The geometry optimizations and frequency calculations were performed with the conductor-like polarizable continuum model (CPCM)^[10] with the Gaussian-defined solvent parameters for dichloromethane. The calculated electrochemical potentials were calculated in the same manner as described by Batista and coworkers^[11] and Gillmore and coworkers.^[8, 9]

X-Ray Crystallography. X-ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at a temperature of 143(1) or 100 (1) K. In all cases, rotation frames were integrated using SAINT,^[32] producing a listing of unaveraged F² and σ (F²) values which were then passed to the SHELXTL^[33] program package for further processing and structure solution on a Dell Pentium 4 computer. The intensity data were corrected for Lorentz and polarization effects and for absorption using TWINABS^[34] or SADABS.^[35] The structures were solved by direct methods (SHELXS-97).^[36] Refinement was by full-matrix least squares based on F² using SHELXL-97.^[36] All reflections were used during refinements. The weighting scheme used was w=1/[σ^2 (F_o²)+ (0.0907P)^2 + 0.3133P] where P = (F_o² +

 $2F_c^2$)/3. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model.

Synthetic Details and Characterization

Walter Dorfner and Alan Dai designed, synthesized, and characterized Ce(O-DiNOx)₂, the model complex reported here. The synthetic details were included because the complex was included in the correlations provided in this chapter. We intend to publish this work in *Inorg. Chem.* where Walter Dorfner and Alan Dai also will be authors.

Compound bis(2-bromobenzyl) ether was synthesized according to literature procedures.^[37]

Synthesis of Bis(2-*tert*-butylhydroxylaminobenzyl) ether (ODiNOx). The synthesis of ODiNOx was accomplished by modifying a related procedure. A 100 mL Schlenk flask was charged in an inert atmosphere glovebox with bis(2-bromobenzyl) ether (3.65 g, 10.3 mmol, 1.00 equiv) and 20 mL of Et₂O. The flask was cooled to -20 °C under inert atmosphere on a Schlenk line. A 1.6 M solution of ^{*n*}BuLi in hexanes (14.1 mL, 22.6 mmol, 2.2 equiv) was added dropwise to the solution using a syringe and the resulting colorless solution was stirred for 2 h. A 50 mL Schlenk flask was charged in a glovebox with 2-methyl-2-nitrosopropane (2.25 g, 25.8 mmol, 2.50 equiv) and 10 mL of Et₂O. The blue solution of 2-methyl-2-nitrosopropane was cooled to -20 °C on a Schlenk line and was added *via* cannula transfer into the solution of lithiated starting material. The resulting green solution was stirred overnight at RT. The solution was warmed slowly to RT and a degassed, saturated solution of NH₄Cl was added (20 mL) to quench the

reaction. The aqueous layer was removed and the organic volatiles were removed under reduced pressure. The resulting tan solid was brought into a dry box and used as isolated. Yield 1.92 g, 8.50 mmol, 82.5 %; ¹H NMR (300 MHz, benzene- d_6) δ 10.22 (s, 2H, OH), 7.99 (d, *J* = 7.6 Hz, 2H), 7.83 (d, *J* = 7.6 Hz, 2H), 7.40 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.29 (dd, *J* = 7.6, 7.6 Hz, 2H), 5.03 (s, 4H), 1.26 (s, 18 H); ¹³C NMR (75 MHz, pyridine- d_5) δ 149.7, 136.8, 128.4, 127.6, 127.5, 126.3, 69.4, 61.1, 26.6 ppm.



Figure 6.4.1. ¹H NMR spectrum of **O-DiNOx** in pyridine- d_5 .



Figure 6.4.2. ¹³C NMR spectrum of O-DiNOx in pyridine-*d*₅.

Synthesis of Ce(ODiNOx)₂. The synthesis of **Ce(ODiNOx)**₂ was accomplished by dissolving **ODiNOx** (0.100 g, 0.268 mmol, 1.0 equiv) in 3 mL of THF in a glovebox. This solution was then stirred with a suspension of PbO₂ (0.385 g, 1.61 mmol, 6.0 equiv) overnight. The solution was filtered through a pipette filled with celite to yield an orange filtrate. To this filtrate was then added **ODiNOx** (0.300 g, 0.805 mmol, 3.0 equiv). This solution was diluted to 10 mL of THF and added to a 100 mL Schlenk flask. A 100 mL Schlenk flask was also prepared with Ce(N(SiMe₃)₂)₃ (0.367 g, 0.537 mmol, 2.0 equiv). Both flasks were transferred from the glovebox to a Schlenk line where both were cooled to -78 °C under positive N₂ pressure. The cerium solution was then transferred to the flask containing **ODiNOx** *via* cannula. The solution turned dark brown and was warmed

to room temperature while stirring. Volatiles were removed *in vacuo* and the flask was transferred back into the glovebox. The complex was purified by layering 10 mL of pentane on top of a solution of **Ce(ODiNOx)**₂ in 5 mL of DCM. X-ray quality crystals were grown in the same manner. Crystalline yield: 46 %.





X-ray Structural Parameters.

Table 6.4.1. Crystallographic parameters for Ce(O-DiNOx)₂.

	Ce(O-DiNOx) ₂ (UPenn 4633)	
Empirical formula	$C_{88}H_{120}O_{12}N_8Ce_2$	
Formula weight	1762.16	
Temperature (K)	100(1)	
Wavelength (Å)	0.71073	
Crystal system	Triclinic	
Space group	PT	
Cell constants		
a (Å)	12.2290(5)	
b (Å)	13.6519(5)	

c (Å)	25.4521(10)
α (°)	83.478(2)
β (°)	84.513(2)
γ (°)	76.166(2)
V (Å ³)	4088.9(3)
Ζ	2
$\rho_{calc} (mg/cm^3)$	1.431
μ (Mo K α) (mm ⁻¹)	1.166
F(000)	1832
Crystal size (mm ³)	0.30 x 0.10 x 0.03
Theta range for data collection	1.54 to 27.56°
Index ranges	-15 \leq h \leq 15, -17 \leq k \leq 17, -31 \leq l \leq 33
Reflections collected	137767
Independent collections	18699 [R(int) = 0.0286]
Completeness to theta = 27.66° and 27.55°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max and min. transmission	0.7456 and 0.6790
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	18699 / 0 / 1015
Goodness-of-fit on F ²	1.189
Final R indices [I>2sigma(I)]	R1 = 0.0313, $wR2 = 0.0739$
R indices (all data)	R1 = 0.0358, wR2 = 0.0755
Largest diff. peak and hole $(e.Å^{-3})$	1.921 and -1.209

Electrochemistry



Figure 6.4.4. Cyclic voltammetry of $Ce(O-DiNOx)_2$ in 0.1 M [*n*NPr₄][BAr^F₄] in

dichloromethane. Scan rate was 50 mV/s.



Figure 6.4.5. Scan rate dependence of Ce(**O-DiNOx**)₂ (top) in 0.1 M [*n*NPr₄][BAr^F₄] in dichloromethane. Scan rate ranged from 50–1000 mV/s. At bottom, i_p vs. $v^{1/2}$ plot.



Figure 6.4.6. Cyclic voltammetry of Ce[N(SiMe₃)₂]₃F in 0.1 M [nNPr₄][BAr^F₄] in dichloromethane. Scan rate was 100 mV/s.



Figure 6.4.7. Scan rate dependence of Ce[N(SiMe₃)₂]₃F (top) in 0.1 M [*n*NPr₄][BAr^F₄] in dichloromethane. Scan rate ranged from 25–1000 mV/s. At bottom, i_p vs. $v^{1/2}$ plot.



Figure 6.4.8. Cyclic voltammetry of Ce[N(SiMe₃)₂]₃Cl in 0.1 M [nNPr₄][BAr^F₄] in dichloromethane. Scan rate was 100 mV/s.



Figure 6.4.9. Scan rate dependence of Ce[N(SiMe₃)₂]₃Cl (top) in 0.1 M [*n*NPr₄][BAr^F₄] in dichloromethane. Scan rate ranged from 25–1000 mV/s. At bottom, i_p vs. $v^{1/2}$ plot.



Figure 6.4.10. Cyclic voltammetry of Ce[N(SiMe₃)₂]₃Br in 0.1 M [nNPr₄][BAr^F₄] in dichloromethane. Scan rate was 100 mV/s.



Figure 6.4.11. Scan rate dependence of Ce[N(SiMe₃)₂]₃Br (top) in 0.1 M [*n*NPr₄][BAr^F₄] in dichloromethane. Scan rate ranged from 25–1000 mV/s. At bottom, i_p vs. $v^{1/2}$ plot.



Figure 6.4.12. Cyclic voltammetry of Li(THF)[Ce(N^{*i*}Pr₂)₄] in 0.1 M [nNPr₄][BAr^F₄] in dichloromethane. Scan rate was 100 mV/s.



Figure 6.4.13. Scan rate dependence of Li(THF)[Ce(N^{*i*}Pr₂)₄] (top) in 0.1 M $[nNPr_4][BAr^F_4]$ in dichloromethane. Scan rate ranged from 25–1000 mV/s. At bottom, i_p

vs. $v^{1/2}$ plot.



Figure 6.4.14. Cyclic voltammetry of $Ce(N^iPr_2)_4$ in 0.1 M [*n*NPr₄][BAr^F₄] in THF. Scan rate was 100 mV/s.



Figure 6.4.15. Scan rate dependence of $Ce(N^iPr_2)_4$ (top) in 0.1 M [$nNPr_4$][BAr^F₄] in

THF. Scan rate ranged from 25–1000 mV/s. At bottom, i_p vs. $v^{1/2}$ plot.

Computational Details

 $Ce^{IV} (CPCM = DCM) + e_{-} \xrightarrow{\Delta G_{DCM}} Ce^{III} (CPCM = DCM)$

Table 6.4.2. Computed Thermal Free Energies, G, and ΔG values for the series of 4-

G _{Ce} ^{III}		ΔG
-99417.2380	-99413.2366	-4.0014
-51204.2999	-51200.31404	-3.9859
-44677.8244	-44674.45087	-3.3735
-154185.2653	-154180.7421	-4.5232
-96736.8355	-96732.4658	-4.3697
-86931.3171	-86927.0988	-4.2183
-96613.2054	-96608.7901	-4.4154
-95279.7735	-95275.1229	-4.6506
-77755.3807	-77752.0522	-3.3285
-81958.0929	-81954.7793	-3.3136
-82430.8400	-82426.8266	-4.0134
	G_{Ce}^{III} -99417.2380 -51204.2999 -44677.8244 -154185.2653 -96736.8355 -86931.3171 -96613.2054 -95279.7735 -77755.3807 -81958.0929 -82430.8400	$\begin{array}{c} \mathbf{G_{Ce}^{III}} & \mathbf{G_{Ce}^{IV}} \\ \hline & -99417.2380 & -99413.2366 \\ \hline & -51204.2999 & -51200.31404 \\ \hline & -44677.8244 & -44674.45087 \\ \hline & -154185.2653 & -154180.7421 \\ \hline & -96736.8355 & -96732.4658 \\ \hline & -86931.3171 & -86927.0988 \\ \hline & -96613.2054 & -96608.7901 \\ \hline & -95279.7735 & -95275.1229 \\ \hline & -77755.3807 & -77752.0522 \\ \hline & -81958.0929 & -81954.7793 \\ \hline & -82430.8400 & -82426.8266 \\ \hline \end{array}$

coordinate and pseudo-4-coordinate cerium complexes. Units are in eV.
Calculated LUMO orbitals



Figure 6.4.16. LUMO orbitals of the following complexes: (a) $Ce^{IV}[N(SiHMe_2)_2]_4$, (b) $Li(THF)[Ce^{IV}(N^iPr_2)_4]^+$, and (c) $Ce[N(SiMe_3)_2]_3F$.

Computed Geometry Optimizations of Ce(IV) Complexes in CPCM =

Dichloromethane

Table 6.4.3. Optimized	coordinates of	$Ce[N(SiHMe_2)_2]_4.$
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Ce	0.003017558	-0.001223726	-0.003931926
Si	-2.292336548	2.441220192	0.022834990
Н	-1.583134718	2.203495763	1.327525390
Si	-1.792676573	1.299842504	-2.802066798
Н	-1.103792879	0.070473495	-3.309495767
Si	-2.286316305	-2.453995525	-0.029919972
Н	-1.586857401	-2.215562688	-1.339956108
Si	-1.791474981	-1.298253818	2.791421292
Н	-1.107803201	-0.063336698	3.291326276
Si	2.283394347	-0.106249579	-2.495365767

Н	1.607328474	1.227521955	-2.329344453
Si	1.811283562	-2.837154075	-1.127693434
Н	1.089707197	-3.253516355	0.116081264
Si	1.803223997	2.844303885	1.128789043
Н	1.098545161	3.262093196	-0.124267542
Si	2.256663366	0.117855247	2.509020466
Н	1.571517743	-1.210758345	2.340703656
Ν	-1.492026049	1.354465026	-1.081411158
Ν	-1.493364232	-1.359195601	1.070486701
Ν	1.496705976	-1.129663567	-1.322175710
Ν	1.483738503	1.137315708	1.323348631
С	-2.107444235	4.277729882	-0.394990869
Н	-1.060706273	4.550783834	-0.566183059
Н	-2.490111661	4.892801425	0.429369738
Н	-2.678551192	4.539169055	-1.294415405
С	-4.124327996	2.078467060	0.330836610
Н	-4.732888643	2.284479896	-0.557505086
Н	-4.498526438	2.711577817	1.145653033
Н	-4.285990857	1.033090385	0.615167134
С	-3.624890752	1.131207658	-3.255664867
Н	-4.092204725	0.278745404	-2.749881666
Н	-3.726001702	0.977575564	-4.337812016
Н	-4.194883183	2.031477909	-2.995438357
С	-1.073298919	2.777365063	-3.743271306
Н	-1.569414946	3.714362406	-3.463558325
Н	-1.204897686	2.639560079	-4.824351051
Н	-0.001405564	2.892064687	-3.545869925
С	-4.122914643	-2.109345992	-0.331512521
Н	-4.728517533	-2.323772582	0.556571501
Н	-4.490894501	-2.745220297	-1.146899171

Н	-4.295842804	-1.065275570	-0.613871999
С	-2.083556232	-4.287820022	0.391613443
Н	-1.032915540	-4.550765969	0.553060521
Н	-2.468593552	-4.907359885	-0.428236016
Н	-2.643816442	-4.552954710	1.296854520
С	-3.623880256	-1.136249262	3.247198455
Н	-4.096410573	-0.289776239	2.736383318
Н	-3.725917140	-0.976454656	4.328345003
Н	-4.189177753	-2.041417567	2.993395928
С	-1.064942151	-2.768163486	3.738953601
Н	-1.561213699	-3.707537618	3.466648503
Н	-1.192202348	-2.624144728	4.819726873
Н	0.006076086	-2.882396031	3.537548460
С	4.129450040	0.187014331	-2.194704029
Н	4.325394454	0.500795749	-1.163404469
Н	4.493677428	0.978260225	-2.862754184
Н	4.722393672	-0.713825887	-2.390254660
С	2.045571016	-0.641824877	-4.295478624
Н	2.594206546	-1.566189526	-4.513784597
Н	2.422551332	0.134087035	-4.973771259
Н	0.988516114	-0.811210583	-4.527497866
С	3.639997027	-3.258535665	-0.868628251
Н	4.235128272	-3.063631328	-1.768810605
Н	3.744020939	-4.324286690	-0.627643017
Н	4.077002823	-2.682763083	-0.045093014
С	1.145259727	-3.899659551	-2.546924427
Н	0.076742029	-3.721063192	-2.712930595
Н	1.277668479	-4.964824523	-2.316301346
Н	1.671372156	-3.694782695	-3.486915442
С	3.636022350	3.262131054	0.893314634

Η	4.219604397	3.062368447	1.800032301
Н	3.746936240	4.328466206	0.657050100
Н	4.081211661	2.688075600	0.072763234
С	1.119648458	3.910138896	2.537255533
Н	0.049747082	3.730619419	2.690863708
Н	1.253969022	4.975003951	2.306060184
Н	1.634227051	3.707462067	3.483773706
С	2.004155091	0.656891172	4.305300292
Н	2.554323330	1.579489877	4.526225284
Н	2.373870687	-0.119348844	4.987465123
Н	0.945969855	0.830256227	4.529480021
С	4.103657253	-0.186304898	2.224980773
Н	4.305901352	-0.499071496	1.194905554
Н	4.461037087	-0.978832445	2.895089967
Н	4.697941704	0.712235985	2.426540910

Table 6.4.4. Optimized coordinates of $Li(THF)[Ce(N^{i}Pr_{2})_{4}]^{+}$.

