EXPLORING THE USE OF TRANSITION METALS IN THE SYNTHESIS OF NOVEL METAL-LIGAND MULTIPLE BONDS, AZIDE COMPLEXES, AND UNPRECEDENTED REACTIVITY WITH THE

PHOSPHAETHYNOLATO REAGENT

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ABSTRACT

EXPLORING THE USE OF TRANSITION METALS IN THE SYNTHESIS OF NOVEL METAL-LIGAND MULTIPLE BONDS, AZIDE COMPLEXES, AND UNPRECEDENTED REACTIVITY WITH THE PHOSPHAETHYNOLATO REAGENT

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Investigation of transition metal nitrides by synthetic and physical chemists alike over the past several decades has revealed the relevance of this ubiquitous functional group to industrial and biological processes, as well as their applications in materials and surface chemistry. The research detailed herein involves the synthesis and reactivity of an anionic titanium nitride supported by two PN⁻ ligands (PN⁻ = (N-(2-(diisopropylphosphino)-4-methylphenyl)-2,4,6-trimethylanilide). Topics will include the nucleophilic, electrophilic, and radical transformations observed in the reactivity of this rare functional group. Also using the PN⁻ ligand, the synthesis of a molecular zirconium nitride complex is presented, including the description of the first structurally characterized terminal zirconium nitride, as well as studies that determined this nitride is within the category of a superbase (-36 to -43 p K_b units). The first structurally characterized mononuclear, terminal titanium methylidene stabilized by the PN⁻ ligand will is also described, in addition to spectroscopic characterization. The stabilization of unique oxidation states of zirconium and hafnium are also presented, supported by the PN⁻ ligand. Uranium chemistry of the PN⁻ ligand involving transient nitrides, conducted in collaboration with the Schelter group, is also described. Nearly all of these complexes were scrutinized using computational methods.

A thorough investigation of the reactivity of the phosphaethynolate reagent $Na(OCP)(1,4-dioxane)_{2.5}$ with early transition metals will also be a focus of this thesis. This reagent has gained popularity in recent years due to its diverse reactivity and valuable products within the organic and inorganic communities alike. In reactivity with transition metal scaffolds, we are interested in the use of this reagent both as a P-atom source via salt metathesis and decarbonylation reactions, as well as for the design of novel transition metal scaffolds incorporating this motif. The reactivity of this reagent with scandium, titanium, and vanadium is presented, as well as the characterization of the products isolated in these reactions by spectroscopic and computational methods. The reactivity of the analogue, arsenic Na(OCAs)(dioxane)_{2.5} (arsaethynolate), is also considered.

With access to such unstable and previously unisolable complexes, the work contained herein in one of few comprehensive reports on the reactivity, spectral characterization, and computational elucidation of such rare metal-ligand multiple bonds, and exploration of the products formed in reactivity of these complexes.

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The facilities at Penn and collaborations I have participated in outside of Penn have also allowed me to fully characterize my compounds, and to expand my research horizons. For this I am incredibly grateful. Here at Penn, I have learned in the classroom and also from my experiences as a TA. Teaching has been an integral part of my development as a scientist, often learning as I teach others. As I've learned from grad school, if you think you understand something, you should teach it, and you'll find out you only had a surface understanding of the material before. Along these lines, I have had the good fortune of working with the Penn Center for Teaching and Learning to train new TAs as they arrive at Penn. Given my status as an NSF predoctoral fellow, I was also able to work with students on crafting their own fellowships, which has helped me to develop fellowship writing skills for future endeavors. At Penn, I have been able to participate in a collaboration within the department with Prof. Eric Schelter and his students. Since our office is next door to Prof. Don Berry, I have enjoyed the many discussions I have had with him about my research over the past four years. I have also appreciated the help of Dr. Pat Carroll and Dr. Mike Gau for their assistance in crystallography. I would like to thank the late Dr. George Furst for his help and expertise in NMR spectroscopy. I learned a great deal from him and feel lucky to have been in the last generation of new graduate students to work with him. I would also like to thank Dr. Jun Gu for her NMR expertise. I have learned many techniques from her that I will continue to teach others. Internationally, I have been able to participate in collaborations that have deeply enriched my Ph.D. experience. I would like to thank Dr. Balazs Pinter, with whom I have collaborated for theoretical calculations, as well as Prof. Mookie Baik and students in his lab for computational collaboration as well. I have also been fortunate to collaborate with many others abroad including the lab of Prof. Bas de Bruin, Prof. Hansgörg Grützmacher, and Prof. Karsten Meyer. These interactions have been instrumental in the characterization of the compounds I have synthesized during my Ph.D. Finally, I would like to thank all the friendly staff at Penn Chemistry including Dr. Kersten Forsthoefel, Chris Jeffrey, Chris Sabella, Clare Din, Lautrelle Smith-Gary, Robert Wertz, Kristen Hughes, Judith Currano, Carol Hantraft, Ana-Rita Mayol, Karen Knoepp-Carraro, Bruno Fiorenza, Cuong Nguyen, and Andrei Korchynsky. Whether I have worked with these individuals directly, or enjoyed friendly conversation in the halls, I appreciate what all these individuals do to keep the chemistry department running smoothly. From (before) day one, I have also appreciated the constant support of Graduate Coordinator Kristen Muscat. Every chemistry department could use a Kristen; I certainly know my graduate school experience has been better with her presence at Penn. I also would like to thank Yvonne Kline, who I interacted with quite a bit to place orders for the lab. Also, as safety officer I met with EHRS Sr. Lab