Ce	-0.832474650	-0.006126752	0.001311499
0	4.248784775	-0.166851959	-0.092499635
N	0.829417783	1.056769358	1.290035558
N	-2.126731603	1.637136611	-0.858808504
N	0.793971782	-1.095807727	-1.287593939
N	-2.215895910	-1.581846171	0.848556896
С	1.283844724	2.467416143	1.251719543
Н	0.558256317	3.097691711	1.789466531
С	1.329702695	2.987811584	-0.193263253
Н	2.154381950	2.544551374	-0.764812888
Н	1.494020121	4.071599225	-0.190695214
Н	0.397163601	2.796371512	-0.732170303

С	2.659533065	2.713026180	1.907455701
Н	2.655883012	2.501995151	2.979938491
Н	2.949837042	3.763439521	1.781249033
Н	3.432757246	2.089305976	1.441667325
С	0.570190909	0.495390717	2.634878453
Н	-0.206350263	-0.290905877	2.495122059
С	-0.051273199	1.470899499	3.656204837
Н	-0.916733654	1.997769736	3.239711565
Н	0.668703202	2.220616489	3.998805661
Н	-0.389129853	0.914652204	4.537357353
С	1.751844045	-0.268545303	3.272324854
Н	1.441779716	-0.727407814	4.219619394
Н	2.594481205	0.396725853	3.482095044
Н	2.103624543	-1.073052084	2.618505132
С	0.579204523	-0.515886283	-2.633273649
Н	-0.180368313	0.287620572	-2.501657938
С	-0.043899454	-1.468923366	-3.674479142
Н	-0.929540108	-1.978859566	-3.279682392
Н	0.665875385	-2.232547510	-4.007948663
Н	-0.350389802	-0.898407214	-4.558016835
С	1.793232294	0.220172162	-3.240673731
Η	1.515513549	0.687046941	-4.194080945
Η	2.623859544	-0.465378508	-3.432413757
Η	2.149701107	1.015655075	-2.578595743
С	1.207471715	-2.519259257	-1.250062228
Η	0.483385021	-3.120854873	-1.821564534
С	1.176920312	-3.053407597	0.189615511
Н	1.972126066	-2.621649662	0.809647292
Н	1.330161566	-4.138827167	0.185810731
Н	0.216851982	-2.856518878	0.676476673

С	2.599006327	-2.795105794	-1.857318993
Н	2.635860056	-2.579409840	-2.928665083
Н	2.859007715	-3.853222512	-1.727645468
Н	3.366046542	-2.188839252	-1.361434243
С	-2.670803651	2.407900954	0.277473192
Н	-2.165521951	2.029846318	1.187104614
С	-4.182858583	2.193360109	0.505485102
Н	-4.772592653	2.604320044	-0.321988124
Н	-4.506901885	2.699544379	1.422720705
Н	-4.420035032	1.129738477	0.597030123
С	-2.354724350	3.918098632	0.239819018
Н	-2.707418568	4.398798011	1.159902342
Н	-2.859361676	4.407217808	-0.600937198
Н	-1.280982013	4.100663089	0.147784363
С	-2.633053189	2.067069736	-2.179816780
Н	-3.484002808	2.744022621	-2.022840525
С	-3.173882344	0.885990159	-3.002201761
Н	-2.389159480	0.154448564	-3.228021997
Н	-3.577721178	1.238160090	-3.959228351
Н	-3.973930631	0.369088964	-2.463183159
С	-1.589861064	2.862685179	-2.988502404
Н	-1.244128717	3.739485255	-2.432993782
Н	-2.021636858	3.208131050	-3.936212670
Н	-0.714102578	2.247540805	-3.225585469
С	-2.837825617	-2.288189434	-0.289621172
Н	-2.363338472	-1.893959527	-1.208427361
С	-4.347866818	-2.008288875	-0.445648950
Н	-4.544022828	-0.933164613	-0.485862156
Н	-4.921529913	-2.429606513	0.387715426
Н	-4.726817795	-2.463412007	-1.368524895

С	-2.707655253	-2.021390521	2.172134174
Η	-3.576638095	-2.676042273	2.021323553
С	-1.670402857	-2.855699357	2.948136568
Η	-2.092304394	-3.201347474	3.900187030
Η	-0.772093769	-2.269636104	3.175028515
Н	-1.362221388	-3.734988979	2.374346062
С	-3.204494819	-0.839673381	3.020368828
Н	-2.396770758	-0.132694403	3.241954620
Н	-3.603288165	-1.194379864	3.978636641
Н	-3.997689552	-0.294269862	2.499744645
С	5.076268855	-0.779090778	0.933587933
Н	5.159960475	-1.851410258	0.719053476
Н	4.574307763	-0.644872377	1.894696153
С	6.428093212	-0.076381189	0.834848274
Н	6.417442515	0.857082058	1.409048516
Η	7.245763980	-0.699844140	1.206588158
С	6.525079019	0.217326494	-0.670357775
Н	6.845741911	-0.678038471	-1.214422590
Н	7.218311958	1.028792889	-0.907659978
С	5.080953725	0.573285474	-1.028576673
Η	4.879226806	1.642351705	-0.893807854
Η	4.795536429	0.281572576	-2.042322259
Li	2.268972071	-0.023793064	0.032225516
С	-2.574777105	-3.808666787	-0.318847014
Η	-1.504390318	-4.029423687	-0.288671672
Η	-2.989023120	-4.245965954	-1.235028303
Н	-3.052233522	-4.310677346	0.530237863

Table 6.4.5. O	ptimized	coordinates	of Ce	$(N'Pr_2)_{4.}$
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Ce	-0.000464000	-0.003068000	-0.000875000
N	0.585010000	-1.739447000	1.371048000
С	-0.067472000	-2.976040000	1.838238000
Н	0.433152000	-3.318252000	2.756357000
С	0.042476000	-4.134517000	0.825346000
Н	-0.493240000	-3.897856000	-0.099909000
Н	1.086110000	-4.337753000	0.567339000
С	-1.539478000	-2.736970000	2.217535000
Н	-1.620893000	-1.987950000	3.012038000
Н	-2.121476000	-2.382399000	1.357988000
С	1.900943000	-1.477580000	1.979365000
Н	2.289535000	-0.562970000	1.493930000
С	2.956336000	-2.575192000	1.721638000
Н	2.692395000	-3.505493000	2.237960000
Н	3.050841000	-2.794638000	0.654047000
С	1.845137000	-1.163721000	3.491536000
Η	1.504156000	-2.031041000	4.069154000
Н	1.164472000	-0.332162000	3.693746000
N	-0.525333000	1.706913000	1.429863000
С	0.145398000	2.932361000	1.901028000
Η	-0.316836000	3.250429000	2.847545000
С	-0.006583000	4.116634000	0.923815000
Н	0.490908000	3.905186000	-0.028393000
Н	-1.059928000	4.324898000	0.714245000
С	1.631779000	2.685932000	2.212622000
Н	1.746316000	1.917060000	2.983733000
Η	2.176981000	2.354009000	1.320867000
С	-1.818425000	1.433516000	2.080874000

Н	-2.228866000	0.533537000	1.586187000
С	-2.880391000	2.538814000	1.891660000
Н	-2.594875000	3.455524000	2.420699000
Н	-3.015676000	2.785204000	0.834424000
С	-1.706299000	1.079455000	3.580902000
Н	-1.340549000	1.930346000	4.167853000
Н	-1.020886000	0.241388000	3.734351000
Ν	-1.754037000	-0.537189000	-1.373271000
С	-2.991742000	0.131999000	-1.812295000
С	-4.145824000	-0.009854000	-0.798171000
Н	-4.349592000	-1.061059000	-0.573751000
С	-2.751004000	1.615325000	-2.142110000
Н	-2.006804000	1.722192000	-2.938091000
Н	-2.388906000	2.165062000	-1.264965000
С	-1.501786000	-1.836476000	-2.020225000
Н	-0.586670000	-2.243901000	-1.551451000
С	-2.601355000	-2.895495000	-1.785829000
Н	-3.533855000	-2.614449000	-2.288950000
Н	-2.814611000	-3.019493000	-0.719987000
С	-1.195960000	-1.738828000	-3.531966000
Н	-2.064446000	-1.375793000	-4.094226000
Н	-0.361422000	-1.057417000	-3.718920000
Ν	1.697421000	0.573520000	-1.424907000
С	2.916635000	-0.084764000	-1.928395000
Н	3.227975000	0.407477000	-2.861852000
С	4.109378000	0.031963000	-0.956803000
Н	3.903552000	-0.494190000	-0.018835000
Н	4.323888000	1.077436000	-0.716206000
С	2.664174000	-1.559458000	-2.287910000
Н	1.887141000	-1.646570000	-3.054388000

Н	2.341982000	-2.136064000	-1.412250000
С	1.417608000	1.884270000	-2.036174000
Н	0.519421000	2.278413000	-1.525368000
С	2.522918000	2.941586000	-1.823160000
Н	3.436108000	2.673524000	-2.367209000
Н	2.776723000	3.045237000	-0.764068000
С	1.054712000	1.815678000	-3.536950000
Н	1.902619000	1.470113000	-4.140208000
Н	0.217302000	1.132993000	-3.705951000
Н	-3.339112000	-0.336656000	-2.745184000
Н	-3.903956000	0.494719000	0.143074000
Н	-3.847928000	2.215171000	2.295112000
Н	-2.687278000	0.800381000	3.985481000
Н	0.443677000	5.026539000	1.342469000
Н	2.112271000	3.605220000	2.570888000
Н	2.840389000	-0.892398000	3.865445000
Н	3.938354000	-2.259643000	2.095400000
Н	-0.391685000	-5.054956000	1.237939000
Н	-2.006027000	-3.664837000	2.572080000
Н	5.014058000	-0.408695000	-1.396545000
Н	3.578917000	-2.027917000	-2.672901000
Н	2.194923000	3.920375000	-2.194687000
Н	0.770676000	2.807617000	-3.910236000
Н	-0.932897000	-2.724225000	-3.936471000
Н	-2.290913000	-3.867337000	-2.189089000
Н	-5.067448000	0.438828000	-1.192095000
Н	-3.679660000	2.096752000	-2.473987000

Table 6.4.6.	Optimized	coordinates	of Ce	N((SiMe ₃))2	₃ Br
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Ce	0.003045000	0.000871000	0.006980000
Br	-0.005716000	-0.009947000	-2.803480000
Si	-2.463581000	-2.439387000	-0.812699000
Si	-0.600925000	-3.113212000	1.495154000
Ν	-1.123787000	-1.954386000	0.257542000
С	-3.482897000	-0.957241000	-1.418355000
Н	-3.965852000	-0.434508000	-0.584478000
Н	-4.278890000	-1.335272000	-2.073676000
Н	-2.902842000	-0.228485000	-1.992762000
С	-1.825704000	-3.395495000	-2.321097000
Н	-1.138085000	-2.783292000	-2.913425000
Н	-2.664566000	-3.685619000	-2.967476000
Н	-1.300102000	-4.311266000	-2.026662000
С	-3.749241000	-3.554698000	0.039480000
Н	-4.221335000	-3.061928000	0.897009000
Н	-3.349273000	-4.515925000	0.378893000
Н	-4.539992000	-3.770609000	-0.691432000
С	-1.862437000	-3.359265000	2.894752000
Н	-2.768016000	-3.884772000	2.579084000
Н	-2.164738000	-2.400582000	3.330753000
Н	-1.394004000	-3.953210000	3.690934000
С	-0.186134000	-4.814475000	0.758903000
Н	0.583915000	-4.738897000	-0.017662000
Н	-1.058068000	-5.308012000	0.315494000
Н	0.199358000	-5.473405000	1.547923000
С	0.965880000	-2.506022000	2.378543000
Н	1.820904000	-2.348057000	1.715819000
Н	1.248311000	-3.277293000	3.107467000

Н	0.803375000	-1.580601000	2.946401000
Si	-0.903930000	3.336663000	-0.836822000
Si	-2.371072000	2.085855000	1.520032000
Ν	-1.131763000	1.949113000	0.257424000
С	0.877473000	3.462517000	-1.479045000
Н	1.587270000	3.647522000	-0.663868000
Н	0.933974000	4.319272000	-2.163571000
Н	1.209773000	2.578264000	-2.031563000
С	-2.079255000	3.239833000	-2.322372000
Н	-1.900712000	2.332884000	-2.909672000
Н	-1.927874000	4.105458000	-2.980650000
Н	-3.129341000	3.241235000	-2.007895000
С	-1.211735000	5.020848000	-0.005462000
Н	-0.535224000	5.196676000	0.838575000
Н	-2.238580000	5.161265000	0.347661000
Н	-1.014925000	5.801805000	-0.752180000
С	-1.930051000	3.320492000	2.895308000
Н	-1.923044000	4.361697000	2.562129000
Н	-0.947728000	3.099766000	3.328488000
Н	-2.673838000	3.233458000	3.698668000
С	-4.066768000	2.565171000	0.810262000
Н	-4.397635000	1.854241000	0.044103000
Н	-4.069595000	3.563997000	0.359860000
Н	-4.816256000	2.563793000	1.612489000
С	-2.611086000	0.438719000	2.434152000
Н	-2.908163000	-0.392662000	1.789644000
Н	-3.409784000	0.589157000	3.172655000
Н	-1.718867000	0.128420000	2.993627000
Si	3.352290000	-0.878764000	-0.838369000
Si	2.991117000	1.012123000	1.520430000

Ν	2.258979000	0.003218000	0.258407000
С	2.590121000	-2.500177000	-1.469549000
Н	2.427374000	-3.211759000	-0.651477000
Η	3.299588000	-2.961456000	-2.169300000
Η	1.644335000	-2.366124000	-2.002311000
С	3.828076000	0.191263000	-2.330113000
Η	2.941303000	0.490574000	-2.898263000
Η	4.489765000	-0.369255000	-3.003607000
Η	4.358632000	1.099754000	-2.022542000
С	4.976526000	-1.429356000	-0.013694000
Η	4.803577000	-2.103867000	0.832545000
Η	5.601814000	-0.600774000	0.334884000
Η	5.558325000	-1.984091000	-0.762123000
С	3.840922000	0.020103000	2.900408000
Η	4.749471000	-0.493212000	2.574027000
Η	3.164951000	-0.730760000	3.324798000
Η	4.120860000	0.709313000	3.708377000
С	4.249303000	2.247253000	0.813038000
Η	3.797019000	2.885173000	0.044504000
Η	5.120678000	1.755848000	0.365776000
Η	4.616022000	2.900634000	1.615440000
С	1.672130000	2.038134000	2.424976000
Н	1.103316000	2.710396000	1.775587000
Η	2.193602000	2.656069000	3.168002000
Η	0.953937000	1.419514000	2.979340000

 Table 6.4.7. Optimized coordinates of Ce[N(SiMe₃)₂]₃Cl.

Ce	-0.003948030	0.001855376	-0.137555634
Cl	0.005378599	-0.005121090	-2.795693186

Si	-0.188725576	-3.158680701	1.370339063
Si	1.720090801	-2.987457967	-0.998420401
Si	-2.652025331	1.732805581	1.378767618
Si	-3.444129196	0.012439161	-1.009110025
Si	2.834071237	1.417290235	1.370023525
Si	1.730618830	2.983397172	-0.996329305
Ν	0.586032349	-2.177998607	0.111739659
Ν	-2.184738462	0.581726709	0.113169637
Ν	1.592492440	1.597322817	0.114543402
С	-1.522558274	-2.161331143	2.283169706
С	0.998406156	-3.726144596	2.740833883
С	-1.052857722	-4.692878716	0.656634045
С	2.688193395	-4.412468104	-0.188624723
С	0.806867069	-3.720382390	-2.490599065
С	3.074719719	-1.816500054	-1.629482512
С	-1.126530054	2.375981929	2.309664738
С	-3.751189814	0.978450776	2.732699016
С	-3.537974474	3.257719636	0.671819167
С	-5.168244676	-0.117769739	-0.214678185
С	-3.610589261	1.177226600	-2.497289352
С	-3.097736654	-1.741965491	-1.646821729
С	2.661154924	-0.244394916	2.272030678
С	2.719505289	2.719654040	2.748625886
С	4.593271248	1.460346001	0.654123327
С	2.472263862	4.535702314	-0.182727526
С	2.829419721	2.559097594	-2.482804464
С	0.042775738	3.567181925	-1.640915084
Н	-1.111123434	-1.314187663	2.847747087
Н	-1.988396568	-2.831867981	3.017616371
Н	-2.315857900	-1.778900624	1.633916758

Н	1.741457026	-4.452221195	2.400314002
Η	0.413924964	-4.199052465	3.541409559
Η	1.534548743	-2.876808634	3.179363535
Η	-1.798851003	-4.418168650	-0.098584635
Η	-1.573438492	-5.230260546	1.460046301
Η	-0.352850207	-5.395792703	0.191373727
Η	3.303577666	-4.069370484	0.650977066
Η	3.367072194	-4.828119847	-0.945268844
Η	2.056919576	-5.233280677	0.167460674
Н	0.076805012	-4.478111092	-2.183605795
Η	1.519443754	-4.201884140	-3.173202102
Η	0.274638098	-2.943938864	-3.050180388
Η	2.691029218	-0.956690775	-2.187588531
Η	3.728426678	-2.383532087	-2.305654410
Η	3.697894797	-1.443490388	-0.808327678
Η	-0.605323077	1.588568284	2.869865792
Н	-1.476643819	3.108125361	3.049155076
Н	-0.392200982	2.875424799	1.670480334
Η	-4.755643106	0.721053072	2.385074263
Η	-3.858011338	1.706659494	3.547886032
Η	-3.298804619	0.073624132	3.154210032
Н	-2.920131735	3.770232877	-0.075017640
Η	-3.745925051	3.971424230	1.479730054
Н	-4.494357119	3.010351043	0.197703497
Н	-5.184169123	-0.823342013	0.623874470
Н	-5.860595222	-0.498002447	-0.977707647
Η	-5.567437376	0.838872979	0.138810610
Н	-3.903384133	2.187594485	-2.188390648
Η	-4.378976688	0.804745365	-3.187570180
Н	-2.668005854	1.251373879	-3.049492236

Η	-2.155222125	-1.834658570	-2.195163852
Н	-3.907703982	-2.022868365	-2.333054319
Η	-3.093751621	-2.473138766	-0.829321669
Η	1.721731145	-0.331885667	2.832947153
Н	3.473879658	-0.302514525	3.008291686
Н	2.743356752	-1.116554830	1.617187576
Н	2.961840168	3.732101999	2.412659501
Η	3.427548528	2.455326216	3.545515371
Н	1.716403134	2.743073145	3.190307328
Н	4.735819285	0.684505737	-0.107229017
Η	5.320593229	1.278000734	1.456103619
Н	4.842466911	2.424528412	0.196821461
Η	1.863370643	4.892028673	0.656347432
Н	2.490347171	5.333529496	-0.937324999
Н	3.498818400	4.403862094	0.175592664
Н	3.849889393	2.305641996	-2.172503344
Н	2.892228552	3.416515383	-3.165811089
Η	2.424555792	1.709808162	-3.043358288
Н	-0.500206156	2.807876381	-2.212336431
Н	0.209779019	4.423653578	-2.307579499
Н	-0.602297353	3.909969506	-0.823407256

Table 6.4.8. Optimized coordinates of Ce[N(SiMe₃)₂]₃F.

Ce	0.004907391	-0.002109651	-0.045151688
Si	2.944557800	-1.600446238	-1.176191227
Si	3.209041029	0.130017800	1.337183330
Si	-2.842967643	-1.750336329	-1.192928067
Si	-1.510308609	-2.829557260	1.342337014
Si	-0.085827193	3.334878399	-1.185412691

Si	-1.720130077	2.715119404	1.328228280
F	0.003602808	0.003183518	-2.118783995
Ν	2.209038922	-0.597293426	0.082781750
Ν	-1.619440431	-1.609277439	0.077133192
Ν	-0.587918411	2.203649336	0.079616283
С	1.785058183	-2.998611378	-1.728421612
Н	1.547330278	-3.674145681	-0.898014686
Н	2.285550210	-3.592988508	-2.504320642
Н	0.843043102	-2.634874834	-2.151496918
С	3.377314562	-0.568954492	-2.709153497
Н	2.471848801	-0.124712898	-3.137721551
Н	3.844847922	-1.195055904	-3.480294402
Н	4.072950743	0.244073411	-2.470741853
С	4.532884393	-2.485929631	-0.614983022
Н	5.330928802	-1.806042136	-0.297863238
Н	4.918676319	-3.069103333	-1.461971787
Н	4.342144237	-3.187768204	0.205098558
С	4.667391592	1.123496958	0.630436977
Н	5.361999074	0.503694683	0.052302237
Н	5.238773700	1.584670258	1.446819098
Н	4.317559540	1.928797202	-0.026467616
С	3.889675421	-1.131249056	2.584698348
Н	3.080719345	-1.726869080	3.024551789
Н	4.396634158	-0.603399253	3.403604845
Н	4.611513480	-1.823334918	2.139544555
С	2.184279295	1.356720871	2.368498823
Н	1.729961354	2.156512380	1.773057359
Н	2.855542757	1.832290433	3.095465271
Н	1.388176199	0.870464369	2.948863038
С	-2.137402589	-2.624473929	-2.721838854

Н	-1.293864325	-2.056555153	-3.129603210
Н	-2.899508528	-2.712217915	-3.507194403
Н	-1.782804095	-3.634805121	-2.485101067
С	-3.488431799	-0.050175847	-1.737600171
Н	-3.962547070	0.481366674	-0.903669373
Н	-4.250524985	-0.189357722	-2.515854298
Н	-2.710882393	0.597749863	-2.153040126
С	-4.400368318	-2.703848701	-0.656870169
Н	-4.204004220	-3.733242974	-0.337981034
Н	-5.083714553	-2.753281651	-1.515243140
Н	-4.931782262	-2.194819707	0.155535287
С	-1.348785467	-4.591847094	0.648808069
Н	-2.215801410	-4.892393387	0.049722834
Н	-1.250054724	-5.312595191	1.471146604
Н	-0.459741595	-4.686806719	0.013949758
С	0.036624430	-2.532613066	2.409822259
Н	0.973855702	-2.530301969	1.841501499
Н	0.102705929	-3.348775065	3.141288021
Н	-0.015572166	-1.597497583	2.983605287
С	-2.969901718	-2.792755639	2.557547612
Н	-3.107143144	-1.790120970	2.980187125
Н	-2.770674850	-3.479724706	3.390741895
Н	-3.915815359	-3.094277554	2.097440837
С	-0.133650905	5.159574890	-0.646526553
Н	-1.126034929	5.505092729	-0.337791338
Н	0.176039352	5.777658330	-1.499962157
Н	0.564297833	5.362330921	0.173918697
С	-1.182318216	3.166269510	-2.725100301
Н	-1.109570844	2.152392788	-3.133717748
Н	-0.869284790	3.870419343	-3.506999385

Η	-2.236668404	3.365088483	-2.498014415
С	1.711801144	3.041917455	-1.718240523
Н	2.407467213	3.190520285	-0.883492348
Η	1.974313389	3.767531898	-2.499438839
Н	1.883596019	2.042660409	-2.130414290
С	-0.982572559	3.966523478	2.553452474
Н	-0.051519652	3.588006966	2.991637277
Н	-1.690879360	4.137507791	3.374982849
Н	-0.766749888	4.936481885	2.094855817
С	-2.249971634	1.227830111	2.392988855
Н	-2.702157975	0.411642476	1.818106086
Н	-3.002571947	1.577126016	3.111893981
Η	-1.422353598	0.809524079	2.982099206
С	-3.318349019	3.449784799	0.607990120
Η	-3.138881926	4.351557961	0.011613182
Η	-4.005008645	3.722778605	1.420067754
Н	-3.833947278	2.725870381	-0.034141601

Table 6.4.9. O	ptimized coordinate	es of Ce(OAr) ₄ .	OAr = 2,6-di	phenylphenol
-----------------------	---------------------	------------------------------	--------------	--------------

4782000
4868000
6398000
)870000
7879000
7832000
2984000
227000
1443000
2727000

Н	5.211030000	2.176932000	-3.158096000
С	3.430355000	1.716634000	-2.054894000
С	1.138743000	4.305932000	-0.363403000
С	0.419341000	5.394436000	-0.888325000
Н	0.588019000	5.695740000	-1.918810000
С	-0.501850000	6.093041000	-0.104784000
Н	-1.045606000	6.931020000	-0.532881000
С	-0.722729000	5.718371000	1.222688000
Н	-1.435567000	6.264137000	1.834721000
С	-0.021133000	4.633481000	1.755985000
Н	-0.182952000	4.334067000	2.788156000
С	0.896162000	3.932464000	0.970583000
Н	1.457317000	3.110180000	1.402409000
С	3.639864000	0.255979000	-2.262586000
С	4.864865000	-0.328603000	-1.897413000
Н	5.610775000	0.278327000	-1.392073000
С	5.133221000	-1.670962000	-2.171717000
Н	6.086496000	-2.101113000	-1.876022000
С	4.182334000	-2.455375000	-2.828590000
Н	4.391362000	-3.497921000	-3.052343000
С	2.961731000	-1.885314000	-3.201149000
Н	2.221966000	-2.478575000	-3.732259000
С	2.688618000	-0.545318000	-2.914953000
Н	1.747002000	-0.110144000	-3.231958000
С	-2.332603000	-1.290640000	-2.258076000
С	-2.194661000	-1.130655000	-3.667174000
С	-3.154755000	-1.704294000	-4.515053000
Н	-3.044147000	-1.571766000	-5.587905000
С	-4.251619000	-2.398712000	-4.013057000
Н	-4.988011000	-2.826412000	-4.687107000

С	-4.397019000	-2.527569000	-2.634199000
Н	-5.247321000	-3.068540000	-2.227873000
С	-3.454946000	-1.995485000	-1.741846000
С	-1.095166000	-0.346863000	-4.297383000
С	-0.829104000	0.980862000	-3.917445000
Н	-1.392236000	1.423016000	-3.102016000
С	0.113606000	1.748322000	-4.604525000
Н	0.293274000	2.776161000	-4.300421000
С	0.817757000	1.202877000	-5.681701000
Н	1.550401000	1.800943000	-6.216647000
С	0.573885000	-0.118930000	-6.062397000
Н	1.119415000	-0.556622000	-6.894269000
С	-0.372569000	-0.884393000	-5.377721000
Н	-0.558685000	-1.910497000	-5.683658000
С	-3.689996000	-2.198580000	-0.284605000
С	-4.919110000	-1.814347000	0.278919000
Н	-5.647711000	-1.300358000	-0.341610000
С	-5.213296000	-2.080169000	1.617495000
Н	-6.169191000	-1.769483000	2.030984000
С	-4.284524000	-2.747441000	2.419327000
Н	-4.513392000	-2.964478000	3.459108000
С	-3.060316000	-3.139238000	1.870203000
Н	-2.337960000	-3.678734000	2.477148000
С	-2.761390000	-2.861591000	0.533925000
Н	-1.817502000	-3.192925000	0.115330000
0	1.369254000	-1.451423000	0.791175000
0	-1.363970000	0.817598000	1.445823000
С	2.268758000	-2.303595000	1.305491000
С	2.106477000	-3.709380000	1.134823000
С	3.046870000	-4.578410000	1.709313000

Н	2.917717000	-5.648055000	1.568113000
С	4.147533000	-4.101646000	2.414909000
Н	4.868203000	-4.792138000	2.843159000
С	4.317504000	-2.726799000	2.553914000
Н	5.171578000	-2.340147000	3.103278000
С	3.396462000	-1.813138000	2.021341000
С	1.002778000	-4.316305000	0.338426000
С	0.257842000	-5.387207000	0.864378000
Н	0.431330000	-5.702401000	1.889893000
С	-0.695058000	-6.050761000	0.088341000
Н	-1.257906000	-6.875661000	0.517220000
С	-0.923366000	-5.657836000	-1.232658000
Н	-1.661044000	-6.176332000	-1.838966000
С	-0.197055000	-4.589746000	-1.766573000
Н	-0.364519000	-4.276274000	-2.793615000
С	0.752187000	-3.923719000	-0.988432000
Н	1.331559000	-3.114862000	-1.421359000
С	3.661298000	-0.362212000	2.236274000
С	4.906116000	0.175592000	1.866075000
Н	5.624629000	-0.458055000	1.353943000
С	5.228494000	1.505416000	2.143130000
Н	6.196158000	1.898886000	1.843136000
С	4.312810000	2.323971000	2.808171000
Н	4.563666000	3.356761000	3.034109000
С	3.073070000	1.800602000	3.186168000
Н	2.360385000	2.420278000	3.724063000
С	2.746112000	0.473348000	2.897270000
Н	1.790425000	0.074405000	3.218248000
С	-2.268428000	1.342207000	2.286257000
С	-2.123686000	1.168133000	3.692990000

С	-3.064818000	1.754791000	4.552801000
Н	-2.949053000	1.610899000	5.623637000
С	-4.150535000	2.475980000	4.064991000
Н	-4.872506000	2.913704000	4.748143000
С	-4.303567000	2.619249000	2.688411000
Н	-5.145137000	3.181706000	2.293202000
С	-3.379929000	2.075257000	1.783908000
С	-1.037022000	0.355324000	4.307957000
С	-0.806360000	-0.975782000	3.917797000
Н	-1.387669000	-1.399203000	3.105454000
С	0.125972000	-1.768967000	4.589720000
Н	0.278614000	-2.798703000	4.277427000
С	0.854601000	-1.246272000	5.661826000
Н	1.579283000	-1.864189000	6.184909000
С	0.645423000	0.078369000	6.052959000
Н	1.210213000	0.498393000	6.881070000
С	-0.290701000	0.869577000	5.383415000
Н	-0.449380000	1.897927000	5.697245000
С	-3.623462000	2.299804000	0.330390000
С	-4.864879000	1.947722000	-0.227103000
Н	-5.598188000	1.440031000	0.392970000
С	-5.165005000	2.236991000	-1.559643000
Н	-6.130471000	1.951006000	-1.968708000
С	-4.230256000	2.896594000	-2.360940000
Н	-4.463988000	3.132241000	-3.395574000
С	-2.993607000	3.256453000	-1.818050000
Н	-2.265818000	3.789631000	-2.424115000
С	-2.688647000	2.954742000	-0.488453000
Н	-1.735074000	3.262377000	-0.074013000

Table 6.4.10.	Optimized	coordinates	of Li(THF);	Ce(MBP)	$(THF)_{2}^{\dagger}$
	- p		===(===)2	-L (-()2J ·

Ce	-0.035558581	-0.940362280	-0.049866270
0	0.630283574	1.029363215	-1.075843171
0	1.877157594	-1.303180723	0.957611358
0	-1.366988746	-2.799594773	1.347416327
0	1.915690149	4.270650919	-0.517290192
С	1.802951285	1.128937313	-1.774476162
С	1.832719622	1.255504441	-3.199265744
С	3.095044946	1.280189369	-3.811388785
Н	3.155759997	1.361412822	-4.890138288
С	4.304587781	1.215939334	-3.107967592
С	4.239328891	1.168454212	-1.716788571
Н	5.159409924	1.158378931	-1.135900217
С	3.017116330	1.138237063	-1.040774621
С	3.024598071	1.214809715	0.483095330
Н	3.491435668	2.167104662	0.763175655
Н	2.000393625	1.250607598	0.858957833
С	3.774118387	0.102423397	1.179604273
С	3.148793902	-1.151993005	1.395797516
С	3.867360905	-2.183479962	2.075250848
С	5.181375109	-1.899958191	2.475267969
Н	5.747687054	-2.667207230	2.990385095
С	5.813903374	-0.670668535	2.264628462
С	5.078636166	0.326005851	1.622733999
Н	5.524290857	1.306866929	1.465429907
С	0.560995851	1.385097980	-4.075303492
С	-0.225072453	0.057031682	-4.090048926
Н	0.404026941	-0.769607450	-4.440904729
Н	-1.083639550	0.134319330	-4.769032968

Н	-0.612544552	-0.192743975	-3.101270034
С	-0.364935830	2.509848771	-3.554273795
Н	-0.777964059	2.259950345	-2.575769408
Н	-1.204618095	2.651358557	-4.245744070
Н	0.171461022	3.463710966	-3.480656238
С	0.899580442	1.731322160	-5.543077178
Н	1.469973772	2.663411929	-5.627763318
Н	-0.034066865	1.861726526	-6.101318694
Н	1.465117491	0.935715062	-6.040356522
С	5.628597884	1.200554617	-3.837394021
Н	5.579066205	1.768684058	-4.772984440
Н	5.931816977	0.177175540	-4.098076788
Н	6.428988792	1.626861396	-3.222924830
С	3.246665928	-3.554769290	2.412890259
С	2.814196498	-4.277666841	1.117425888
Н	2.126836210	-3.672101274	0.526201252
Н	2.328639531	-5.232798242	1.356437291
Н	3.691413539	-4.498853194	0.496758492
С	2.042729641	-3.342706973	3.359273852
Н	2.372482427	-2.874264223	4.294410041
Н	1.579746475	-4.304390943	3.614881274
Н	1.285686335	-2.698407150	2.910068250
С	4.229357477	-4.496916548	3.141131855
Н	5.116736023	-4.717004631	2.536912880
Н	3.723916442	-5.448420333	3.342642308
Н	4.559534436	-4.090580088	4.103643744
С	7.241100764	-0.439045349	2.704951327
Н	7.506316358	-1.074548909	3.556875505
Н	7.406603330	0.604458856	2.995737617
Н	7.953366197	-0.664761271	1.899178834

Н	-2.017661589	-5.657206582	2.890116066
С	-3.197128571	-3.828472971	2.507660300
Н	-3.784026501	-3.623130105	3.407078661
С	-2.722325348	-2.534517136	1.830829872
Н	-3.340962303	-2.242305480	0.980238469
Н	-2.655998547	-1.698927887	2.528582773
С	2.315256718	5.107698586	0.600017710
Н	2.913918464	4.498661934	1.287999411
Н	1.412428662	5.442980708	1.115667500
С	3.134153722	6.249800855	-0.004387635
Н	3.882387322	6.634691842	0.693988619
Н	2.479355281	7.078757175	-0.296378106
Li	0.377460227	3.015899032	-0.326935713
С	3.744952587	5.587268453	-1.248551189
Н	4.055204382	6.305697372	-2.012403249
Н	4.614386082	4.979362446	-0.973158839
С	2.602317733	4.693458905	-1.725400772
Н	1.894500902	5.250167035	-2.353127780
Н	2.928829658	3.799172596	-2.257815549
0	-0.941490455	0.278768660	1.448008159
0	-1.924751372	-1.103000177	-1.131411185
0	1.096582389	-2.817357179	-1.689903864
0	-1.019110465	4.308123241	0.257333775
С	-1.966184676	0.916731521	2.057418908
С	-1.989068840	1.104735323	3.474116480
С	-3.132091777	1.703384295	4.020567768
Н	-3.189325054	1.848051692	5.093247232
С	-4.218658545	2.142999548	3.253787955
С	-4.125962921	2.013852100	1.868614710
Н	-4.931025136	2.395441565	1.244081626

С	-3.019334483	1.420776222	1.253494953
С	-2.938288643	1.414469186	-0.268667967
Н	-3.268603542	2.402464197	-0.610757532
Н	-1.898680519	1.315693209	-0.580750874
С	-3.780950642	0.376995206	-0.989408137
С	-3.223425130	-0.855670584	-1.419170904
С	-4.034664859	-1.776910171	-2.156324888
С	-5.369256898	-1.418438015	-2.388010578
Н	-6.006471874	-2.098005009	-2.941550946
С	-5.939260913	-0.214650431	-1.959465162
С	-5.115698878	0.675933711	-1.274027152
Н	-5.515766869	1.638520213	-0.960995928
С	-0.813648163	0.696187912	4.391906631
С	-0.666248227	-0.842050117	4.423712740
Н	-1.564410755	-1.304955811	4.850731728
Н	0.187012447	-1.127253270	5.051473763
Н	-0.509258242	-1.258204303	3.428015326
С	0.502125724	1.348584306	3.902032567
Н	0.750211406	1.045599781	2.884084583
Н	1.331577332	1.059390855	4.559202838
Н	0.421420475	2.442569408	3.927868233
С	-1.021402770	1.157921314	5.851228362
Н	-1.137141973	2.245064028	5.928343563
Н	-0.142440808	0.875344436	6.441594005
Н	-1.892516117	0.684745269	6.317787432
С	-5.441630142	2.740681597	3.910929031
Н	-5.177972102	3.310495399	4.808990153
Н	-6.150949752	1.961329654	4.221903270
Н	-5.976277708	3.410079900	3.228451795
С	-3.500672865	-3.115130181	-2.713765261

С	-3.021703302	-4.017395303	-1.555012688
Н	-2.251461188	-3.525982545	-0.960873688
Н	-2.615875730	-4.958771434	-1.946665523
Н	-3.859957679	-4.267029971	-0.892665439
С	-2.344276952	-2.848173901	-3.704350531
Н	-2.688823989	-2.222704617	-4.536527720
Н	-1.983373469	-3.794561557	-4.127388276
Н	-1.508006747	-2.341094316	-3.222787476
С	-4.574957397	-3.910936106	-3.486940874
Н	-5.431591174	-4.175409513	-2.856868129
Н	-4.131058951	-4.846364878	-3.846317966
Н	-4.945544627	-3.365761491	-4.362277997
С	-7.393089784	0.099244531	-2.228132505
Н	-7.732823377	-0.345171749	-3.170265158
Н	-7.565891821	1.179771027	-2.280771332
Н	-8.043218642	-0.293650047	-1.434133063
С	0.687526847	-4.195844539	-1.933943049
Н	-0.206488148	-4.173275892	-2.560056701
Н	0.441737122	-4.657914938	-0.975151668
С	1.865169692	-4.867537493	-2.644696845
Н	2.548502317	-5.320133374	-1.918247758
Н	1.531577286	-5.649207432	-3.332858895
С	2.544913162	-3.685988636	-3.352427293
Н	2.015476732	-3.431941874	-4.277797998
Н	3.594071570	-3.875243625	-3.596164810
С	2.387486782	-2.571280624	-2.324465720
Н	3.165244298	-2.614572705	-1.553985852
Н	2.362152893	-1.567772470	-2.753660251
С	-1.533143650	5.269203848	-0.703686290
Н	-2.255328807	4.753672185	-1.347303099

Η	-0.699027144	5.621400068	-1.317549134
С	-2.193878967	6.376324172	0.122048126
Н	-3.030055190	6.840461039	-0.408152159
Н	-1.467019048	7.159263714	0.366010738
С	-2.620034116	5.627598427	1.394328768
Н	-2.764348594	6.286926502	2.254854183
Н	-3.549150036	5.072141214	1.224560293
С	-1.458586661	4.658432960	1.595922170
Н	-0.626405541	5.137838728	2.128082364
Н	-1.732647897	3.736465452	2.109810091
С	-1.037513561	-4.191080722	1.597992369
Н	-1.305107918	-4.789190594	0.718608908
Н	0.036914373	-4.250808323	1.761282472
С	-1.885758142	-4.575066693	2.803015152
Н	-1.423975527	-4.205036380	3.724989074
Н	-3.819923943	-4.415300991	1.824098394

 Table 6.4.11. Optimized coordinates of Ce(MBP)₂(THF)₂.