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Most importantly, I would like to thank my family. My wonderful parents Marie and Richard raised me with strong values for what is most important in life, love, and family. I was always taught to value education from a young age, and no matter what I wanted to do, I knew my parents would support me. In the way of education, although it was always extremely valued in my family, I still appreciate that my parents never pushed me. All they wanted for me was to put in my best effort, but more importantly to follow my own path into doing whatever I wanted to do. If I had decided that it was my dream to work at a music shop or become a chef, they would have respected this decision all the same and supported me. Going into chemistry was something I found I excelled at completely on my own, and decided it was what I enjoyed, and they have supported me through the successes and failures that a life in research brings. This was always the case through middle and high school, onto college and ultimately the decision to move across the country to grad school. They have always been there to support me, even from afar, knowing that I was making the best choice to work on establishing myself for a career I truly enjoy. I really don't know how I would have made it through many long days of my Ph.D. without my mom, my very best friend in life, to talk to over the phone almost every day on my walk to or from work. Or let's be honest, often times both, and maybe at some point in between. My mom truly deserves an honorary Ph.D. for always being there by my side, walking right next to me through life everyday. I know she will always be there. Having her as a role model, a woman who pursued a college degree, has always been a driving force for me to pursue higher education. My dad, who will always be Batman to me, is still the one who I know I can call at 3 am when anything breaks down or goes wrong and he will always be my superhero to help me fix it over the phone. I admire my dad for who he has become. Knowing the circumstances he grew up in, I admire the man he has made himself for the benefit of his family and have looked up to him in times of self doubt. I know my parents are incredibly proud of my academic accomplishments, but I always want them to know how proud and lucky I am to be

their daughter, and to have had such wonderful, hard-working and loving parents raise me. They are both heroes to me for different aspects of their lives, and I hope I continue to make them proud for my choices in life both personally and professionally. My brother Justin has also made a tremendous impact on my life, being my mini-dad since birth and always taking care of me. He was the first friend I ever had, and because we were inseparable for the first (more than a) decade of my life, I still hear him in my head trying to influence my decisions in a way that only a big brother can. I consider myself very lucky to be his little sister. I am so thrilled that during graduate school I got to go back home to California to be at his wedding with my lovely sister-in-law, Farrah, who has truly become a sister to me. More recently, they completely filled my life with joy and changed my outlook on life and the world with the birth of my niece Abigail (Abby). I hope that I can be a good role model for her in her life and be an example of a strong woman pursuing a life in a scientific career. I loved her since the moment I saw her over Facetime in the hospital, and I can't wait to move closer to home so I can get to know her and watch her grow. I hope when she grows up she finds something that excites and inspires her to learn as much as chemistry has in my life. I am lucky to also be close with my Aunts Ellen and Colette, who I have gotten to know even more since moving to the northeast and visiting with them in North Carolina. These visits have made lasting memories that I will carry with me no matter where I ultimately settle down. I know my Uncle Hank is excited to have me moving closer to LA again, where we can continue to make memories. Finally, I would like to thank my grandpa, George, who was an engineer at Hughes Aircraft and loves to talk with me about my science. I know my work makes him proud, and I will always remember how talking about my science with him made him light up like I had never seen in my life before. I am thankful that he is still with us to see me accomplish my goal of getting my Ph.D. and that he knows I made it to this point in my life. My family is small, but we are extremely close, and I am thankful to have all of them in my life.

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Chapter 1:

Titanium Nitrides: Synthesis and Reactivity as Powerful Nucleophiles

Introduction. Investigation of transition metal nitrides by synthetic and physical chemists alike over the past several decades has revealed the relevance of this ubiquitous functional group to industrial and biological processes, as well as their applications in materials and surface chemistry.¹⁻⁷ Nitride reactivity can be tuned with the appropriate transition metal ion to render this site either nucleophilic or electrophilic. High oxidation states, generally, can be stabilized with this type of motif and are known to participate in reactivity spanning various transformations⁸ such as N-atom transfer reactions and nitrile-alkyne cross-metathesis,^{9,10} and also to act as surface supports that engage in important industrial processes such as Haber-Bosch¹¹⁻¹⁴ and hydrodenitrogenation and hydrodesulfurization of crude oil.¹⁵⁻¹⁹ The nitride ligand can also provide a realistic snapshot of the active site of nitrogenases through molecular platforms modeling N₂ reductive splitting reactions.^{6,20} Additionally, nitride-based materials are investigated for use in thin films, often derived *via* chemical vapor deposition and by direct current electron sputtering methods.²¹⁻²⁵ Consequentially, the nitride group is extremely important in small molecule activation, in modeling and performing N₂ to ammonia synthesis, and in producing new materials with important electronic properties or applications.

While the synthesis of both terminally bound as well as bridging metal nitrides are rather routine for groups 6-7 transition metals,^{7,26-29} a convergent synthesis of these highly nucleophilic terminal transition metal nitrides for groups 4 or 5 metals has not been documented until recently, and hence, their reactivity has been rather unexplored.³⁰⁻⁴¹ Of particular interest are group 4 terminally bound Ti nitrides, expected to be highly ionic given the disparity in Pauling electronegativities between Ti (1.5) and N (3.0). Only in certain cases could the nitride ligand be installed with protecting Lewis acidic groups (Figure 1.1).⁴²⁻⁴⁴ However, examples of well-defined group 4 nitrides are indeed known, and can be isolated as dinuclear (Figure 1.1), trinuclear (Figure 1.1), tetranuclear, and even hexanuclear species.⁴²⁻⁵¹ While some of these are only stabilized in cubane-type structures, it can be seen that the closest to a mononuclear nitrido complex was that reported by Lancater and coworkers stabilized by a borane (Figure 1.1). However, with the formation of this Lewis acid-

base adduct, this ultimately renders the nitrido moiety closer to an imido moiety in character. Thus, we focused our attention on group 4, especially on Ti, since studies of mononuclear nitride reactivity in this group have largely evaded the reach of the synthetic chemist until recently.^{52,53} The fact that mononuclear titanium nitrides are exceedingly rare is rather surprising since group 4 nitrides have been proposed in N₂ activation and reductive splitting reactions, and the nitride group is often generated in route to the deposition of thin metal nitride films. The elusive nature of terminal titanium nitrides, adjunct with the wealth of useful reactivity established in midtransition metal nitrides, calls for the attention to probe the nature of this highly polarized bond and to determine the degree of nucleophilicity in this rather uncharacterized motif.



Figure 1.1. Examples of molecular titanium nitrides.

Design of a Robust Ligand Scaffold.

Previously, we reported the synthesis of a dinuclear titanium-nitride complex supported by a sterically encumbering β -diketiminate (BDI) ligand (Figure 1.2, left).⁵² This nitride complex, [K][(^tBunacnac)Ti(N)(Ntolyl₂)] where ^tBunacnac = (ArNC^tBu)₂CH; Ar = 2,6-ⁱPr₂C₆H₃, was synthesized by a rather circuitous route involving the treatement of the chlorido precursor (^tBunacnac)TiCl(Ntolyl₂) with NaN₃, which then lost N₂ to form a transient nitridyl radical complex which than abstracted an H-atom from the ligand scaffold to form (^tBunacnac)Ti≡NH(Ntolyl₂) (in 45% yield, accounting for the destruction of ~50% of the ligand scaffold). Finally, this parent imido ligand was deprotonated with benzylpotassium to form the nitrido complex.



Figure 1.2. Synthesis of molecular titanium nitrides salts using β -diketiminato or phosphino-anilido ligands.

However, due to degradation in this ligand scaffold, as well as other decomposition pathways, reactivity in this system was quite restricted. We turned instead to new PN^{-} (PN^{-}) titanium nitrides supported by two ligands (N-(2-= (diisopropylphosphino)-4-methylphenyl)-2,4,6-trimethylanilide), (Figure 1.2, right), derived from a more direct route *via* reduction of the corresponding azide precursor.^{53,54} This ligand framework was selected as it was speculated to be more robust, lacking vulnerable protons in the ligand backbone, as well as the imine group present in β-diketiminates, which can be split under reducing conditions.⁵⁵ Inspired

by Parkin and Woo's five coordinate $L_nTi=X$ complexes^{56,57} ($L_n^{2^-} = meso$ -substituted porphyrin, octamethyldibenzotetraaza[14]annulene; X = chalcogen or imide group), we hypothesized that two PN⁻ ligands could enforce a pseudo tetragonal ligand field environment suitable for the construction of a terminally bound nitride or other isoelectronic atoms or groups. Figure 1.3 depicts a simplified d-orbital splitting diagram for a square planar Ti⁴⁺ fragment supported by four σ donor nitrogen ligands, two of which could also serve as π -donors in a transoid orientation, akin to the ubiquitous porphyrin scaffold. For a d^0 fragment, the empty and hybridized dz^2 as well as π -like dxz and dyz orbitals are available to form a triple bond with an incoming axial ligand. Further evidence that a chelating ligand such as PN⁻ could enable a more robust Ti-X multiple bond (such as a nitride) derived from the fact that terminally bound chalcogenido complexes of the Ti⁴⁺ ion supported by two monoanionic benzamidinato ligands could be isolated as demonstrated in the work by Arnold, with one example of these complexes being $L_2Ti(\mu-0)_2TiL[\eta^{1} NC(Ph)N(SiMe_3)_2$] (L = PhC(NSiMe_3)_2).⁵⁸⁻⁶⁰ However, unlike the highly constrained porphyrin or octamethyldibenzotetraaza[14]annulene dianion ligands, the use of two chelating ligands allows for a more flexible geometric interplay between trigonal bipyramidal and square pyramidal scaffolds when such a system is confronted by a fifth ligand.



Figure 1.3. Simplified d-orbital splitting diagram for a tetragonal ML₄ fragment (d^0) and its compatibility with a nitride ligand N³⁻. Note that dz² hybrization is shown and the role of the p-orbitals in bonding is omitted for clarity in addition to these being too high in energy.

Isolation of the dinuclear, or mononuclear titanium nitride complexes having the anionic core $[(PN)_2Ti \equiv N]^-$, presented an exciting opportunity to exploit such functionality, either by salt elimination followed by complete and incomplete N-atom exchange. This chapter discusses the reactivity of the dinuclear nitride complex $[\mu_2-K(OEt_2)]_2[(PN)_2Ti\equiv N]_2$ (**1.3**) including the access to a rare parent imide ligand, in addition to a variety of other uncommon imide species. In addition to examining the basicity of this nitride, we report salt elimination reactions, some of which result in complete N-atom transfer to the substrate. In conjunction with solution-state spectroscopic studies of these species we also report solid state ¹⁵N NMR spectroscopy (*via* MAS) to further elucidate the electronic nature of the Ti-N_{nitride} bond and the effect on this bond by cation coordination. Finally, with the aid of theory

we also report a detailed study of the $Ti-N_{nitride}$ multiple bond and the role of the counter cation in the $Ti-N_{nitride}$ bonding.