Ce	0.004487416	0.006932005	-0.436620062	
0	-0.749167519	1.486144916	0.939867759	
0	-1.972197918	-0.916822534	-0.527175398	
0	1.975937688	0.943925363	-0.524194920	
0	0.763096274	-1.471177301	0.937842201	
0	-1.162772171	1.633601643	-2.179190875	
0	1.177938587	-1.617834320	-2.179477170	
С	-1.601461184	2.095544774	1.786730944	
С	-1.481527971	3.485439751	2.098457403	
С	-2.437126106	4.033792341	2.964347521	
Н	-2.379313687	5.087142357	3.214435610	

С	-3.469275821	3.291293562	3.550758428
С	-3.527066062	1.928105001	3.264126359
Н	-4.291063148	1.315756213	3.739852435
С	-2.620959086	1.317746258	2.392448613
С	-2.711276429	-0.184297516	2.162888633
Н	-1.717207764	-0.582788365	1.950051792
Н	-3.025370490	-0.638162452	3.111075709
С	-3.696178378	-0.653463665	1.096383101
С	-5.049656155	-0.750186206	1.434331594
Н	-5.361483443	-0.447832097	2.432374221
С	-6.003777780	-1.233220136	0.540645864
С	-5.552653752	-1.677169674	-0.708747124
Н	-6.290766001	-2.093528223	-1.385260289
С	-4.211736304	-1.627602054	-1.109237849
С	-3.269614572	-1.056307894	-0.196186057
С	-0.341616876	4.369771528	1.540892424
С	-0.387413630	5.807736342	2.101933097
Н	-0.292813071	5.828458711	3.193630218
Н	-1.308721330	6.333642958	1.826496440
Н	0.451365352	6.378430827	1.687119524
С	1.033875595	3.778422297	1.931109088
Н	1.181441661	2.787562134	1.501745320
Н	1.127379066	3.703101017	3.021536379
Н	1.838538958	4.431863286	1.570524011
С	-0.444795176	4.484729046	0.002251098
Н	0.369899674	5.110286109	-0.384472745
Н	-1.392611218	4.956579328	-0.285919741
Н	-0.383727322	3.509810311	-0.483537728
С	-4.481203175	3.950431579	4.460587033
Н	-5.310870656	4.391756906	3.890706920

Н	-4.029245952	4.759370583	5.045908353
Н	-4.918811164	3.230169245	5.160664609
С	-7.470710190	-1.286961737	0.903169999
Н	-7.963591489	-2.159661435	0.459377559
Н	-8.009536034	-0.398386310	0.545349932
Н	-7.612837674	-1.334226277	1.988474696
С	-3.783023683	-2.231331222	-2.466935978
С	-4.967005310	-2.858761478	-3.233871634
Н	-5.443745687	-3.667464639	-2.668691472
Н	-4.598144320	-3.285769687	-4.173743282
Н	-5.734258440	-2.118674106	-3.488537883
С	-3.177345523	-1.148766654	-3.390065776
Н	-3.928124937	-0.385419774	-3.629212537
Н	-2.851013916	-1.598786231	-4.336922866
Н	-2.321804482	-0.653199484	-2.929134696
С	-2.752728888	-3.361219626	-2.225561359
Н	-1.870045102	-2.993263496	-1.700084134
Н	-2.434968338	-3.795350952	-3.182456418
Н	-3.196416521	-4.164950828	-1.625379059
С	3.277689833	1.060872583	-0.201279402
С	4.225237044	1.608535681	-1.123385588
С	5.568872241	1.637094631	-0.730019314
Н	6.310611259	2.036143564	-1.412977525
С	6.018613423	1.192985668	0.519852564
С	5.061130554	0.730810138	1.420939071
Н	5.373168312	0.426904805	2.418433417
С	3.704377123	0.656345797	1.090732240
С	2.717061702	0.207266876	2.163603271
Н	1.725719591	0.610250405	1.946636683
Н	3.035022175	0.669920336	3.106261487

С	2.617908834	-1.291500739	2.410255586
С	3.512585343	-1.894272006	3.298871306
Н	4.272833310	-1.278424107	3.776101913
С	3.447660100	-3.253826548	3.600659218
С	2.418823717	-3.999603745	3.012641528
Н	2.354491925	-5.049535434	3.275197038
С	1.473880497	-3.458454321	2.130587495
С	1.602942510	-2.073286034	1.802113471
С	3.799685829	2.211431988	-2.482354097
С	2.798153220	3.366255573	-2.239683968
Н	2.483517456	3.802553785	-3.196594557
Η	3.264454634	4.162525804	-1.646690509
Н	1.911102669	3.019837640	-1.707049911
С	3.161539512	1.137500930	-3.393510196
Н	2.845178652	1.588058469	-4.343229690
Η	2.293305731	0.671279470	-2.926402290
Н	3.890052544	0.350921281	-3.626466039
С	4.991963034	2.805282815	-3.263266874
Н	5.740513739	2.045876759	-3.517056684
Н	5.491391695	3.608071636	-2.709309345
Η	4.625712782	3.232212917	-4.204154808
С	7.488140231	1.223922565	0.874461435
Η	7.636758709	1.268178887	1.958992120
Н	7.991904801	2.089345817	0.428603703
Н	8.011357356	0.327547723	0.512985471
С	4.447905046	-3.905242810	4.528785576
Η	4.881141460	-3.177814660	5.224174055
Н	5.281667353	-4.356673412	3.972952987
Н	3.987107245	-4.705133455	5.119641847
С	0.333262273	-4.344661681	1.577223184

С	0.371763025	-5.777024376	2.153023769
Н	1.293051461	-6.308320874	1.887978665
Н	-0.466511521	-6.349454986	1.739576341
Н	0.271229741	-5.786458918	3.244320207
С	-1.040919261	-3.743961756	1.957488007
Н	-1.847426559	-4.396936667	1.600203410
Н	-1.182822131	-2.756374221	1.518631287
Н	-1.137699472	-3.657989450	3.046816012
С	0.439399233	-4.475651180	0.040214537
Н	1.385728834	-4.954244958	-0.241511410
Н	0.382540320	-3.505307309	-0.455076469
Н	-0.377076836	-5.101811971	-0.341929461
С	-0.688945042	2.015023963	-3.502331232
Н	-0.306937575	1.120019846	-4.000364066
Н	-1.590182443	3.385729200	-4.948331883
С	-2.684136812	3.239770627	-3.033467077
Н	-2.249195844	4.197402268	-2.726242604
Н	-3.740992674	3.399908928	-3.264504974
С	-2.489946214	2.190008782	-1.942440572
Н	-2.505672107	2.591108393	-0.928419422
Н	-3.219694885	1.379227447	-2.019732365
С	2.519734945	-2.152531634	-1.956035215
Н	2.464537122	-2.810531718	-1.086544357
Н	3.188433628	-1.319394941	-1.733187330
С	2.892415288	-2.904250586	-3.239814871
Н	3.489394044	-3.795929311	-3.029508952
Н	3.471347851	-2.258958905	-3.909654836
С	1.525856752	-3.228395131	-3.865268967
Н	1.574928301	-3.391126655	-4.945606192
Н	1.085595151	-4.117356075	-3.400113540

С	0.715394527	-1.988648858	-3.503474403
Η	0.915519208	-1.162041636	-4.197388710
Η	-0.360633854	-2.156160832	-3.443309104
Η	0.129227326	2.730684735	-3.377013540
С	-1.892856791	2.641076463	-4.206852982
Н	-2.484273941	1.871456259	-4.714853737

Table 6.4.12. Optimized coordinates of Ce(O-DiNOx)₂.

Ce	0.002468000	-0.709195000	-0.119209000
0	-1.700959000	1.516823000	-0.046258000
0	-0.226221000	-1.285839000	2.046920000
0	-1.574491000	-2.060695000	-0.940773000
0	1.922928000	0.817174000	1.350062000
0	1.432152000	-2.188766000	-0.996229000
0	0.966448000	0.820557000	-1.375992000
Ν	-1.431577000	-0.546393000	2.190596000
Ν	-2.012907000	-1.090582000	-1.882037000
Ν	2.095349000	-2.232824000	0.253404000
N	0.933723000	2.119025000	-1.921456000
С	-2.499961000	-1.398779000	2.873604000
С	-2.724027000	-2.675560000	2.050586000
Н	-2.853215000	-2.449970000	0.990927000
Н	-3.624821000	-3.179303000	2.419981000
Н	-1.888659000	-3.371021000	2.154690000
С	-3.819438000	-0.610439000	2.919596000
Н	-3.714931000	0.347203000	3.438631000
Н	-4.563718000	-1.200566000	3.465192000
Н	-4.212066000	-0.429850000	1.914143000
С	-2.092191000	-1.804519000	4.304085000

Н	-1.103702000	-2.273258000	4.303409000
Н	-2.813781000	-2.534122000	4.688574000
Н	-2.080501000	-0.954980000	4.993053000
С	-1.136955000	0.703291000	2.872666000
С	-0.307635000	0.731250000	4.002901000
Н	0.143666000	-0.192055000	4.342947000
С	-0.054861000	1.925591000	4.674367000
Н	0.577172000	1.923907000	5.558501000
С	-0.613416000	3.117941000	4.208165000
Н	-0.425570000	4.054555000	4.725395000
С	-1.386973000	3.102386000	3.049145000
Н	-1.782387000	4.034476000	2.655134000
С	-1.649444000	1.909610000	2.358667000
С	-2.462760000	1.972421000	1.090764000
Н	-3.376872000	1.379617000	1.169988000
Н	-2.758834000	3.013130000	0.905321000
С	-1.878422000	-1.615004000	-3.305279000
С	-2.720548000	-2.879315000	-3.570529000
Н	-2.539841000	-3.630103000	-2.795375000
Н	-2.425506000	-3.308771000	-4.534440000
Н	-3.791961000	-2.667225000	-3.620272000
С	-0.402896000	-1.963056000	-3.538497000
Н	0.241668000	-1.120135000	-3.283420000
Н	-0.248728000	-2.201295000	-4.597011000
Н	-0.094557000	-2.822777000	-2.941751000
С	-2.300351000	-0.496328000	-4.272193000
Н	-3.352175000	-0.221554000	-4.148998000
Н	-2.164952000	-0.842602000	-5.302521000
Н	-1.689006000	0.401650000	-4.136129000
С	-3.351083000	-0.640977000	-1.533567000

С	-4.407848000	-1.540637000	-1.336977000
Н	-4.215913000	-2.604934000	-1.381121000
С	-5.697588000	-1.077397000	-1.073026000
Н	-6.506554000	-1.789399000	-0.933798000
С	-5.945681000	0.294680000	-0.995763000
Н	-6.949676000	0.663190000	-0.805549000
С	-4.883375000	1.189266000	-1.126797000
Н	-5.059424000	2.256597000	-1.015536000
С	-3.578159000	0.739119000	-1.372468000
С	-2.418676000	1.703955000	-1.290249000
Н	-1.669264000	1.557718000	-2.065098000
Н	-2.775120000	2.740771000	-1.337948000
С	2.106790000	-3.658780000	0.807703000
С	0.659456000	-4.163573000	0.861323000
Н	0.044765000	-3.486633000	1.456048000
Н	0.642606000	-5.153677000	1.330694000
Н	0.228068000	-4.248733000	-0.138246000
С	2.929501000	-4.622591000	-0.068787000
Н	2.589661000	-4.582076000	-1.108278000
Н	2.785558000	-5.646088000	0.295043000
Н	4.001347000	-4.408413000	-0.037561000
С	2.675379000	-3.624992000	2.235236000
Н	3.700889000	-3.244562000	2.264073000
Н	2.687519000	-4.643318000	2.639280000
Н	2.050916000	-3.009342000	2.889895000
С	3.415194000	-1.635450000	0.137612000
С	4.273954000	-1.974935000	-0.916987000
Н	3.919175000	-2.643564000	-1.691537000
С	5.568595000	-1.458708000	-0.974436000
Н	6.225568000	-1.742331000	-1.792221000
С	6.018264000	-0.590695000	0.023244000
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Н	7.030465000	-0.197307000	-0.003951000
С	5.140520000	-0.198147000	1.033430000
Н	5.465130000	0.525126000	1.777881000
С	3.826997000	-0.686688000	1.092699000
С	2.836297000	-0.057360000	2.049947000
Н	2.190159000	-0.779120000	2.544660000
Н	3.372446000	0.526864000	2.810205000
С	1.899851000	2.267595000	-3.074037000
С	1.569696000	1.183276000	-4.109526000
Н	1.795838000	0.187508000	-3.725947000
Н	2.167485000	1.344835000	-5.013584000
Н	0.511393000	1.219707000	-4.387513000
С	1.692877000	3.642038000	-3.736629000
Н	0.657252000	3.771830000	-4.067685000
Н	2.340689000	3.707854000	-4.617363000
Н	1.951003000	4.469342000	-3.070280000
С	3.378007000	2.129342000	-2.658609000
Н	3.665329000	2.901528000	-1.936737000
Н	4.023777000	2.241360000	-3.537510000
Н	3.572492000	1.144217000	-2.225000000
С	0.963679000	3.123674000	-0.895324000
С	0.168785000	4.261944000	-1.122818000
Н	-0.421443000	4.300533000	-2.031575000
С	0.113060000	5.314938000	-0.212824000
Н	-0.505212000	6.182146000	-0.429682000
С	0.832455000	5.236926000	0.980774000
Н	0.794857000	6.043726000	1.707146000
С	1.596174000	4.098909000	1.232397000
Н	2.159417000	4.030023000	2.160215000

С	1.685954000	3.035146000	0.320714000
С	2.611263000	1.899210000	0.682330000
Η	3.123537000	1.508583000	-0.193175000
Н	3.371693000	2.284287000	1.374715000

Computed Geometry Optimizations of Ce(III) Complexes in CPCM =

Dichloromethane

Table 6.4.13. Optimized coordinates of $Ce[N(SiHMe_2)_2]_4^-$.

Ce	-0.018698760	-0.000016996	-0.000014124
Si	-2.388343721	-1.093796986	-2.274437186
Si	-1.896584252	1.866293897	-2.643453961
Si	2.481417628	2.229908767	-1.235349767
Si	1.871951273	2.531974360	1.746792678
N	-1.637370798	0.382521575	-1.806757377
N	1.620961313	1.826663025	0.197953950
С	-2.148613103	-1.600053187	-4.092499350
Н	-2.634538425	-0.894274853	-4.778272577
Н	-2.576117680	-2.593277422	-4.283154806
Н	-1.083917839	-1.636799398	-4.352331116
С	-4.242784699	-1.239905581	-1.878048766
Н	-4.438883532	-1.022637367	-0.820863797
Н	-4.604785658	-2.256363190	-2.083196391
Н	-4.843817911	-0.545285584	-2.477264338
С	-3.613899418	2.065295928	-3.444972149
Н	-3.834021289	1.283908723	-4.182239519
Н	-3.672081218	3.031987402	-3.963189762
Н	-4.411312598	2.045321779	-2.691159999
С	-1.658064751	3.387641303	-1.536831301

Н	-2.443378282	3.445337530	-0.772797156
Н	-1.705688692	4.305526515	-2.138124376
Н	-0.693388289	3.373016267	-1.018348957
С	2.402039448	4.056699059	-1.764437765
Н	1.369423406	4.411403140	-1.859297465
Н	2.897217889	4.198021156	-2.734390129
Н	2.909897198	4.704131961	-1.037666890
С	4.323324963	1.750208353	-1.265324150
Н	4.905386535	2.324521172	-0.533669593
Н	4.752935264	1.944629741	-2.257346698
Н	4.467852403	0.686564189	-1.042065163
С	3.672400338	2.550527224	2.365846502
Н	4.121268415	1.550468215	2.335825467
Н	3.717097914	2.907029264	3.403658567
Н	4.302751748	3.215223687	1.761472854
С	1.209789903	4.305271594	1.938998480
Н	1.755908454	5.007819000	1.296615020
Н	1.312246820	4.652970274	2.975682371
Н	0.149046574	4.364926021	1.667628661
Н	-1.728296816	-2.175360372	-1.458669890
Н	-0.922457124	2.042639866	-3.787454993
Н	1.850700414	1.442985606	-2.356941783
Н	1.114076534	1.700481974	2.748105297
Si	-2.388206019	1.093821899	2.274471821
Si	-1.896765807	-1.866333834	2.643358286
Si	2.481369319	-2.230008655	1.235415454
Si	1.872088954	-2.531914473	-1.746765722
Ν	-1.637409846	-0.382557501	1.806713534
Ν	1.620962186	-1.826709190	-0.197900687
С	-2.148410703	1.599963655	4.092557575

Η	-2.634422752	0.894212198	4.778297316
Н	-2.575793189	2.593231315	4.283260573
Н	-1.083711201	1.636567311	4.352391929
С	-4.242632566	1.240160062	1.878106790
Н	-4.438766726	1.022973728	0.820911507
Н	-4.604521689	2.256644289	2.083319938
Н	-4.843732433	0.545567816	2.477288680
С	-3.614108803	-2.065168894	3.444858937
Н	-3.834140131	-1.283787933	4.182160688
Н	-3.672412229	-3.031877227	3.963031109
Н	-4.411515162	-2.045060825	2.691042861
С	-1.658412081	-3.387682886	1.536705500
Н	-2.443741922	-3.445286142	0.772681012
Н	-1.706122416	-4.305574670	2.137982308
Н	-0.693741705	-3.373142804	1.018213588
С	2.402011941	-4.056831142	1.764399521
Н	1.369400435	-4.411560671	1.859208669
Н	2.897161611	-4.198193039	2.734361067
Н	2.909905708	-4.704217857	1.037612713
С	4.323265500	-1.750268859	1.265500932
Н	4.905377979	-2.324519352	0.533838195
Н	4.752828635	-1.944745276	2.257533180
Н	4.467777927	-0.686606279	1.042320131
С	3.672584635	-2.550381277	-2.365687664
Н	4.121423940	-1.550313007	-2.335553798
Н	3.717368323	-2.906799575	-3.403524690
Н	4.302908120	-3.215109437	-1.761320128
С	1.209990085	-4.305215761	-1.939147825
Н	1.756080098	-5.007793911	-1.296773561
Н	1.312538312	-4.652834963	-2.975849395

Н	0.149227771	-4.364921190	-1.667864933
Н	-1.728037673	2.175348360	1.458747430
Н	-0.922670948	-2.042806938	3.787367139
Н	1.850591954	-1.443158731	2.357021387
Н	1.114275886	-1.700377324	-2.748088480

Table 6.4.14. Optimized coordinates of Li(THF)[Ce(N^{*i*}Pr₂)₄].