Results and Discussion

Synthesis of a Titanium Dinitrogen Complex and a Titanium Nitride.

Recently, we reported that the azide complex $(PN)_2Ti(N_3)$ (1.2), readily prepared from $(PN)_2$ TiCl (1.1) and NaN₃, could undergo reductive extrusion of N₂ with KC₈ in Et₂O to form the nitride salt $[\mu_2-K(OEt_2)]_2[(PN)_2Ti\equiv N]_2$ (**1.3**) along with graphite (Scheme 1.1).⁵³ This route circumvents a radical mechanism commonly observed in the formation of the parent imido (*t*^{Bu}BDI)Ti≡NH(Ntolyl)₂,⁵² which results in much lower yield due to the sacrificial H-atom source deriving from the ligand scaffold. In addition, the introduction of the nitride group directly from reduction of the azide skips an additional deprotonation step involving the parent imido. To our surprise however, we found that the dinitrogen complex $(PN)_2Ti=N=N=Ti(PN)_2$ (1.4) (note that this was originally synthesized by Dr. Maria Carroll, a species prepared in 49% yield from KC₈ reduction of (PN)₂TiCl under N₂, cannot be fragmented with excess reductant (such as KC₈) to form two equivalents of complex **1.3**. This route would undoubtedly provide a more atom economical route to **1.3** using a vast resource such as atmospheric N₂. Complex **1.4** is a diamagnetic species, displaying one single PN chemical environment by both ¹H and ³¹P NMR spectra, and as shown in Figure 1.4, its solid-state structural diagram reveals a topologically linear TiN₂Ti moiety where the N–N bond has been partially reduced by 2e⁻ (1.252(8) Å versus 1.0976 Å in free N_2). Although a formal N_2^{4-} ligand would intuitively account for its diamagnetic nature, the observed N–N and Ti–N distances and computed bond orders argue for **1.4** possessing two Ti(III) centers that strongly antiferromagnetically couple, i.e. its core can be best characterized formally as Ti=N=Ti. In stark contrast to **1.4**, Fryzuk and co-workers have observed N₂ splitting reactions with low-valent titanium reagents, via reduction of (NPN)TiCl₂ (NPN²⁻ = PhP(CH₂SiMe₂NPh)₂), to produce 7

transient titanium nitrides which then undergo insertion into the Ti–P linkages of the ligand.⁶¹ For us, we attribute the lack of reactivity in **1.4** to being reduced is likely to be kinetic as well as thermodynamic in nature. Akin to vanadium(II) dinitrogen complexes prepared in our group, we propose the rigid PN ligands in a putative species such as 1.4^{2^-} (1.4^{2^-} represents **1.4** being reduced by two electrons) to disfavor the mixing of triplet and singlet subspaces that is critical for the dinitrogen cleavage process.⁶² In addition, the reactive nature of **1.3** suggests the formation of a nitride from N₂ to be thermodynamically less stable than 1.4^{2^-} , a common trait also observed in vanadium nitrides versus dinitrogen complexes. Compound **1.4** is remarkably stable, failing to react with electrophiles as well as reductants, and further attempts to functionalize the N₂ have been unsuccessful. Arnold and coworkers have observed formation of a similar complex to **1.4** using benzamidinate ligands.⁵⁹



Scheme 1.1. Synthesis of complex 1.3 from reductive splitting of an azido complex
1.2 (synthesized from chloride complex 1.1) with KC₈. Also shown is the attempted synthesis of 1.3 from reductive splitting of N₂ in 1.4 with excess KC₈.



Figure 1.4. Solid state structure of complex **1.4** showing thermal ellipsoids at the 50% probability level. Selected metrical parameters (distances Å in and angles in °) are shown in Table 1.1. Two molecules of residual benzene were removed for clarity.

Reactivity Studies of the Titanium Nitride with Electrophiles.

Although bridging derivatives of group 4 methyl imides have been reported,^{63,64} terminally bound examples are unknown. Accordingly, we treated compound **1.3** with MeI in toluene at 25 °C causing an immediate color change from orange to dark red. Workup of the reaction mixture and recrystallization of the solid from pentane at -35 °C allowed for the isolation of the methyl-imide complex (PN)₂Ti \equiv NMe (**1.5**)

in ~95% yield (Scheme 1.2). The ³¹P NMR spectrum of **1.5** features a singlet at 12.45 ppm, shifted slightly upfield from **1.3** (7.23 ppm), while the methyl imide resonance is observed at 2.63 ppm in the ¹H NMR spectrum and correlated to a resonance at 57.4 ppm in the ¹³C NMR spectrum. A solid-state structural analysis confirmed the monomeric nature of **1.5** (Figure 1.6), and revealed a short Ti–N distance of 1.709(3) Å with a linear Ti–N–Me angle of 178.5(4)° (Table 1.1). While the geometry of **1.3** ($\tau_5 = 0.529$) is between idealized trigonal bipyramidal ($\tau_5 = 1$) and square pyramidal ($\tau_5 = 0$), conversion to the imide species **1.5** ($\tau_5 = 0.721$) alters the geometry more towards a trigonal bipyramidal environment.