Ce	-0.875600034	0.014707558	0.035742942
0	4.265166923	-0.095954154	-0.094148802
N	1.058280207	0.802016392	1.430451270
N	-2.148396791	1.874807190	-0.718284396
N	0.909135097	-1.055016755	-1.371938797
N	-2.460129954	-1.635228609	0.689125338
С	1.481833619	2.207245207	1.552735491
Н	0.739841590	2.789566303	2.130214308
С	1.539573212	2.850646841	0.157562954
Н	2.329739278	2.396867576	-0.456664513
Н	1.767666434	3.921155006	0.234591288
Н	0.586962717	2.750038313	-0.374469024
С	2.843912997	2.431823020	2.249347692
Н	2.829092266	2.122223055	3.298527113
Н	3.117156083	3.495680871	2.226874063
Н	3.631535906	1.863706697	1.738735653
С	0.787653072	0.094825097	2.693720349
Н	0.070575076	-0.717847814	2.443597706
С	0.082457337	0.925490516	3.788741851
Н	-0.797165832	1.445607885	3.390966055
Н	0.747842311	1.679070870	4.224618727
Н	-0.252660250	0.273132110	4.603837357
С	1.986186994	-0.668435714	3.309803997

Н	1.662184104	-1.278006719	4.164824164
Н	2.765450823	0.014460895	3.663070245
Н	2.437066785	-1.344074287	2.574331522
С	0.683660265	-0.370163309	-2.658776013
Н	0.007221061	0.486226018	-2.441459464
С	-0.057029362	-1.192390359	-3.736119550
Н	-0.968068440	-1.650754553	-3.333985757
Н	0.570004634	-1.993298035	-4.143836010
Н	-0.346475682	-0.545402273	-4.572645935
С	1.924146142	0.309033316	-3.288689946
Н	1.641105392	0.887755437	-4.178962827
Н	2.678296732	-0.424132783	-3.592943030
Н	2.390688892	1.002475153	-2.580808778
С	1.227342754	-2.490678304	-1.459848542
Н	0.468304867	-3.019783627	-2.063885443
С	1.171741635	-3.127624087	-0.062183291
Н	1.948662791	-2.718354333	0.598852388
Н	1.339455273	-4.209960808	-0.124969784
Н	0.196943276	-2.965990532	0.411350032
С	2.596411517	-2.823857656	-2.098818651
Н	2.646892767	-2.518214635	-3.148317087
Н	2.788509504	-3.905014026	-2.063452000
Н	3.406331007	-2.313600472	-1.561287492
С	-2.672637441	2.595014970	0.447829673
Н	-2.209778696	2.129109826	1.340624728
С	-4.200227868	2.446841557	0.655578680
Н	-4.762913155	2.904170813	-0.167655375
Н	-4.525562522	2.934204659	1.584566539
Н	-4.478719741	1.388784441	0.707178262
С	-2.283047789	4.089828921	0.526624757

Н	-2.617738476	4.535097327	1.473036947
Н	-2.745439784	4.662925854	-0.286421227
Н	-1.197750993	4.213082837	0.452423110
С	-2.603778003	2.404023323	-2.008650806
Н	-3.456003558	3.087163533	-1.855842165
С	-3.119991679	1.286919842	-2.935161068
Н	-2.329906762	0.555629555	-3.149762778
Н	-3.463386200	1.689939144	-3.897662251
Н	-3.954640347	0.750879201	-2.470075883
С	-1.521478594	3.227821148	-2.742710351
Н	-1.171857514	4.058855419	-2.121837697
Н	-1.902257355	3.643075754	-3.686780608
Н	-0.652489354	2.600397587	-2.979399418
С	-3.091913666	-2.204362852	-0.505273906
Н	-2.612961609	-1.716901191	-1.378358977
С	-4.601683288	-1.891099800	-0.644375675
Н	-4.776576728	-0.810834935	-0.597738025
Н	-5.185164870	-2.362086105	0.156291064
Н	-4.998354210	-2.262212080	-1.598863014
С	-2.957422745	-2.177854374	1.957974776
Н	-3.868592872	-2.773664633	1.783503852
С	-1.953757742	-3.129240136	2.646894433
Н	-2.369226765	-3.552513142	3.572583502
Н	-1.031013889	-2.595468544	2.909018293
Н	-1.681506906	-3.957793863	1.984998647
С	-3.362108421	-1.056188322	2.933739121
Н	-2.507468786	-0.404070611	3.156542068
Н	-3.725647974	-1.461060824	3.888174632
Н	-4.152839532	-0.432848757	2.501833720
С	5.133605570	-0.817969240	0.815162150

Η	5.183647407	-1.867129934	0.497104708
Н	4.691403734	-0.768244507	1.812798126
С	6.494501888	-0.133629926	0.705486805
Н	6.535074225	0.743467909	1.361604680
Н	7.317503270	-0.802222174	0.973060413
С	6.514907968	0.294919749	-0.769741602
Н	6.788262572	-0.552138149	-1.409062142
Н	7.209876819	1.114423357	-0.972793617
С	5.059318027	0.701778595	-1.011707248
Н	4.889156410	1.759790277	-0.779605037
Н	4.714403831	0.501760265	-2.029008757
Li	2.241373133	-0.171878755	-0.002886452
С	-2.857224514	-3.721063309	-0.703398021
Н	-1.786574546	-3.951610469	-0.695984147
Н	-3.278537633	-4.068147391	-1.656462084
Н	-3.332647928	-4.302352722	0.096488973

Table 6.4.15. Optimized coordinates of $Ce(N^iPr_2)_4^-$.

Ce	0.000279000	0.002222000	-0.003772000
N	-0.436220000	-0.290039000	2.360477000
С	-1.428720000	-1.049968000	3.122953000
Η	-1.513451000	-0.649544000	4.148852000
С	-1.066174000	-2.546223000	3.277405000
Η	-1.020349000	-3.031264000	2.294631000
Н	-0.087721000	-2.665961000	3.753937000
С	-2.835168000	-0.925532000	2.504587000
Н	-3.159490000	0.121167000	2.487421000
Н	-2.840341000	-1.293588000	1.470412000
С	0.450352000	0.538396000	3.179787000
Н	1.173697000	1.000811000	2.482284000

С	1.307940000	-0.230460000	4.214824000
Н	0.680408000	-0.680205000	4.994485000
Н	1.872957000	-1.035070000	3.732000000
С	-0.252597000	1.724455000	3.888839000
Н	-0.992174000	1.374249000	4.620072000
Н	-0.773076000	2.352919000	3.158370000
Ν	-0.912285000	2.196408000	-0.473150000
С	-0.310023000	3.513016000	-0.693467000
Н	-1.062707000	4.308771000	-0.553115000
С	0.243535000	3.696347000	-2.126376000
Н	1.042392000	2.970552000	-2.322729000
Н	-0.541673000	3.537266000	-2.872807000
С	0.807923000	3.804418000	0.327394000
Н	0.413754000	3.791989000	1.350010000
Н	1.599119000	3.045670000	0.265698000
С	-2.376716000	2.194973000	-0.468209000
Н	-2.686858000	1.139984000	-0.348621000
С	-3.041876000	2.674069000	-1.782235000
Н	-2.837592000	3.736309000	-1.966313000
Н	-2.663845000	2.105558000	-2.638893000
С	-3.015896000	2.948389000	0.726106000
Н	-2.782147000	4.020225000	0.697032000
Н	-2.642467000	2.548300000	1.674793000
Ν	-1.013338000	-1.737412000	-1.349871000
С	-1.799025000	-1.738847000	-2.585407000
С	-3.288629000	-1.388495000	-2.358497000
Н	-3.748610000	-2.078749000	-1.643750000
С	-1.203223000	-0.782867000	-3.637753000
Н	-0.181531000	-1.080887000	-3.899446000
Н	-1.162615000	0.244239000	-3.251925000

С	-0.708151000	-3.071228000	-0.826936000
Н	-0.170261000	-2.916168000	0.126986000
С	-1.940142000	-3.939444000	-0.470267000
Н	-2.513612000	-4.201892000	-1.368185000
Н	-2.609504000	-3.404708000	0.212062000
С	0.255652000	-3.903590000	-1.710770000
Н	-0.188129000	-4.125879000	-2.689552000
Н	1.188992000	-3.356556000	-1.880779000
Ν	2.358973000	-0.171880000	-0.543009000
С	3.522018000	-0.713318000	0.163006000
Н	4.350160000	-0.895353000	-0.544565000
С	4.083232000	0.246850000	1.238344000
Н	3.332063000	0.429064000	2.016671000
Н	4.349158000	1.214052000	0.799348000
С	3.211190000	-2.078594000	0.807597000
Н	2.918966000	-2.809762000	0.045329000
Н	2.382639000	-1.992321000	1.522405000
С	2.650778000	0.322787000	-1.890389000
Н	1.708247000	0.753054000	-2.276991000
С	3.688830000	1.470039000	-1.963635000
Н	4.683823000	1.124725000	-1.655840000
Н	3.402082000	2.297860000	-1.305997000
С	3.044312000	-0.778397000	-2.908442000
Н	3.983747000	-1.270252000	-2.625744000
Н	2.265369000	-1.546512000	-2.962525000
Н	-1.788015000	-2.741913000	-3.047181000
Н	-3.384372000	-0.374301000	-1.951452000
Н	-4.133279000	2.552263000	-1.744845000
Н	-4.110659000	2.852991000	0.720957000
Н	0.658963000	4.703659000	-2.278530000

Η	1.274155000	4.783950000	0.150740000
Н	0.468316000	2.353213000	4.429766000
Н	2.022481000	0.437956000	4.714762000
Н	-1.808617000	-3.084914000	3.884809000
Н	-3.579119000	-1.507206000	3.066909000
Н	4.979921000	-0.164435000	1.725328000
Н	4.078433000	-2.477803000	1.352231000
Н	3.779921000	1.860689000	-2.986570000
Н	3.184608000	-0.361539000	-3.915488000
Н	0.503331000	-4.864710000	-1.239060000
Н	-1.638899000	-4.879651000	0.011948000
Н	-3.865874000	-1.431921000	-3.294023000
Η	-1.803330000	-0.767505000	-4.558412000

Table 6.4.16. Optimized coordinates of Ce[N(SiMe₃)₂]₃Br⁻.

Ce	0.001240000	-0.001655000	0.100934000
Br	0.097847000	0.023347000	3.047509000
Si	-1.651259000	-3.166025000	0.838295000
Si	-2.718672000	-1.719439000	-1.581943000
N	-1.574772000	-1.830726000	-0.279353000
С	0.071412000	-3.662856000	1.486328000
Н	0.739910000	-3.952836000	0.665525000
Н	-0.023470000	-4.528733000	2.155674000
Н	0.558925000	-2.863092000	2.055782000
С	-2.730466000	-2.781176000	2.361775000
Н	-2.334955000	-1.917647000	2.909406000
Н	-2.761936000	-3.633365000	3.054535000
Н	-3.763769000	-2.551711000	2.071269000
С	-2.354289000	-4.791710000	0.118453000

Н	-1.750607000	-5.169902000	-0.715320000
Н	-3.387750000	-4.697666000	-0.235357000
Η	-2.347124000	-5.559361000	0.904403000
С	-2.587935000	-3.095702000	-2.900224000
Η	-2.883472000	-4.081425000	-2.526745000
Н	-1.562215000	-3.178172000	-3.280678000
Η	-3.238459000	-2.855635000	-3.752664000
С	-4.536414000	-1.706288000	-0.995183000
Н	-4.729197000	-0.865383000	-0.316537000
Н	-4.802785000	-2.625496000	-0.458492000
Н	-5.224323000	-1.610494000	-1.846226000
С	-2.483703000	-0.116207000	-2.583853000
Н	-2.522818000	0.791828000	-1.972553000
Н	-3.277636000	-0.047356000	-3.339698000
Η	-1.526419000	-0.106867000	-3.122933000
Si	3.600308000	0.227935000	0.738313000
Si	2.824045000	-1.539414000	-1.573795000
Ν	2.375459000	-0.432747000	-0.311605000
С	3.153991000	1.971904000	1.365473000
Н	3.030756000	2.676730000	0.533247000
Н	3.965499000	2.351757000	2.001087000
Н	2.235843000	1.987858000	1.963564000
С	3.915624000	-0.855662000	2.274610000
Н	3.000462000	-0.963131000	2.868252000
Н	4.687152000	-0.414887000	2.920869000
Η	4.254563000	-1.860580000	1.992005000
С	5.317421000	0.463464000	-0.069967000
Η	5.280095000	1.142002000	-0.930775000
Η	5.768520000	-0.477089000	-0.407783000
Н	6.000327000	0.905713000	0.668394000

С	3.890920000	-0.791319000	-2.970588000
Н	4.900381000	-0.519311000	-2.646031000
Н	3.420268000	0.110417000	-3.382083000
Н	3.990105000	-1.515850000	-3.790762000
С	3.763295000	-3.076317000	-0.938258000
Н	3.163851000	-3.632300000	-0.205804000
Н	4.708890000	-2.809120000	-0.450080000
Н	4.000302000	-3.762291000	-1.762818000
С	1.293398000	-2.205101000	-2.491668000
Н	0.549160000	-2.664671000	-1.832692000
Н	1.614692000	-2.964393000	-3.217457000
Н	0.782110000	-1.415832000	-3.059888000
Si	-1.987992000	2.985659000	0.790722000
Si	-0.144552000	3.197157000	-1.588123000
Ν	-0.838922000	2.260422000	-0.300238000
С	-3.246200000	1.719544000	1.460615000
Н	-3.823059000	1.260310000	0.647711000
Н	-3.959002000	2.227027000	2.124742000
Н	-2.777602000	0.914980000	2.039445000
С	-1.156649000	3.795313000	2.303275000
Н	-0.583723000	3.056001000	2.875189000
Н	-1.902253000	4.238694000	2.977531000
Н	-0.467462000	4.593990000	2.000372000
С	-3.080086000	4.353661000	0.021728000
Н	-3.677468000	3.981573000	-0.819462000
Н	-2.503199000	5.214675000	-0.336166000
Н	-3.779419000	4.723797000	0.783928000
С	-1.368735000	3.744424000	-2.948281000
Н	-2.100592000	4.480175000	-2.599628000
Н	-1.924260000	2.885630000	-3.345359000

Η	-0.817003000	4.196169000	-3.784369000
С	0.735084000	4.782783000	-0.987981000
Н	1.537398000	4.548230000	-0.276728000
Н	0.044166000	5.470927000	-0.484894000
Н	1.185629000	5.325595000	-1.830021000
С	1.166717000	2.196357000	-2.541154000
Н	1.947752000	1.770061000	-1.902262000
Н	1.654075000	2.851410000	-3.275914000
Н	0.715618000	1.366381000	-3.102526000

 Table 6.4.17. Optimized coordinates of Ce[N(SiMe₃)₂]₃Cl⁻.

Ce	0.004572000	-0.017232000	-0.286045000	
Cl	0.098274000	-0.074925000	-3.077470000	
Si	0.565109000	3.104724000	1.491168000	
Si	-1.072177000	3.382573000	-1.028572000	
Si	2.373534000	-2.148056000	1.430974000	
Si	3.562271000	-0.654151000	-0.901539000	
Si	-3.111806000	-0.959610000	1.391339000	
Si	-2.365946000	-2.664600000	-0.980601000	
N	-0.253693000	2.384126000	0.139583000	
N	2.213296000	-0.972820000	0.158575000	
N	-2.000452000	-1.364335000	0.119149000	
С	1.468308000	1.796154000	2.544193000	
С	-0.566786000	3.997917000	2.744583000	
С	1.900920000	4.370213000	0.977778000	
С	-1.759520000	5.033913000	-0.353387000	
С	0.047029000	3.868337000	-2.493771000	
С	-2.609013000	2.521557000	-1.760635000	
С	0.727551000	-2.425191000	2.351807000	
С	3.587146000	-1.668453000	2.825603000	

С	2.916502000	-3.871625000	0.811363000
С	5.285749000	-0.850973000	-0.097270000
С	3.579226000	-1.799488000	-2.424670000
С	3.571474000	1.138612000	-1.549050000
С	-2.519853000	0.552984000	2.381963000
С	-3.344681000	-2.307437000	2.725225000
С	-4.860197000	-0.522355000	0.757312000
С	-3.433770000	-4.072271000	-0.250305000
С	-3.306235000	-2.075680000	-2.530933000
С	-0.793911000	-3.559356000	-1.583376000
Н	0.767311000	1.105851000	3.032606000
Н	2.028930000	2.302466000	3.341426000
Н	2.178485000	1.191523000	1.968831000
Н	-1.019349000	4.908807000	2.339535000
Н	0.012960000	4.282728000	3.633528000
Н	-1.380170000	3.341202000	3.076900000
Н	2.665401000	3.904055000	0.342838000
Н	2.409617000	4.788711000	1.856813000
Η	1.476078000	5.209758000	0.413197000
Н	-2.502225000	4.878360000	0.438314000
Η	-2.257674000	5.572992000	-1.170905000
Η	-0.981496000	5.695054000	0.046267000
Н	0.916051000	4.448429000	-2.157133000
Н	-0.497435000	4.481465000	-3.225028000
Η	0.420004000	2.978302000	-3.013874000
Н	-2.370868000	1.605929000	-2.313901000
Н	-3.112575000	3.202332000	-2.460560000
Н	-3.332570000	2.263697000	-0.976382000
Н	0.430534000	-1.542205000	2.933897000
Н	0.857840000	-3.250296000	3.064874000

Н	-0.111987000	-2.680321000	1.696136000
Н	4.629960000	-1.629133000	2.495141000
Н	3.524890000	-2.402205000	3.641196000
Н	3.334679000	-0.686793000	3.245763000
Н	2.209425000	-4.270450000	0.072665000
Н	2.967339000	-4.587633000	1.642895000
Н	3.905382000	-3.847756000	0.337019000
Н	5.422894000	-0.174491000	0.755156000
Н	6.055683000	-0.603333000	-0.840854000
Н	5.487065000	-1.870398000	0.252664000
Н	3.648617000	-2.853506000	-2.127355000
Н	4.434473000	-1.582121000	-3.079152000
Н	2.663667000	-1.677610000	-3.015214000
Н	2.669784000	1.396546000	-2.115993000
Н	4.430199000	1.280326000	-2.219299000
Н	3.673663000	1.860289000	-0.728391000
Н	-1.602107000	0.335413000	2.944553000
Н	-3.289445000	0.828537000	3.115638000
Н	-2.317919000	1.430173000	1.758398000
Н	-3.869218000	-3.194637000	2.356540000
Н	-3.928312000	-1.902233000	3.563600000
Н	-2.376944000	-2.635347000	3.125290000
Н	-4.833397000	0.333813000	0.070596000
Н	-5.526492000	-0.258716000	1.589884000
Н	-5.323100000	-1.358344000	0.217912000
Н	-2.949590000	-4.556561000	0.606181000
Н	-3.583680000	-4.840412000	-1.021337000
Н	-4.426489000	-3.738550000	0.074153000
Н	-4.274152000	-1.631959000	-2.264487000
Н	-3.501061000	-2.909419000	-3.219315000

Η	-2.729625000	-1.319021000	-3.075621000
Н	-0.131077000	-2.923544000	-2.181305000
Н	-1.081228000	-4.411528000	-2.214536000
Н	-0.214056000	-3.957324000	-0.740647000

Table 6.4.18. Optimized coordinates of Ce[N(SiMe₃)₂]₃F⁻.