Treatment of **1.3** with certain azide reagents can also result in salt elimination. For example, combining **1.3** with N₃SiMe₃ yields KN₃ along with the trimethylsilylimide $(PN)_2Ti=N{SiMe_3}$ (1.6) in ~90% yield as a deep red colored material (Scheme 1.2). Complex **1.6** shows similar spectroscopic features to **1.5** with the trimethyl resonance being observed at 0.217 ppm in the ¹H NMR spectrum. An IR spectrum of the reaction mixture confirms the formation of KN₃ (v_{N3} = 2030 cm⁻¹). The synthesis of complex **1.6** was also confirmed by monitoring reactivity of **1.3** with Me₃SiCl by ¹H NMR spectroscopy. To probe the reaction mechanism with Me₃SiN₃ (Scheme 1.3), a ¹⁵N enriched sample of **1.3**, $[\mu_2$ -K(OEt₂)]₂[(PN)₂Ti \equiv ¹⁵N]₂ (**1.3**)-¹⁵N was prepared and treated with Me₃SiCl to independently prepare (PN)₂Ti= 15 N{SiMe₃} (1.6)-¹⁵N. As expected, a resonance at 534 ppm in ¹⁵N NMR was attributable to the imide isotopomer species **1.6**-¹⁵N. A further experiment of **1.3**-¹⁵N with Me₃SiN₃ reproduced the signal for **1.6**-¹⁵N in the ¹⁵N NMR spectrum, showing that this reaction is proceeding by salt elimination rather than by cycloaddition and silutropic shifts (Scheme 1.3). This mechanism follows the predicted behavior in reactivity with regard to the nucleophilic nitride attacking at the electrophilic silyl group of the azide. Consistent with our hypothesis, there was no reactivity between **1.3** and adamantyl azide or trisylazide. The solid-state structure of 1.6 shows an overall similar geometry to **1.5** but where the Ti–N distance has now been elongated to 1.730(2) Å, consistent with the presence of an electrophilic SiMe₃ group. This is similar to reported Ti–N distances in Ti=NSiMe₃ functionalities,⁶⁵⁻⁶⁹ although some shorter derivatives have been reported with distances as low as ~1.6 Å.⁷⁰ The Ti–N–Si is slightly bent at nitrogen at 168.06(1)° (Figure 1.6, Table 1.1). In stark contrast to **1.5**, the geometry of **1.6** remains quite similar to **1.3**, confined between trigonal bipyramidal and square pyramidal ($\tau_5 = 0.557$).

In the pursuit of rare functional imide groups we treated complex **1.3** with ClPⁱPr₂. Upon addition of the electrophile, the reaction mixture changed color from orange to dark green. Workup of the reaction mixture allowed for isolation of a green colored solid in 94.1% yield and ¹H, ³¹P and ¹³C NMR spectral data were consistent with formation of the phosphonylimide $(PN)_2Ti=N\{P'Pr_2\}$ (1.7) (Scheme 1.2). Phosphonylimides of early transition metals are rare functionalities, with only a few reported examples.^{71,72} The ³¹P NMR spectrum features a broadened resonance $(\Delta v_{1/2} = 16 \text{ Hz})$ attributable to the phosphonylimide at 152 ppm. Interestingly, the resonance for the P of the PN ligand appears as two broadened features centered at 13.73 ppm $\Delta v_{1/2}$ = 30 Hz. Although quite broad, it is clear that these two signals account for two separate *PN* ligand resonances, indicating a solution-state behavior that renders these two resonances inequivalent. Additionally, when cooled, the broadened resonances slightly sharpen although P-P coupling with phosphonylimide was unresolved, as shown in Figure 1.5, with a sample measured at 219 K in toluene d_8 . We propose that, unlike other imides reported in these studies, the phosphonylimide results in inequivalency in the PN ligands due to steric clash of ⁱPr groups of the phosphonylimide with the 'Pr groups of the PN ligand. The molecular structure of **1.7** features a Ti–N–P angle of 162.21(6)° and elongation of the Ti–N bond to 1.753(3) Å (Figure 1.6, Table 1.1).



Figure 1.5. ³¹P{¹H} NMR spectrum of **1.7**, taken at 219 K in C₇D₈, 162 MHz.

This latter metrical parameter is similar to hydrazido complexes reported by Mountford and Odom, with Ti=N distances varying from 1.703-1.76 Å. Shorter Ti–N distances have been reported in some instances, attributable to NR₃⁺ groups on the imido moiety.⁷³⁻⁷⁷ Complex **1.7** crystallizes in a monoclinic crystal system in the space group I2/a, and the molecule lies along a two-fold axis. Consequently, this two-fold axis causes disorder in the ^{*i*}Pr groups of the phosphonyl group. Hence, we restrain ourselves from discussing metrical parameters. However, the gross solid-state structure of **1.7** reveals a bent TiN^{*i*}Pr₂ moiety thus rendering both phosphorus groups on the PN ligands inequivalent (Figure 1.6).



Scheme 1.2. Synthesis of compounds **1.5-1.9** from **1.3** and various electrophiles. All reactions were performed in toluene at 25 °C due to the insolubility of **1.3** in aliphatic solvents.

Early-transition borylimidos are rare functional groups in inorganic chemistry. Only two examples of titanium have been reported, both being derived from nonconventional routes involving B–B, B–H, and B–C bond activation reactions.^{52,78} Our ability to prepare nitride **1.3** allows us to explore simple salt-metathesis reactions to construct these types of functionalities. Hence, treating **1.3** with ClBcat (cat = catechol) resulted in clean conversion to the borylimido (PN)₂Ti=N{Bcat} (**1.8**) in ~89% yield after subsequent workup of the reaction mixture (Scheme 1.2). Unlike the phosphonylimide, the borylimido does not display any unusual NMR spectroscopic features, with a ³¹P NMR spectrum featuring one singlet resonance at 17.19 ppm. A solid-state structural study of **1.8** shows a topologically linear Ti=N=B (175.00(1)°) due to the Lewis acidic nature of the boryl group. Consequently, the former titanium nitride distance Ti–N has elongated to 1.7312(2) Å, akin to **1.6** (Figure 1.7, Table 1.1). In accord with these other rare examples, the linear character of the Ti=N=B bond angle demonstrates delocalized π electrons in these bonds. It should also be noted that crystal of the Ti(III) complex one [(PN)₂Ti=N{Bcat}][K(dme)₄] was also isolated, although it is likely attributable to residual **1.3** remaining in the solution during crystallization. Although the formulation of this complex is unknown, it presents another unique example of a titanium imido complex. Further crystallographic information on this complex can be found in the Appendix of Molecules.⁷⁹