Ce	-0.000143000	0.002434000	-0.122641000
Si	0.771309000	3.392872000	-1.161637000
Si	-0.900141000	3.174801000	1.379650000
Si	2.565968000	-2.297907000	-1.211743000
Si	3.215048000	-0.867949000	1.393320000
Si	-3.321684000	-1.013975000	-1.179034000
Si	-2.333977000	-2.376429000	1.350373000
F	0.000955000	-0.024642000	-2.255223000
Ν	0.003789000	2.471960000	0.089268000
Ν	2.143797000	-1.236491000	0.091313000
Ν	-2.156639000	-1.212490000	0.089082000
С	2.523016000	2.741140000	-1.548259000
Н	3.166968000	2.787603000	-0.659795000
Н	2.995750000	3.351649000	-2.329984000
Н	2.522820000	1.702482000	-1.902496000
С	-0.203176000	3.335580000	-2.798714000
Н	-0.329993000	2.294526000	-3.116659000
Н	0.313136000	3.879977000	-3.601226000
Н	-1.202050000	3.776987000	-2.685983000
С	1.040264000	5.245182000	-0.769452000
Н	0.109011000	5.775531000	-0.537057000
Н	1.488709000	5.740651000	-1.641543000
Н	1.724015000	5.390554000	0.075852000

С	-2.376096000	4.246261000	0.808921000
Н	-2.055329000	5.098131000	0.196596000
Н	-2.930599000	4.648536000	1.667861000
Н	-3.080362000	3.658553000	0.206324000
С	0.122120000	4.253389000	2.580182000
Н	0.975056000	3.691611000	2.983230000
Н	-0.493203000	4.575035000	3.431847000
Н	0.518912000	5.155082000	2.100050000
С	-1.662858000	1.822051000	2.490813000
Н	-2.312958000	1.130133000	1.940591000
Н	-2.273074000	2.294980000	3.271761000
Н	-0.898011000	1.223383000	3.004826000
С	3.153710000	-1.353576000	-2.760811000
Н	2.365336000	-0.669002000	-3.095260000
Н	3.387657000	-2.034881000	-3.590412000
Н	4.052866000	-0.758191000	-2.555310000
С	1.080185000	-3.359381000	-1.763588000
Н	0.696891000	-3.974441000	-0.938712000
Н	1.377393000	-4.040947000	-2.572417000
Н	0.252388000	-2.747348000	-2.139347000
С	3.934839000	-3.572871000	-0.813569000
Н	4.879790000	-3.108598000	-0.507078000
Н	4.142708000	-4.177966000	-1.706783000
Н	3.630879000	-4.261145000	-0.015511000
С	4.896840000	-0.151947000	0.834650000
Н	5.455085000	-0.853016000	0.201666000
Н	5.532410000	0.091339000	1.697075000
Н	4.757647000	0.770343000	0.255313000
С	2.473053000	0.453811000	2.556287000
Н	2.245724000	1.396981000	2.043355000

Н	3.192223000	0.681206000	3.354425000
Н	1.550763000	0.110111000	3.044802000
С	3.606558000	-2.340779000	2.545799000
Н	2.683706000	-2.783989000	2.942421000
Н	4.210122000	-2.012164000	3.403091000
Н	4.161557000	-3.135980000	2.036350000
С	-5.094924000	-1.591811000	-0.755160000
Н	-5.147197000	-2.652740000	-0.481999000
Н	-5.746994000	-1.446835000	-1.627400000
Н	-5.524472000	-1.015783000	0.073647000
С	-2.827595000	-1.936375000	-2.772529000
Н	-1.850923000	-1.576251000	-3.114953000
Н	-3.554608000	-1.775331000	-3.580415000
Н	-2.748585000	-3.018671000	-2.605839000
С	-3.531151000	0.818355000	-1.667020000
Н	-3.865402000	1.423165000	-0.814145000
Н	-4.287496000	0.917661000	-2.457713000
Н	-2.603643000	1.261822000	-2.046952000
С	-3.780019000	-2.035748000	2.551578000
Н	-3.703876000	-1.027887000	2.980212000
Н	-3.768186000	-2.751110000	3.385434000
Н	-4.757917000	-2.112665000	2.063466000
С	-0.790476000	-2.426170000	2.472958000
Н	0.132372000	-2.656320000	1.924879000
Н	-0.920567000	-3.206694000	3.234613000
Н	-0.632891000	-1.479810000	3.008343000
С	-2.553670000	-4.170983000	0.729187000
Н	-3.449350000	-4.286960000	0.106028000
Н	-2.643053000	-4.874177000	1.568523000
Н	-1.693126000	-4.485934000	0.124298000

Table 6.4.19.	Optimized coo	ordinates of	$Ce(OAr)_4$,	, OAr = 2, 6-di	phenylphenol.
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Ce	0.001222000	-0.005485000	-0.000860000
0	-1.415620000	1.220423000	1.294954000
0	1.475040000	-1.270238000	1.197523000
С	-2.297321000	1.819763000	2.074910000
С	-2.187473000	3.214692000	2.376189000
С	-3.122023000	3.819352000	3.230595000
Н	-3.020624000	4.881692000	3.439861000
С	-4.185787000	3.106698000	3.779419000
Н	-4.904023000	3.596613000	4.430901000
С	-4.315366000	1.754711000	3.466640000
Н	-5.137890000	1.179723000	3.885859000
С	-3.394861000	1.096287000	2.639123000
С	-1.125907000	4.076840000	1.785766000
С	-0.386078000	4.954075000	2.599384000
Н	-0.534956000	4.930321000	3.676001000
С	0.531198000	5.852321000	2.048494000
Н	1.089824000	6.518741000	2.701013000
С	0.731153000	5.893394000	0.666975000
Н	1.442682000	6.592374000	0.235475000
С	0.010296000	5.021966000	-0.155236000
Н	0.157017000	5.043601000	-1.232268000
С	-0.902517000	4.122211000	0.397636000
Н	-1.471969000	3.465015000	-0.250430000
С	-3.613499000	-0.353921000	2.372214000
С	-4.855598000	-0.797051000	1.883731000
Н	-5.616658000	-0.062680000	1.633779000
С	-5.122167000	-2.157212000	1.709527000
Н	-6.089732000	-2.471944000	1.326522000

С	-4.150196000	-3.108179000	2.027716000
Н	-4.355591000	-4.167683000	1.899902000
С	-2.910704000	-2.683141000	2.515720000
Н	-2.151409000	-3.412984000	2.785069000
С	-2.642160000	-1.322479000	2.680076000
Н	-1.683341000	-1.009290000	3.079221000
С	2.369770000	-2.041010000	1.788963000
С	2.274256000	-2.346047000	3.184205000
С	3.221836000	-3.193018000	3.778973000
Н	3.131605000	-3.405509000	4.841638000
С	4.284270000	-3.730645000	3.056004000
Н	5.012379000	-4.376736000	3.538395000
С	4.400767000	-3.412545000	1.704034000
Н	5.223412000	-3.821469000	1.121803000
С	3.467768000	-2.591430000	1.055545000
С	1.213972000	-1.766462000	4.055046000
С	0.968514000	-0.381654000	4.093463000
Н	1.519892000	0.270718000	3.425355000
С	0.057073000	0.162787000	4.999754000
Н	-0.106789000	1.237455000	5.015441000
С	-0.640141000	-0.664651000	5.885390000
Н	-1.350327000	-0.239786000	6.589755000
С	-0.418731000	-2.043108000	5.851107000
Н	-0.959344000	-2.699872000	6.528138000
С	0.496484000	-2.585637000	4.945713000
Н	0.661245000	-3.660000000	4.926848000
С	3.674186000	-2.312209000	-0.394108000
С	4.909734000	-1.811435000	-0.842111000
Н	5.674734000	-1.562973000	-0.111209000
С	5.165235000	-1.624184000	-2.202653000

Н	6.128054000	-1.232555000	-2.521226000
С	4.188528000	-1.940899000	-3.149194000
Н	4.385347000	-1.802784000	-4.209034000
С	2.955265000	-2.440467000	-2.719378000
Н	2.192595000	-2.708661000	-3.446153000
С	2.697839000	-2.618210000	-1.358177000
Н	1.744169000	-3.026485000	-1.041168000
0	-1.458866000	-1.227802000	-1.250176000
0	1.407034000	1.296032000	-1.239071000
С	-2.357496000	-1.842193000	-1.998077000
С	-2.239312000	-3.236593000	-2.299014000
С	-3.194140000	-3.855748000	-3.119948000
Н	-3.086360000	-4.917379000	-3.329571000
С	-4.284573000	-3.158398000	-3.635019000
Н	-5.017925000	-3.659557000	-4.260595000
С	-4.420978000	-1.807054000	-3.322244000
Н	-5.264415000	-1.244137000	-3.715517000
С	-3.482152000	-1.134350000	-2.527606000
С	-1.145726000	-4.082264000	-1.744348000
С	-0.424864000	-4.953005000	-2.581714000
Н	-0.614334000	-4.936215000	-3.652040000
С	0.525179000	-5.835846000	-2.062347000
Н	1.067906000	-6.497538000	-2.732870000
С	0.777903000	-5.867831000	-0.689223000
Н	1.515131000	-6.554778000	-0.282253000
С	0.076352000	-5.002825000	0.156140000
Н	0.264348000	-5.017099000	1.226867000
С	-0.869328000	-4.118375000	-0.365432000
Н	-1.422992000	-3.466223000	0.301052000
С	-3.709891000	0.313439000	-2.255379000

С	-4.945564000	0.743350000	-1.739313000
Н	-5.692832000	0.000958000	-1.471823000
С	-5.223562000	2.100683000	-1.560885000
Н	-6.185902000	2.405062000	-1.156907000
С	-4.270029000	3.062087000	-1.902568000
Н	-4.484642000	4.119429000	-1.771906000
С	-3.036996000	2.650303000	-2.417557000
Н	-2.292591000	3.388203000	-2.705916000
С	-2.756594000	1.292537000	-2.585820000
Н	-1.803973000	0.989737000	-3.006994000
С	2.278931000	2.066961000	-1.863505000
С	2.138064000	2.362938000	-3.256895000
С	3.062844000	3.209494000	-3.886867000
Н	2.937357000	3.415564000	-4.947270000
С	4.146438000	3.754636000	-3.201831000
Н	4.856225000	4.400491000	-3.711122000
С	4.307529000	3.444782000	-1.852523000
Н	5.147034000	3.859840000	-1.299444000
С	3.398569000	2.624779000	-1.169339000
С	1.053320000	1.773973000	-4.090704000
С	0.820105000	0.386990000	-4.121659000
Н	1.401222000	-0.260496000	-3.474165000
С	-0.118039000	-0.165742000	-4.995000000
Н	-0.272227000	-1.241907000	-5.005632000
С	-0.854612000	0.655405000	-5.854233000
Н	-1.585820000	0.223994000	-6.532644000
С	-0.644731000	2.035799000	-5.827359000
Н	-1.215008000	2.687602000	-6.484564000
С	0.297546000	2.586535000	-4.955222000
Н	0.453861000	3.662289000	-4.942462000

С	3.652220000	2.354995000	0.274529000
С	4.903668000	1.862029000	0.685515000
Η	5.646068000	1.612964000	-0.068132000
С	5.203145000	1.682897000	2.038133000
Н	6.177388000	1.297120000	2.327863000
С	4.255418000	2.000038000	3.013578000
Н	4.486439000	1.868301000	4.067316000
С	3.006693000	2.491473000	2.620582000
Η	2.266056000	2.759705000	3.369770000
С	2.705130000	2.660895000	1.267473000
Η	1.739626000	3.062222000	0.978896000

 Table 6.4.20. Optimized coordinates of Li(THF)₂[Ce(MBP)₂(THF)₂].

Ce	-0.013894100	-0.839065155	0.016165001
0	-0.596160796	1.128953670	1.278161916
0	-2.116271081	-1.167433063	-0.873170915
0	1.058894116	-2.742141666	-1.680262090
0	-1.453933415	4.072392821	-0.066315364
С	-1.708829132	1.207946651	2.043422159
С	-1.644091529	1.278370359	3.474877892
С	-2.853264178	1.280026435	4.187173700
Н	-2.827066973	1.322421645	5.270368434
С	-4.113266472	1.236110666	3.579231027
С	-4.149747094	1.228432352	2.186208120
Н	-5.111727980	1.225504599	1.676168661
С	-2.985482723	1.226393871	1.412528947
С	-3.125474172	1.341496352	-0.104821906
Н	-3.566368871	2.323404015	-0.317362595
Н	-2.134870449	1.347722048	-0.560686510
С	-3.981778007	0.292346755	-0.780376303

С	-3.405952757	-0.957150212	-1.148507441
С	-4.234554009	-1.917874624	-1.816022831
С	-5.573835129	-1.579353487	-2.063314990
Н	-6.212740350	-2.296540735	-2.568171893
С	-6.145871820	-0.353688834	-1.707934208
С	-5.317600785	0.574472620	-1.073660648
Н	-5.716643082	1.552813497	-0.805550180
С	-0.305377187	1.383727533	4.246709453
С	0.560888767	0.122993969	4.034278846
Н	0.022123621	-0.779025699	4.349387424
Н	1.477256606	0.188546858	4.635938746
Н	0.855629843	0.003591150	2.991575569
С	0.482665888	2.628626351	3.777959653
Н	0.713035238	2.567073528	2.713957029
Н	1.427467012	2.710071577	4.331235475
Н	-0.091440573	3.545892823	3.958606457
С	-0.512253245	1.532783921	5.770579897
Н	-1.098791355	2.422872124	6.025709637
Н	0.466349084	1.632521418	6.254478412
Н	-1.006782111	0.658752156	6.209960000
С	-5.379636287	1.195151161	4.405783352
Н	-5.258228309	1.729056498	5.355538719
Н	-5.674206930	0.165275273	4.653420032
Н	-6.222177327	1.648221562	3.870785370
С	-3.690455210	-3.287140330	-2.274843367
С	-3.182611451	-4.082306296	-1.049688977
Н	-2.438669324	-3.511298342	-0.492562216
Н	-2.739749356	-5.037104145	-1.364223705
Н	-4.015600847	-4.311554871	-0.372682621
С	-2.549101229	-3.078259544	-3.297332178

Н	-2.925727367	-2.557751081	-4.186688953
Н	-2.144369556	-4.045216278	-3.625043975
Н	-1.740251301	-2.482312340	-2.872680940
С	-4.758672191	-4.160529430	-2.966267350
Н	-5.603959338	-4.382389844	-2.304631273
Н	-4.307088017	-5.117119709	-3.255717880
Н	-5.150285078	-3.693306184	-3.877205878
С	-7.602539991	-0.055192306	-1.986099224
Н	-7.973986277	-0.629576038	-2.842648782
Н	-7.761044452	1.008201147	-2.202122178
Н	-8.245569302	-0.304855449	-1.129617179
Н	1.374238194	-5.594887600	-3.329781819
С	2.640604178	-3.792404504	-3.148014012
Н	3.056823071	-3.579021785	-4.136538677
С	2.324948382	-2.504915611	-2.367931979
Н	3.084473429	-2.262216377	-1.620967039
Н	2.181389368	-1.639723266	-3.019889457
С	-2.038632581	4.746143491	-1.205797266
Н	-2.805784861	4.091732726	-1.637485063
Н	-1.258217892	4.909811187	-1.953849274
С	-2.642355204	6.046274523	-0.666198744
Н	-3.510395761	6.371341651	-1.246788685
Н	-1.898412183	6.851255462	-0.684185521
Li	0.019772853	2.549107103	-0.006139292
С	-2.983061520	5.668567382	0.783290249
Η	-3.069491463	6.533201467	1.447707676
Н	-3.923780963	5.107274895	0.824145310
С	-1.808055226	4.764768831	1.153336872
Н	-0.945539126	5.353095666	1.493445350
Н	-2.046714838	4.012251610	1.907774774

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0	2.074171723	-1.184216999	0.928048098
0	-1.065444484	-2.739090149	1.723316957
0	1.517917088	4.051869036	0.045375548
С	1.714594862	1.148745269	-2.052435408
С	1.641668114	1.196084953	-3.484424557
С	2.845857745	1.165393662	-4.204322652
Н	2.813124232	1.189759480	-5.287916635
С	4.109079495	1.110417512	-3.603923919
С	4.154753201	1.123465446	-2.211284575
Н	5.120050536	1.109312410	-1.707807528
С	2.995724160	1.152352332	-1.430334057
С	3.146608871	1.278350880	0.085271381
Н	3.613172873	2.250524185	0.286292815
Н	2.158375518	1.312752571	0.544811786
С	3.980756160	0.217091039	0.770671017
С	3.373863835	-1.005915573	1.177626758
С	4.184676190	-1.975086151	1.855466306
С	5.537112821	-1.671015417	2.073584019
Н	6.162317643	-2.394693007	2.586167582
С	6.139397442	-0.471578810	1.680634377
С	5.328803626	0.465913966	1.037670626
Н	5.752180351	1.425822011	0.741729668
С	0.299968893	1.309050860	-4.249808908
С	-0.589507985	0.071028143	-4.001901940
Н	-0.067662373	-0.849313932	-4.291015766
Н	-1.505020382	0.136748436	-4.604827812
Н	-0.885562468	-0.013085845	-2.956097770
С	-0.460006896	2.579493016	-3.804482525
Н	-0.675733708	2.549953342	-2.735980524

Н	-1.411213131	2.662883339	-4.346418200
Н	0.127068696	3.481509145	-4.017932195
С	0.498636575	1.417976673	-5.778068125
Н	1.099388849	2.290783874	-6.058510000
Н	-0.481347068	1.524182600	-6.257773281
Н	0.974268344	0.524728153	-6.199396775
С	5.368848638	1.034062611	-4.438066186
Н	5.254538055	1.564789524	-5.390537655
Н	5.637000054	-0.004099173	-4.681179194
Н	6.225366149	1.469960257	-3.911113841
С	3.608677904	-3.315713452	2.358505903
С	3.057288435	-4.129906805	1.165079310
Н	2.319657864	-3.555371059	0.603755135
Н	2.591598602	-5.060742043	1.515552581
Н	3.871341588	-4.403436874	0.481302007
С	2.491383358	-3.047299987	3.393270426
Η	2.893416079	-2.499602201	4.254809109
Н	2.078521401	-3.994505063	3.765857375
Н	1.683634484	-2.455542691	2.961093663
С	4.663096546	-4.200919249	3.056537352
Н	5.492382103	-4.461980806	2.389016602
Η	4.189875822	-5.137507638	3.375204616
Н	5.080325274	-3.723108648	3.950515331
С	7.608509428	-0.210555823	1.929481873
Η	7.975744839	-0.773748310	2.795242073
Η	7.802242965	0.852716616	2.115165709
Н	8.230350587	-0.501824662	1.070508657
С	-0.730753331	-4.152057916	1.808711163
Н	0.251474516	-4.233415828	2.278757252
Н	-0.674268745	-4.560662235	0.796433848

С	-1.830456252	-4.803213902	2.656560639
Н	-2.628734970	-5.196450681	2.017509064
Н	-1.443584539	-5.627087453	3.263020114
С	-2.352311841	-3.624824864	3.492898478
Н	-1.693606761	-3.435265229	4.348385374
Н	-3.368837921	-3.777931792	3.866745213
С	-2.268507168	-2.475641140	2.494387487
Н	-3.128412371	-2.466854173	1.814155301
Н	-2.162167613	-1.489469969	2.950378761
С	2.185862837	4.682910662	1.164527960
Н	2.838575213	3.937968137	1.633229589
Н	1.434132899	4.996281036	1.895077176
С	2.983423398	5.858481265	0.583539152
Н	3.916584989	6.031599327	1.127047330
Н	2.392153173	6.780502664	0.622586664
С	3.199628749	5.428076802	-0.875969675
Н	3.389123206	6.268185320	-1.550394813
Н	4.037622913	4.725885533	-0.954132070
С	1.884514618	4.716826071	-1.183500885
Н	1.100233834	5.436541309	-1.456101893
Н	1.958697929	3.954922843	-1.962036053
С	0.673573194	-4.122408416	-1.867053791
Н	1.087677908	-4.731472612	-1.052606839
Н	-0.414613835	-4.169655679	-1.834127541
С	1.282563263	-4.511596915	-3.208342134
Н	0.668406889	-4.120488964	-4.027520845
Н	3.366319767	-4.404439612	-2.601399954