Figure 1.6. Solid state X-ray structure of complexes **1.5-1.7** (Left to Right) depicting thermal ellipsoids at the 50% probability level. H atoms and the substituents of one depicted PN ligand have been omitted for clarity. A molecule of pentane has been omitted from **1.5** and **1.7** for clarity.

Terminally bound imides with a hydrogen substituent (referred to as a parent imide) are exceptionally rare in early transition metals, with the only documented examples for group 4 at the time this work was done being (BDI)Ti \equiv NH(Ntolyl₂)^{52,80,81} $(BDI^{-} = [ArNCMe]_2CH \text{ or } [ArNC^tBu]_2CH; \text{ Ar } = 2,6^{-i}Pr_2C_6H_3), \text{ and } trans-$ TiCl₂(NH)(OPPh₃)₂.⁸¹Not surprisingly, pK_a information on parent imides is unknown, but one would expect the imide moiety to be a weak acid given the highly polarized nature of the nitride group. Conversely, the basicity of terminal nitride anions is also unknown. While these species have rarely been reported, it has been hypothesized that some parent imide complexes exist as transient, non-isolable intermediates.¹⁴ Since formation of **1.3** does not traverse through a parent imide, we treated this species with a weak acid not only to allow us entry to this rare moiety but also to provide some information about the basicity of the nitride ligand in **1.3**. Hence, exploring various sources of a proton established HN{SiMe₃}₂ ($pK_a = 25.8$, THF)⁸² to cleanly yield the parent imide (PN)₂Ti=NH (1.9) in ~84% (Scheme 1.2). The imide resonance was observed in the ¹H NMR spectrum as a broad feature at 5.07 ppm $(\Delta v_{1/2} = 9.1 \text{ Hz})$ while the ³¹P NMR spectrum displayed a singlet at 15.66 ppm, a resonance shifted downfield from **1.3**. Characterization by single crystal X-ray crystallography revealed that compared to all other compounds synthesized in reactivity with **1.3**, complex **1.9** favors a more trigonal bipyramidal geometry, $(\tau_5 =$ 0.769), which contrasts the geometry observed for the few known group 4 transition metal parent imides having coordination numbers of four and five.⁸¹ One notable feature is the nearly linear orientation of the phosphine groups (P–Ti–P, 177.16(3)°) when associated to other (PN)₂Ti scaffolds (Table 1.1). It is also noted that single crystal X-ray diffraction revealed that for this parent imide species, the molecule also co-crystallizes in a 4:1 ratio with a secondary product in which the N atom of the imide has inserted into the phosphorous arm of the PN ligand, and the H atom of the parent imide has formed a bond to titanium. The metal-hydride bond that is observed as a result of this transformation will be discussed in Chapter 2. While the ylide Ph_3PCH_2 (p $K_b = -22$, DMSO) failed to deprotonate the imide, attempts to use stronger bases resulted in decomposition products presumably due to the reactivity of the titanium nitride product. It was found independently that complex **1.9** gradually decomposes over time thus precluding reactivity with stronger bases. However, 15

attempts to protonate the nitride with diisopropylamine, HN^iPr_2 (p $K_a = 36$, THF),⁸³ resulted in no reaction. This observation allowed us to narrow the p K_a range of the parent imide to within 26-36 based on these set of control experiments. Given these p K_a ranges for the nitride, we are able to estimate the p K_b of **1.3** on the order of -20, in accord with such a moiety being a strong base and nucleophile as demonstrated through our reactivity.



Scheme 1.3. Above: Proposed mechanism for formation of **1.6**, traversing through an azametallacycle (upper). This mechanism was proved incorrect *via* ¹⁵N-labeling experiments (lower).



Figure 1.7. Solid state X-ray structure of complexes **1.8** and **1.9** depicting thermal ellipsoids at the 50% probability level. H atoms and the substituents of one depicted PN ligand have been omitted for clarity.

Table 1.1. Selected metrical parameters for complexes **1.3-1.9** showing bond distances in Å and angles in degrees. X represents the substituent on the nitride or formal nitride ligand.

For **1.3**, X = K; **1.4**, X = N; **1.5**, X = C; **1.6**, X = Si; **1.7**, X = P; **1.8**, X = B; **1.9**, X = H. τ_5 Represents $(\beta - \alpha)/60$ where $\beta > \alpha$ are the two greatest valence angles of the coordination center.⁸⁴