Table 6.4.21.	Optimized	coordinates	of Ce	(MBP)	2(THF	$)_2^{-}$.
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Ce	-0.019003234	0.074363850	0.358041358
0	0.845103422	1.480043613	-1.222625129
0	2.051570102	-0.942872523	0.620574468
0	-2.088027272	1.142812812	0.413487212
0	-0.895529124	-1.553044826	-0.971151178
0	1.111836485	1.829283505	2.119036863
0	-1.271392299	-1.355025689	2.357914807
С	1.869355595	1.987317713	-1.904271800
С	1.911850275	3.374772204	-2.276090473
С	3.045342729	3.846341472	-2.950679894
Н	3.097765541	4.894334245	-3.228196303
С	4.126117282	3.031447577	-3.309818914
С	4.035876204	1.675977395	-2.993400479
Н	4.839977285	1.007548349	-3.298648766
С	2.943673349	1.139315892	-2.304987181
С	2.891686966	-0.369520692	-2.071840385
Н	1.860430941	-0.664586013	-1.868496561
Н	3.172181706	-0.851312031	-3.018929927
С	3.805675729	-0.938353010	-0.991770829
С	5.132178500	-1.233829965	-1.318857387
Н	5.477059617	-1.036060896	-2.333440545
С	6.024025689	-1.787162827	-0.398796138
С	5.525694129	-2.084510375	0.874994200
Н	6.210482033	-2.541184960	1.582735205
С	4.201481415	-1.841624210	1.263681171
С	3.312861498	-1.224408588	0.317819956
С	0.730876835	4.328644025	-1.979295587
С	0.955533940	5.746524451	-2.547179866

Н	1.087585556	5.738986110	-3.635419802
Н	1.826964724	6.239851529	-2.100742528
Η	0.078136927	6.365615001	-2.324485484
С	-0.562053417	3.781902410	-2.631951675
Н	-0.789640820	2.779106083	-2.269297108
Н	-0.452785060	3.740210762	-3.723182743
Н	-1.411709039	4.439709757	-2.405477010
С	0.526431425	4.483562009	-0.454014841
Н	-0.341522233	5.124233131	-0.247954771
Н	1.404792508	4.956357830	0.004313866
Н	0.366111944	3.518179472	0.027027551
С	5.338974201	3.602775599	-4.010978674
Н	6.088606374	3.979482880	-3.299621886
Н	5.069989749	4.442637679	-4.662933316
Н	5.838376340	2.846840326	-4.628500594
С	7.469736981	-2.051747176	-0.757947691
Н	7.873205052	-2.907536824	-0.203434560
Н	8.117185027	-1.191682764	-0.531444699
Н	7.585509374	-2.262432446	-1.827888943
С	3.712078318	-2.270808702	2.665420162
С	4.820324574	-2.938076300	3.507402814
Н	5.207823208	-3.848488508	3.035616764
Η	4.408922638	-3.222884289	4.483465895
Η	5.664314014	-2.262609863	3.690494184
С	3.215499759	-1.044917598	3.467620713
Н	4.038848746	-0.338815815	3.636491773
Η	2.840652016	-1.357766325	4.451931063
Н	2.418449652	-0.522361270	2.937083341
С	2.569709460	-3.305090515	2.520571849
Н	1.744083354	-2.896136362	1.936200117

Н	2.192010336	-3.602752712	3.508179218
Н	2.933087714	-4.209696659	2.016644002
С	-3.378518531	1.205265305	0.112035495
С	-4.331470753	1.829199033	0.991027912
С	-5.685625993	1.802984682	0.634228141
Н	-6.416690077	2.257861751	1.295488195
С	-6.160958293	1.231107851	-0.552470478
С	-5.213723439	0.693231240	-1.424241364
Н	-5.546805020	0.285535012	-2.378097257
С	-3.848230518	0.667956327	-1.125483135
С	-2.877959134	0.137506771	-2.180539134
Н	-1.876509918	0.519511837	-1.971249378
Н	-3.181394994	0.571247798	-3.143597350
С	-2.812650597	-1.373786430	-2.372219659
С	-3.746020679	-1.991778127	-3.209988113
Н	-4.505365001	-1.376023712	-3.691042528
С	-3.727932993	-3.364095281	-3.462467527
С	-2.701766971	-4.111307648	-2.871710884
Н	-2.671480046	-5.174346206	-3.088945591
С	-1.718369922	-3.555182529	-2.042804668
С	-1.783839890	-2.149022353	-1.761544822
С	-3.880455380	2.552664455	2.281012002
С	-2.867251968	3.667283004	1.923347444
Н	-2.519358023	4.175194006	2.833192337
Н	-3.338060501	4.421884448	1.280251743
Н	-2.004919651	3.256677543	1.396226361
С	-3.238251925	1.553128373	3.271537703
Н	-2.867022109	2.081051440	4.160541389
Н	-2.409054798	1.014492134	2.811400860
Н	-3.981271780	0.818561294	3.608441976

С	-5.050485942	3.231814378	3.024204194
Н	-5.801703721	2.508972300	3.363410097
Н	-5.554213925	3.981586111	2.403145449
Н	-4.663030351	3.744633694	3.913019525
С	-7.639614202	1.201115730	-0.871603502
Н	-7.815954900	1.184205056	-1.953685737
Н	-8.159377599	2.075789788	-0.461975870
Н	-8.135954415	0.312470436	-0.454251056
С	-4.774329450	-4.023253655	-4.334060721
Н	-5.192410730	-3.317554898	-5.061609105
Н	-5.618131446	-4.411830906	-3.745062704
Н	-4.359545426	-4.871782320	-4.891540401
С	-0.584288387	-4.440829576	-1.476945952
С	-0.680572447	-5.906024454	-1.953396271
Н	-1.608502110	-6.389359448	-1.625518905
Н	0.154504876	-6.476979294	-1.529863090
Н	-0.618068951	-5.991118114	-3.044616307
С	0.789565116	-3.903231339	-1.945046558
Н	1.600326359	-4.520708733	-1.535809889
Н	0.939064606	-2.873186321	-1.620321654
Н	0.862250247	-3.938238472	-3.039584376
С	-0.638177184	-4.466144807	0.068741031
Н	-1.581100973	-4.910562942	0.412747428
Н	-0.557888888	-3.461016248	0.484690832
Н	0.183223309	-5.075017610	0.469766685
С	0.616924637	2.291103714	3.400692322
Н	0.181283250	1.437813538	3.928165313
Н	1.530490699	3.683042791	4.823811270
С	2.659325056	3.430380266	2.938408253
Н	2.261967553	4.389289982	2.585769069

Η	3.715773092	3.567496034	3.186698011
С	2.451387840	2.344199623	1.883722392
Н	2.494667745	2.708947372	0.856032806
Η	3.160927900	1.519202486	2.000699299
С	-2.605011255	-1.897864427	2.138567477
Н	-2.537993910	-2.600108640	1.303926784
Н	-3.269932655	-1.077358735	1.860589218
С	-3.005058000	-2.585415526	3.451385322
Η	-3.601972366	-3.485219905	3.276986398
Η	-3.592896272	-1.905699462	4.078692242
С	-1.649357853	-2.878347238	4.114697701
Η	-1.714593216	-2.990888210	5.200906565
Н	-1.201684812	-3.788002373	3.698252954
С	-0.835853658	-1.655291528	3.701354483
Н	-1.049517698	-0.797294205	4.354064764
Н	0.242657445	-1.821640450	3.673154326
Η	-0.169752641	3.032929030	3.223003360
С	1.823070319	2.903116147	4.114812024
Н	2.377249467	2.132000959	4.662032487

Table 6.4.22. Optimized coordinates of $Ce(O-DiNOx)_2^-$.

Ce	0.122863000	-0.719716000	-0.308000000
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0	-0.500531000	-1.562535000	1.808703000
0	-1.428275000	-1.944580000	-1.568007000
0	2.025260000	0.642318000	1.607283000
0	1.754873000	-2.117797000	-1.219968000
0	1.111098000	1.215016000	-1.198843000
Ν	-1.814570000	-1.021837000	2.025457000

Ν	-1.823498000	-0.759898000	-2.263472000
Ν	2.370519000	-2.250755000	0.064670000
Ν	0.963381000	2.610074000	-1.405740000
С	-2.760791000	-2.110819000	2.464882000
С	-2.792292000	-3.178467000	1.357431000
Н	-2.902105000	-2.717895000	0.372384000
Н	-3.631074000	-3.864197000	1.531437000
Н	-1.869789000	-3.763911000	1.349559000
С	-4.171767000	-1.512691000	2.610884000
Н	-4.197545000	-0.694487000	3.338416000
Н	-4.863548000	-2.288238000	2.959547000
Н	-4.545750000	-1.138064000	1.652380000
С	-2.359410000	-2.794799000	3.790071000
Н	-1.309929000	-3.100581000	3.751825000
Н	-2.972172000	-3.691041000	3.945491000
Н	-2.504835000	-2.140697000	4.655816000
С	-1.685689000	0.087542000	2.944078000
С	-0.964576000	-0.014223000	4.146633000
Н	-0.472515000	-0.950467000	4.378749000
С	-0.859396000	1.066387000	5.020310000
Н	-0.310991000	0.955640000	5.952871000
С	-1.456335000	2.287756000	4.695604000
Н	-1.382271000	3.136128000	5.370598000
С	-2.120511000	2.416043000	3.476700000
Н	-2.549137000	3.375317000	3.196540000
С	-2.234001000	1.337049000	2.586572000
С	-2.926212000	1.549328000	1.263016000
Н	-3.719532000	0.813788000	1.108717000
Н	-3.393045000	2.545846000	1.252272000
С	-1.520296000	-0.893031000	-3.745415000

С	-2.211433000	-2.102061000	-4.408420000
Н	-2.038775000	-3.002945000	-3.812680000
Н	-1.789874000	-2.263342000	-5.407574000
Н	-3.289141000	-1.954414000	-4.525628000
С	-0.000544000	-1.071424000	-3.882630000
Н	0.528480000	-0.268043000	-3.363490000
Н	0.282875000	-1.040756000	-4.941558000
Н	0.324881000	-2.025554000	-3.463128000
С	-1.946669000	0.400991000	-4.458523000
Н	-3.028597000	0.559075000	-4.407217000
Н	-1.667881000	0.343523000	-5.516980000
Н	-1.449279000	1.275260000	-4.026345000
С	-3.216251000	-0.484868000	-1.971317000
С	-4.201978000	-1.477138000	-2.096115000
Н	-3.897945000	-2.482692000	-2.356967000
С	-5.548098000	-1.187904000	-1.875744000
Н	-6.294420000	-1.969899000	-1.992249000
С	-5.933584000	0.105712000	-1.513803000
Н	-6.981112000	0.346119000	-1.353625000
С	-4.952097000	1.077672000	-1.323485000
Н	-5.238876000	2.073400000	-0.991620000
С	-3.590143000	0.798200000	-1.521041000
С	-2.557832000	1.819653000	-1.090127000
Н	-1.704673000	1.885552000	-1.762205000
Н	-3.024705000	2.813045000	-1.014490000
С	2.443609000	-3.717607000	0.458889000
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Н	0.396234000	-3.636274000	1.191290000
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6.5 BIBLIOGRAPHY

- [1] L. J. Nugent, R. D. Baybarz, J. L. Burnett, J. L. Ryan, J. Inorg. Nucl. Chem. 1971, 33, 2503-2530.
- S. B. Adler, *Chem. Rev.* 2004, 104, 4791-4844; H. Inaba, H. Tagawa, *Solid State Ionics* 1996, 83, 1-16; M. Mogensen, N. M. Sammes, G. A. Tompsett, *Solid State Ionics* 2000, 129, 63-94.
- [3] J. Kaspar, P. Fornasiero, N. Hickey, *Catal. Today* 2003, 77, 419-449; J. Kaspar,
 P. Fornasiero, *J. Solid State Chem.* 2003, *171*, 19-29.
- [4] T. Bunluesin, R. J. Gorte, G. W. Graham, *Appl. Catal. B* **1998**, *15*, 107-114.

- [5] S. Park, J. M. Vohs, R. J. Gorte, *Nature* 2000, 404, 265-267; C. T. Campbell, C. H. F. Peden, *Science* 2005, 309, 713-714; C. Ratnasamy, J. P. Wagner, *Catal. Rev.* 2009, 51, 325-440; A. Trovarelli, C. de Leitenburg, M. Boaro, G. Dolcetti, *Catal. Today* 1999, 50, 353-367.
- [6] G. A. Molander, *Chem. Rev.* 1992, 92, 29-68; A. K. Das, *Coord. Chem. Rev.* 2001, 213, 307-325.
- [7] N. A. Piro, J. R. Robinson, P. J. Walsh, E. J. Schelter, *Coordin. Chem. Rev.* 2014, 260, 21-36.
- [8] E. J. Lynch, A. L. Speelman, B. A. Curry, C. S. Murillo, J. G. Gillmore, J. Org. Chem. 2012, 77, 6423-6430.
- D. D. Mendez-Hernandez, J. G. Gillmore, L. A. Montano, D. Gust, T. A. Moore,
 A. L. Moore, V. Mujica, J. Phys. Org. Chem. 2015, 28, 320-328.
- [10] A. V. Marenich, J. Ho, M. L. Coote, C. J. Cramer, D. G. Truhlar, *Phys. Chem. Chem. Phys.* 2014, *16*, 15068-15106.
- [11] S. J. Konezny, M. D. Doherty, O. R. Luca, R. H. Crabtree, G. L. Soloveichik, V.
 S. Batista, *J. Phys. Chem. C* 2012, *116*, 6349-6356.
- [12] A. Elkechai, Y. Mani, A. Boucekkine, M. Ephritikhine, *Inorg. Chem.* 2012, *51*, 6943-6952; A. Maccoll, *Nature* 1949, *163*, 178-179; W. L. Dorfner, P. J. Carroll, E. J. Schelter, *Org. Lett.* 2015, *17*, 1850-1853.
- [13] J. A. Bogart, A. J. Lewis, M. A. Boreen, H. B. Lee, S. A. Medling, P. J. Carroll,
 C. H. Booth, E. J. Schelter, *Inorg. Chem.* 2015, *54*, 2830-2837.

- U. J. Williams, D. Schneider, W. L. Dorfner, C. Maichle-Mossmer, P. J. Carroll,
 R. Anwander, E. J. Schelter, *Dalton Trans*. 2014, 43, 16197-16206.
- [15] A. R. Crozier, A. M. Bienfait, C. Maichle-Mossmer, K. W. Tornroos, R. Anwander, *Chem. Commun.* 2013, 49, 87-89.
- [16] D. Schneider, T. Spallek, C. Maichle-Mossmer, K. W. Tornroos, R. Anwander, *Chem. Commun.* 2014, 50, 14763-14766.
- [17] J. E. Kim, P. J. Carroll, E. J. Schelter, *Chem. Commun.* 2015, *51*, Just accepted.
- [18] P. B. Hitchcock, A. G. Hulkes, M. F. Lappert, *Inorg. Chem.* **2004**, *43*, 1031-1038.
- [19] O. Eisenstein, P. B. Hitchcock, A. G. Hulkes, M. F. Lappert, L. Maron, *Chem. Commun.* 2001, 1560-1561.
- [20] P. L. Arnold, Z. R. Turner, N. Kaltsoyannis, P. Pelekanaki, R. M. Bellabarba, R.
 P. Tooze, *Chem. Eur. J.* 2010, *16*, 9623-9629.
- [21] U. J. Williams, J. R. Robinson, A. J. Lewis, P. J. Carroll, P. J. Walsh, E. J. Schelter, *Inorg. Chem.* 2014, 53, 27-29.
- [22] U. J. Williams, P. J. Carroll, E. J. Schelter, *Inorg. Chem.* **2014**, *53*, 6338-6345.
- [23] B. D. Mahoney, N. A. Piro, P. J. Carroll, E. J. Schelter, *Inorg. Chem.* 2013, 52, 5970-5977.
- [24] N. G. Connelly, W. E. Geiger, *Chem. Rev.* **1996**, *96*, 877-910.
- [25] A. E. V. Gorden, J. Xu, G. Szigethy, A. Oliver, D. K. Shuh, K. N. Raymond, J. Am. Chem. Soc. 2007, 129, 6674-6675.
- [26] J. A. Bogart, A. J. Lewis, S. A. Medling, N. A. Piro, P. J. Carroll, C. H. Booth, E. J. Schelter, *Inorg. Chem.* 2013, *52*, 11600-11607.

- [27] W. L. Dorfner, P. J. Carroll, E. J. Schelter, *Dalton Trans.* **2014**, *43*, 6300-6303.
- [28] H. B. Lee, J. A. Bogart, P. J. Carroll, E. J. Schelter, *Chem Commun.* 2014, 50, 5361-5363.
- [29] D. C. Bradley, J. S. Ghotra, F. A. Hart, J. Chem. Soc., Dalton Trans. 1973, 1021-1023.
- [30] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, V. Voth, J. Cioslowski, D. J. Fox, *Vol. Revision D.01*, Gaussian, Inc., Wallingford, CT, **2009**.
- [31] Institute for Theoretical Chemistry, University of Cologne, http://www.tc.uni-koeln.de/PP/clickpse.en.html; X. Cao, M. Dolg, J. Molec. Struct. (Theochem)
 2002, 581, 139-147; M. Dolg, H. Stoll, H. Preuss, J. Chem. Phys. 1989, 90, 1730-1734.
- [32] Bruker, Bruker AXS Inc., Madison, Wisconsin, USA, 2009.

- [33] Bruker, Bruker AXS Inc., Madison, Wisconsin, USA, 2009.
- [34] G. M. Sheldrick, University of Gottingen, Germany, 2008.
- [35] G. M. Sheldrick, University of Gottingen, Germany, 2007.
- [36] G. M. Sheldrick, Acta Cryst. 2008, A64, 112-122.
- [37] Y. Chen, K. Yu, N. Y. Tan, R. H. Qiu, W. Liu, N. L. Luo, L. Tong, C. T. Au, Z.
 Q. Luo, S. F. Yin, *Eur. J. Med. Chem.* 2014, 79, 391-398.

Appendix

Aqueous lanthanide carbonate chemistry. Attempts to isolate and stabilize Tb^{IV} and Pr^{IV} carbonate complexes.