Complex	1.3	1.4	1.5	1.6	1.7	1.8	1.9
Ti-N	1.674(2)	1.832(3)	1.709(3)	1.730(2)	1.753(3)	1.7312(2)	1.747(2)
Ti-N _{PN}	2.173(2)	2.107(3)	2.093(3)	2.095(2)	2.0695(2)	2.0521(1)	2.0605(1)
Ti-N _{PN}	2.170(2)	2.091(2)	2.096(3)	2.0736(2)	2.0695(2)	2.0685(1)	2.0987(2)
Ti-P	2.6779(8)	2.6763(8)	2.6777(1)	2.6917(7)	2.7041(6)	2.6718(5)	2.6810(5)
Ti-P	2.6853(8)	2.7306(8)	2.6824(1)	2.7094(7)	2.7041(6)	2.6532(6)	2.6656(1)
N-X	2.729(2)	1.250(4)	1.431(5)	1.737(2)	1.732(3)	1.395(2)	0.860(0)
P-Ti-P	167.42(3)	166.03(4)	173.14(3)	167.14(3)	171.16(3)	175.289(2)	177.16(3)
Ti-N-X	135.40(1)	1.250(4)	178.5(4)	168.06(1)	162.21(6)	175.00(1)	180.0(0)
N_{PN} - Ti - N_{PN}	135.67(8)	128.79(1)	129.87(1)	134.35(8)	130.02(1)	131.33(6)	130.99(6)
P-Ti-N _{PN}	74.88(6)	76.30(7)	75.24(8)	73.77(6)	75.88(5)	75.27(4)	74.94(4)
P-Ti-N _{PN}	75.11(6)	75.18(7)	75.13(8)	75.46(5)	75.88(5)	76.18(4)	75.70(5)

P-Ti-N	95.83(8)	96.99(2)	93.46(1)	99.59(7)	94.419(2)	92.67(5)	92.52(6)
P-Ti-N	96.75(8)	98.31(2)	93.37(1)	96.25(7)	94.419(2)	91.96(5)	90.22(7)
τ_5	0.529	0.621	0.721	0.557	0.686	0.733	0.769

Complete N-Atom Transfer of the Titanium Nitride.

A salt elimination reaction concurrent with complete N-atom transfer could be accomplished when complex **1.3** was treated with $ClC(0)^{t}Bu$ in toluene. Immediate formation of a purple solution is evidenced upon addition of the acid chloride, and workup of the reaction mixture followed by NMR spectroscopic characterization confirmed this purple species to be the oxo complex $(PN)_2$ Ti $\equiv 0$ (1.10) (Scheme 1.4) in near quantitative yield, 96%. Examination of the reaction mixture also revealed the formation of another product, which was identified as the organic nitrile NC^tBu based on NMR spectroscopic comparison to an authentic sample. The formation of the nitrile was monitored by NMR spectroscopy to be formed in the same ratio as the oxo as identified by integration. A similar transformation involving N for O/Cl exchange was originally reported by Cummins using nitride complexes such as $N \equiv W(N[iPr]Ar)_3$ $(Ar = 3,5-Me_2C_6H_3)$ or the salt $[Na][N=Nb(N[Np]Ar)_3]$ $(Np = CH_2^tBu).^{31,85}$ Likewise, Veige more recently reported N-atom transfer to various acid chlorides using ${[^{t}BuOCO]Mo \equiv N]Na(DMF)}_{2} [^{t}BuOCO^{3-} = 2,6-C_{6}H_{3}(6-^{t}BuC_{6}H_{3}O)_{2}].$ In these studies, the authors were able to isolate the acylimido intermediate [^{*t*}BuOCO]Mo=NC(O)^{*t*}Bu, and mechanistically probe for an azametallacylobutene species en route to N for O exchange.⁸⁶ While we do not observe either of these intermediates, this proposed mechanistic pathway is shown for clarification in Scheme 1.5.



Scheme 1.4. Salt metathesis, and N for O-atom transfer to form the oxo complex 1.10.

Complex **1.10** was characterized by ¹H and ³¹P NMR spectroscopy and the latter displayed a sharp singlet at 13.3 ppm. Although there are no diagnostic signatures in the ¹H NMR spectrum, monitoring the reaction mixture by ¹H NMR spectroscopy revealed clean formation of a resonance at 0.77 ppm consistent with the pivaloyl nitrile (NC^{*t*}Bu). Single crystal X-ray diffraction studies of **1.10** are in accord with a five-coordinate, mononuclear complex having a terminal oxo group, with a Ti \equiv O length of 1.644(2) Å, well within the range of many reported terminal titanium oxo moieties.^{58,87} Rather unsurprisingly, the oxo complex closely parallels the molecular geometry of the parent imide, complex **1.9**, with a τ_5 value of 0.769 and very similar P–Ti–P angle of 179.08(3). Furthermore, we explored the unusual purple color of this Ti(IV) complex *via* UV-vis analysis. The extremely low intensity absorption observed at 550 nm ($\epsilon = 174.8 \text{ M}^{-1} \text{ cm}^{-1}$) possibly corresponds to a similar phenomenon like that observed in MnO₄⁻, where the complex absorbs yellow light to promote a LMCT band.

Complex **1.3** can also transfer the nitride atom to other carbonyl containing groups such as the ketene O=C=CPh₂ (Scheme 1.3). Accordingly, addition of the ketene to **1.3** rapidly produces the signature purple color indicative in formation of **1.10**, as confirmed by both ¹H and ³¹P NMR spectroscopy. However, upon addition of the ketene a salt is also produced which could be readily separated from the mixture *via* filtration. Given the insoluble nature of this yellow solid, we proceeded to treat it

with Me₃SiCl, immediately forming a salt (presumably KCl) and a neutral species which was unequivocally identified to be the azaallene Me₃SiN=C=CPh₂ based on ¹H NMR spectroscopic comparison to a literature report.⁸⁸



Figure 1.8. Solid state X-ray structure of complex **1.10**, depicting thermal ellipsoids at the 50% probability level. H atoms and the substituents of one depicted PN ligand have been omitted for clarity.