A1.1 Introduction

Isolation of Pr^{IV} and Tb^{IV} materials with oxide or fluoride anions has been known for over 70 years, and, unlike their Ln^{III} counterparts, these Ln^{IV} materials are intensely colored.^[1, 2] On the other hand, in molecular chemistry, there currently are no examples of isolable, well-defined molecular Pr^{IV} or Tb^{IV} complexes.^[1] Under aqueous conditions, Pr^{IV} and Tb^{IV} easily oxidize water to evolve O₂ leading to isolation of Pr^{III} or Tb^{III} compounds.^[1] Seminal work by Hobart and coworkers has shown spectroscopic evidence of molecular Pr^{IV} and Tb^{IV} carbonate complexes under basic aqueous conditions.^[3] Similar UV-Vis or EXAFS spectroscopic evidence of Pr^{IV} and Tb^{IV} has also been observed with polyoxometalate anions and mixtures of hydroxide and periodate supporting ligands.^[4]

A1.2 Results

A1.2.1 Repeating and expanding on Hobart and coworkers' results

In an effort to isolate Pr^{IV} and Tb^{IV} species through crystallization, Hobart and coworkers' work was repeated. Originally, hexahydrate CeCl₃, PrCl₃, or TbCl₃ salts were 500

added to an aqueous solution that contained 2–5.5 M K₂CO₃ and 1 M KOH.^[3] Then CeCl₃, PrCl₃, and TbCl₃ were oxidized electrolytically and the UV-Vis spectra were recorded.^[3] Chemically, oxygen in air could oxidize CeCl₃ in a basic carbonate solution, where the originally colorless solution turned bright yellow. Ozonation (+1.24 V versus NHE in 1 M hydroxide solutions) was required to oxidize PrCl₃ and TbCl₃, where the oxidized species turned from light green to bright yellow (Pr) or light yellow to dark reddish-brown (Tb).^[3]

Instead of applying one set voltage, cyclic voltammetry was recorded for the Ce, Tb, and Pr carbonate solutions (Figures A1.2.1–A1.2.3). Cyclic voltammetry and UV-Vis spectroscopy were also recorded for Tb and Pr after the solutions were ozonated for 3 or more hours. Cyclic voltammetry of the Ce aqueous carbonate solution showed a quasireversible wave attributed to Ce^{III/IV} oxidation chemistry. Neither Pr nor Tb- either before or after ozonation- showed any significant features in the cyclic voltammetry within water's solvent window.



Figure A1.2.1. Scan rate dependence of the isolated $Ce^{IV/III}$ reduction potential of 0.1 M CeCl₃•6H₂O in a 5.5 M K₂CO₃ aqueous solution. Scan rates ranged from 25 mV/s–1000 mV/s.



Figure A1.2.2. Cyclic voltammogram of the background (left), a 5.5 M K₂CO₃ and 1 M KOH aqueous solution. At right, the cyclic voltammogram of 0.1 M TbCl₃•6H₂O in a 5.5 M K₂CO₃ and 1 M KOH aqueous solution. Scan rate was 500 mV/s.



Figure A1.2.3. Cyclic voltammogram of the background (left), a $5.5 \text{ M K}_2\text{CO}_3$ and 1 M KOH aqueous solution. At right, the cyclic voltammogram of 0.1 M PrCl₃•6H₂O in a $5.5 \text{ M K}_2\text{CO}_3$ and 1 M KOH aqueous solution. Scan rate was 500 mV/s.

A1.2.2 Switching K₂CO₃ for the hydrogen bond donor guanidine carbonate

To isolate the oxidized Pr and Tb carbonate complexes, we hypothesized that building a hydrogen bonding network in the secondary coordination sphere of the Ln carbonate complex would help crystallize the complex. This strategy was used previously to isolate the first mononuclear Ln tetracarbonate complexes.^[5] To this end, guanidine carbonate and tetramethylguanidinium carbonate was used in place of K₂CO₃. Cyclic voltammetry of Ce and Tb in guanidine carbonate solutions were recorded (Figures A1.2.4 and A1.2.6). Although the Ce^{III/IV} couple of CeCl₃•6H₂O was more reversible in solutions of guanidine carbonate compared to solutions of K₂CO₃, the Ce^{IV} oxidation state was stabilized by 100 mV in K₂CO₃ (Table A1.2.1). Cyclic voltammetry of CeCl₃•6H₂O in aqueous tetramethylguanidinium (HTMG⁺) carbonate was significantly different than either the K_2CO_3 or the $(N_3H_5C)_2CO_3$ solutions, showing only the return reduction of the Ce^{III/IV} couple (Figure A1.2.5).



Figure A1.2.4. Scan rate dependence of the isolated $Ce^{IV/III}$ reduction potential of 0.1 M $CeCl_3 \cdot 6H_2O$ in a 5.5 M $(N_3H_5C)_2CO_3$ aqueous solution, where N_3H_5C is the chemical formula for the guanidinium cation. Scan rates ranged from 25 mV/s–1000 mV/s.



Figure A1.2.5. Cyclic voltammogram of the background (left), a 0.93 M (HTMG)₂CO₃ in water. At right, the cyclic voltammogram of 0.1 M CeCl₃•6H₂O in a 0.93 M (HTMG)₂CO₃ aqueous solution. Scan rate was 250 mV/s.

Similar to the K₂CO₃ solutions, Tb in guanidine carbonate- both before and after ozonolysis- showed no significant features in the cyclic voltammogram within water's solvent window. At first glance, ozonolysis and oxidation of Tb and Pr in guanidine carbonate solutions appeared to be successful, resulting in a bright yellow color upon exposure to ozone over the course of several hours (Figures A1.2.7–A1.2.8). However, control experiments revealed that the yellow color observed for Tb and Pr ozonolysis was due to the guanidine carbonate oxidation and not oxidation of the metal centers (Figures A1.2.7–A1.2.8). Ozonolysis of Tb also failed in an aqueous (HTMG)₂CO₃ solution, where, as seen in the cyclic voltammetry of (HTMG)₂CO₃, the HTMG⁺ was even easier to oxidize by ozone (Figure 1.2.5). We also attempted to oxidize Tb(III) through ozonolysis of a 0.4 M TbCl₃ in an aqueous mixture of 2.4 M (NH₄)₂CO₃ and 1 M KOH, however the solution still appeared colorless after several hours of ozonation.



Figure A1.2.6. Cyclic voltammogram of the background (left), a 5.5 M $(N_3H_5C)_2CO_3$ in water. At right, the cyclic voltammogram of 0.1 M TbCl₃•6H₂O in a 5.5 M $(N_3H_5C)_2CO_3$ aqueous solution. Scan rate was 500 mV/s.



Figure A1.2.7. UV-vis spectra of the following solutions: ozonated 0.0100 g PrCl₃•6H₂O in 5.0 mL of an aqueous solution composed of 2.2 M in guanidine carbonate and 1 M KOH (blue), an ozonated aqueous solution that was 2.2 M in guanidine carbonate and 1 M KOH (red), and 0.0100 g PrCl₃•6H₂O in 5.0 mL of an aqueous solution composed of 2.2 M in guanidine carbonate and 1 M KOH (red), and 0.0100 g PrCl₃•6H₂O in 5.0 mL of an aqueous solution composed of 2.2 M in guanidine carbonate and 1 M KOH (red), and 0.0100 g PrCl₃•6H₂O in 5.0 mL of an aqueous solution composed of 2.2 M in guanidine carbonate and 1 M KOH (green, bottom).



Figure A1.2.8. UV-vis spectra of the following solutions: ozonated 0.0132 g TbCl₃•6H₂O in 5.0 mL of an aqueous solution composed of 2.2 M in guanidine carbonate and 1 M KOH (blue), an ozonated aqueous solution that was 2.2 M in guanidine carbonate and 1 M KOH (red), and 0.0132 g TbCl₃•6H₂O in 5.0 mL of an aqueous solution composed of 2.2 M in guanidine carbonate and 1 M KOH (green, bottom).

Because guanidine carbonate could not be used in ozonolysis solutions, further attempts to install a hydrogen bonding network to isolate Tb^{IV} or Pr^{IV} carbonate complexes included ozonolysis of either Tb or Pr in a K₂CO₃ and KOH solution (using Hobart and coworkers' original conditions), and then adding the hydrogen bonding donors after the ozonolysis. Guanidinium carbonate, tetramethylguanidine, guanidine nitrate, proline, diphenylguanidine, guanidine sulfate, guanidine phosphate, guanidine periodate, 1,3-diethyl-2-thiourea, pyrrole, DBU, thiocarbanilide, piperidine, ethylenediamine, arginine, indole, sarcosine, 2,2'-dipyrrolylmethane, and naphthalene-1,8-diamine were added in to the oxidized Tb or Pr carbonate solutions, but none led to isolation of the Tb^{IV} or Pr^{IV} product.

A1.2.3 Comparing carbonate with other inorganic salts

Next, to compare carbonate to different inorganic anions, guanidine sulfate, guanidine phosphate, and guanidine periodate were tested. Electrochemistry of CeCl₃•6H₂O in solutions of guanidine sulfate, phosphate, or periodate was performed (Figures A1.2.9–A1.2.10). The cyclic voltammetry revealed that the carbonate ligand was by far the best at supporting a higher oxidation state, where Ce^{IV} was stabilized 900 mV using the carbonate ligand compared to the phosphate or sulfate ligands (Table A1.2.1). Cyclic voltammetry of guanidine periodate solutions was unsuccessful as the background had a huge signal. Unfortunately we were unable to isolate any cerium complexes with the periodate, sulfate, or phosphate salts to compare the complexes structurally to the cerium carbonate complex. Because a periodate salt had been previously used to achieve Tb^{IV} and Pr^{IV},^[4] ozonolysis of TbCl₃•6H₂O in a guanidine periodate solution was attempted, but the oxidation failed, yielding only colorless solutions.



Figure A1.2.9. Cyclic voltammogram of the background (left), a 2.2 M $(N_3H_5C)_2SO_4$ in water. At right, the cyclic voltammogram of 0.1 M CeCl₃•6H₂O in a 2.2 M $(N_3H_5C)_2SO_4$ aqueous solution. Scan rate was 500 mV/s.



Figure A1.2.10. Cyclic voltammogram of the background (left), a 2.2 M guanidine phosphate in water. At right, the cyclic voltammogram of 0.1 M CeCl₃•6H₂O in a 2.2 M guanidine phosphate aqueous solution. Scan rate was 500 mV/s.

Table A1.2.1. Summary of cyclic voltammetry data of $CeCl_3 \cdot 6H_2O$ in a variety of aqueous salt solutions. Data was obtained from 100 mV/s scan rates unless otherwise noted. Potentials were recorded versus Ag/AgCl. ^{*a*} The E_{pa} was estimated since the second oxidation feature was ill-defined. ^{*b*} E_{pc} was obtained from a 250 mV/s scan rate.

Salt Solution	$\mathbf{E}_{\mathbf{pa}}$	$\mathbf{E}_{\mathbf{pc}}$	ΔE	E _{1/2}
K ₂ CO ₃	-0.045	-0.42	0.37	-0.23
Guanidine	0.015	-0.26	0.27	-0.12
Carbonate				
(HTMG) ₂ CO ₃		-0.27^{b}		
Guanidine	1.36	0.26	1.1	0.81
Phosphate				
Guanidine	1.32	0.34	0.98	0.83
Sulfate	1.67 ^{<i>a</i>}		1.34 ^{<i>a</i>}	1.00^{a}

A1.2.4 Alternative strong oxidants

Finally, alternative oxidants were used to try to oxidize Tb^{III} or Pr^{III} in aqueous carbonate solutions. Oxidants were selected based on their standard reduction potentials in acidic solutions (Table A1.2.2). Several oxidants with lower oxidizing potential than ozone were chosen, like H₂O₂ (1.78 V versus NHE)^[6] and Na₂S₂O₈ (2.1 V versus NHE),^[7] to see if that lessened the probability that the guanidine carbonate would be oxidized. Addition of H₂O₂ to a solution of TbCl₃•6H₂O and guanidine carbonate resulted in a colorless solution and the precipitation of a white solid. The white solid was likely a terbium(III) oxide or a mixed ligand terbium carbonate oxide complex. Considering the Tb(IV) solid state materials were brightly colored, and the Tb(IV) carbonate solutions were also intensely colored, the colorless solution was an indicator that H_2O_2 was an ineffective oxidant for Tb(III). Na₂S₂O₈ addition led to a yellow solution with guanidine carbonate. However, control experiments showed that the yellow solution was caused by the oxidation of the guanidine carbonate, not Tb(III).

Hydroxyl radicals (2.73 V)^[8] or high valent Fe(IV) produced by Fenton reactions had even higher oxidation potentials than ozone.^[8, 9] Either H_2O_2 was slowly added to an aqueous solution containing 0.1 M LnCl₃•6 H₂O (Ln = Pr, Tb), 0.01 M Fe(C₂O₄)•2H₂O, 2.2 M guanidine carbonate, and 0.2 M KOH; or $Fe(C_2O_4) \cdot 2 H_2O$ was added slowly to an aqueous solution containing 0.1 M LnCl₃•6 H₂O (Ln = Pr, Tb), 0.1 M H₂O₂, 2.2 M guanidine carbonate, and 0.2 M KOH. Both orders of addition led to a brown-orange solution and precipitate with the same UV-Vis spectra (Figures A1.2.11–A1.2.13). A control experiment (Figure A1.2.11) where the LnCl₃ was not added to the mixture showed that the same brown color formed even without Pr or Tb present. Further evidence that oxidation to Ln^{IV} did not occur was found in the UV-Vis spectrum of the Fenton reaction with PrCl₃•6H₂O (Figure A1.2.12). The Pr^{III} f-f transitions were observed in the spectrum, indicating that Pr^{III} was not oxidized (Figures A1.2.12–A1.2.13). The Tb^{III} f-f transitions may be present in the Fenton reaction spectrum with TbCl₃•6H₂O, but the relatively high intensity of the peak that gives rise to the brown-orange color of the solution dominated the UV-Vis spectrum below 400 nm, washing out the weak, LaPorte forbidden f-f transitions (Figures A1.2.12–A1.2.13).

Table A1.2.2. List of oxidants and their standard reduction potentials versus NHE in acidic solutions. $E(NHE) = E(Ag/AgCl) + 0.197 \text{ V}.^{[10] a}$ Value obtained from studies of advanced oxidative processes like Fenton chemistry.

Oxidant	Standard Reduction Potential
	(V versus NHE)
F ₂	2.86 ^[6]
OH radical ^a	2.73 ^[8]
O_3	$2.07^{[6]}$
$S_2O_8^{2-}$	2.1 ^[7]
H_2O_2	1.78 ^[6]
MnO_4^-	$1.70^{[6]}$
Au^+	1.69 ^[6]
O_2	1.23 ^[6]



Figure A1.2.11. The UV-Vis spectrum of a Fenton reaction described in the next sentence. To a 10 mL aqueous solution containing 0.01 M $Fe(C_2O_4) \cdot 2H_2O$, 2.2 M guanidine carbonate, and 0.2 M KOH, 0.1 mL of H_2O_2 was added slowly, resulting in an orange-brown solution.



Figure A1.2.12. The UV-Vis spectra of the Fenton reactions described in the next sentences. At left: to a 10 mL aqueous solution containing 0.1 M PrCl₃•6H₂O, 0.1 M H_2O_2 , 2.2 M guanidine carbonate, and 0.2 M KOH, 0.018 g of Fe(C₂O₄)•2 H₂O was added slowly, resulting in an orange-brown solution. At right: to a 10 mL aqueous solution containing 0.1 M TbCl₃•6 H₂O, 0.1 M H₂O₂, 2.2 M guanidine carbonate, and 0.2 M KOH, 0.018 g of Solution containing 0.1 M TbCl₃•6 H₂O, 0.1 M H₂O₂, 2.2 M guanidine carbonate, and 0.2 M KOH, 0.018 g of Fe(C₂O₄)•2 H₂O was solution containing 0.1 M TbCl₃•6 H₂O, 0.1 M H₂O₂, 2.2 M guanidine carbonate, and 0.2 M KOH, 0.018 g of Fe(C₂O₄)•2 H₂O was solution.



Figure A1.2.13. UV-Vis spectra of the following: at left, an aqueous solution containing 0.1 M $PrCl_3 \cdot 6H_2O$ and 5.5 M K_2CO_3 , and at right, an aqueous solution containing 0.1 M $TbCl_3 \cdot 6H_2O$ and 5.5 M K_2CO_3 .

A1.3 Conclusions

Oxidizing Tb^{III} and Pr^{III} is very difficult- it requires a very specific set of conditions in order to succeed. The ligand, solvent, and supporting cations must be stable to very positive reduction potentials. Since water can eventually reduce the resulting Tb^{IV} and Pr^{IV}, there is a short window of time in which the Tb^{IV} or Pr^{IV} complex can be isolated in aqueous solutions. The CO_3^{2-} and OH^- ligands were strong donors and were difficult to oxidize, as shown in the aqueous electrochemistry collected on CeCl₃ complexes in carbonate solutions. With K⁺ as the countercation, which is extremely difficult to oxidize, the oxidation of Tb^{III} and Pr^{III} through ozonolysis was successful. However, NH_4^+ , $(N_3H_5C)^+$, and $(HTMG)^+$ as the countercations led to undesired sidereactions instead of Tb^{IV} or Pr^{IV}. Even though NH₄⁺ and (N₃H₅C)⁺ both are fairly difficult to oxidize based on cyclic voltammetry, these countercations still were counterproductive in these reactions. Use of sodium persulfate $(Na_2S_2O_8)$ as a strong oxidant is worth revisiting. Na₂S₂O₈, a solid powder, is much easier to handle than ozone, and, like ozone, formed a yellow solution with guanidine carbonate, indicating that it may be potent enough to oxidize Tb(III) and Pr(III). It could be possible to use this oxidant in non-aqueous conditions, or in biphasic reactions with water.

A1.4 BIBLIOGRAPHY

- A. W. G. Platt, *The Rare Earth Elements: Fundamentals and Applications*, John Wiley & Sons Ltd., Chichester, United Kingdom, **2012**.
- [2] J. K. Marsh, J. Chem. Soc. 1946, 15-17.

- [3] D. E. Hobart, K. Samhoun, J. P. Young, V. E. Norvell, G. Mamantov, J. R. Peterson, *Inorg. Nucl. Chem. Lett.* 1980, *16*, 321-328.
- [4] A. L. Hector, W. Levason, Eur. J. Inorg. Chem. 2005, 3365-3370.
- [5] G. S. Goff, M. R. Cisneros, C. Kluk, K. Williamson, B. Scott, S. Reilly, W.
 Runde, *Inorg. Chem.* 2010, 49, 6558-6564; W. Runde, M. P. Neu, C. Van Pelt, B.
 L. Scott, *Inorg. Chem.* 2000, 39, 1050-1051.
- [6] W. C. Lyons, G. J. Plisga, Standard Handbook of Petroleum and Natural Gas Engineering, 2nd ed., Elsevier, Published online by: http://app.knovel.com/hotlink/toc/id:kpSHPNGEEA/standard-handbookpetroleum/standard-handbook-petroleum, 2005.
- [7] P. A. Block, R. A. Brown, D. Robinson, in *Proceedings of the Fourth International Conference on the Remediation of Chlorinated and Recalcitrant Compounds*, Monterey, CA, May 24-27, 2004, pp. Paper 2A-05.
- [8] J. C. Barreiro, M. D. Capelato, L. Martin-Neto, H. C. B. Hansen, *Water Res.* 2007, 41, 55-62.
- [9] H. Bataineh, O. Pestovsky, A. Bakac, *Chem. Sci.* 2012, *3*, 1594-1599; C. Walling,
 Acc. Chem. Res. 1998, *31*, 155-157; M. L. Kremer, *J. Phys. Chem. A* 2003, *107*, 1734-1741.
- [10] A. J. Esswein, Y. Surendranath, S. Y. Reece, D. G. Nocera, *Energy Environ. Sci.***2011**, *4*, 499-504.