Scheme 1.5. Proposed mechanistic route of formation of **1.10**. Acylimido **1B** then converts to azametallacylobutene **1C**. Finally, retrocycloaddition to form NC^{*t*}Bu and **1.10**.

Solid State ¹⁵N NMR Spectroscopic Studies of Titanium Nitrides.

Isolation of dinuclear and mononuclear nitrides of titanium presented us with a rare opportunity to investigate their axial symmetry. Hence, we prepared the 50% ¹⁵N enriched complex **1.3**-¹⁵N and converted it to the terminal nitride [K(2,2,2-Kryptofix)][(PN)₂Ti \equiv ¹⁵N] by addition of the cryptand (2,2,2-Kryptofix = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane).⁵³ We were able to analyze this discrete salt by magic angle spinning (MAS) ¹⁵N NMR spectroscopy. This work was conducted by Prof. Gang Wu. In accord with our expectations,^{38,52} this species reveals a significantly downfield chemical shift ($\delta_{iso} = 902$ ppm), which is attributable to a highly deshielded terminal nitride species (Figure 1.9). As presented

in Figure 1.9, the simulated ¹⁵N NMR solid state spectrum agrees well with experimentally collected values in both solid and solution state phases (δ = 958 ppm).⁵³ Tensor components span a large chemical shift anisotropy (CSA) of nearly 1500 ppm, with $\delta_{11} \approx \delta_{22} = 1392 \pm 50$ and $\delta_{33} = -78 \pm 50$ ppm. Such anisotropy has been similarly observed in other mononuclear metal nitride species, namely ¹⁵N=Mo(N['Bu]Ar')₃ (Ar' = 3,5-Me₂C₆H₃) and [K(OEt₂)]₂[('^{Bu}BDI)Ti=¹⁵N(Ntolyl₂)]₂ ('^{Bu}BDI⁻= [ArNC'^{Bu}]₂CH; Ar = 2,6-'Pr₂C₆H₃), which also have a range of several hundred ppm for CSA in their tensor components.^{52,89-91} The observed ¹⁵N NMR chemical shift tensors were then used to compute the axial symmetry component, $\kappa = 3(\delta_{22} - \delta_{iso})/(\delta_{11} - \delta_{33}) = 1 \pm 0.2$. Gratifyingly, the κ value close to unity supports the triply bound nature of the Ti-nitride moiety in [K(2,2,2-Kryptofix)][(PN)₂Ti=¹⁵N], and which is the favorable bonding due to a pseudo-tetragonal environment shown in Figure 1.3 (*vide supra*). The κ value observed here deviates notably from axial symmetry values reported previously for less-symmetrical Ti-nitride functionalities supported by the BDI ligand,⁵² which system has a $\kappa = 0.64$.



Figure 1.9. Simulated (top) and observed (bottom) solid state MAS ¹⁵N NMR spectrum of $[K(2,2,2-Kryptofix)][(PN)_2Ti\equiv^{15}N]$. Note: small amounts of impurities in observed spectrum are from parent imido complex **1.9**. This is due to formation of this complex during data collection, given the MAS setup is not 100% air free.

Computational Studies Scrutinizing the Titanium Nitride Functionality.

To understand the observed characteristic reactivity and some of the measured physicochemical properties of the titanium nitride functionality Prof. Balazs Pinter carried out a comprehensive computational and theoretical study on the putative anion $[(PN)_2Ti\equiv N]^-$ and complexes **1.3** and $[K(18-crown-6)][(PN)_2Ti\equiv N]$, that we have recently characterized. Using the X-ray structures as guiding geometries, the slightly truncated models were fully optimized using the BLYP functional^{92,93} in combination with the Def2-TZVP(-f) basis set.⁹⁴ The structural modifications included only the replacement of two *para*-methyl substituents to hydrogens in each PN⁻ ligand and were introduced to facilitate an all-electron DFT investigation for systems of the size of 1.3, which still consists of 232 atoms after truncation. Dispersion has been also taken into account during optimizations using Grimme's D3 method.⁹⁵ Dispersion turned out to be a critical component of our computational practice as it significantly contributed to finding accurate equilibrium geometries for both the dimer species, 1.3 and 1.4, and for monometallic systems, that is $[(PN)_2Ti\equiv N]^-$, $[K(18-crown-6)][(PN)_2Ti\equiv N]$. It is important to note that a substantial improvement in the computed distances of weak Ti-P and K+...N interactions was observed for the latter systems when compared to our earlier simulations without dispersion.⁵³ As a matter of fact, the computational protocol outlined at the end of the chapter might offer useful practical solutions to few of the inborn weaknesses of standard DFT for such very extended transition-metal- and alkali-metal-containing systems. For example, one might obtain more realistic results for the notoriously overestimated bond lengths of weak metal-ligand interactions when taking into account inter ligand dispersion as well as one might be able to get rid of the surreal behavior of alkali-metal(s) in simulations, which was recently noted by Holland and co-workers to be detrimental for a systematic computational study on the alkali metal effect on Fe=N=N=Fe functionalities.⁹⁶ As Figure 1.10 reveals, the computed equilibrium structures are very similar to the experimentally determined molecular
geometries established by single crystal X-ray diffraction studies. Also, in excellent agreement with our experiments, calculations predict the ¹⁵N NMR spectroscopic chemical shifts to be 913 ppm, 970 ppm and 878 ppm using the slightly truncated models of $[(PN)_2Ti\equiv N]^-$, $[K(18\text{-crown-6})][(PN)_2Ti\equiv N]$, and **1.3**, respectively. These two benchmarks convincingly imply that our computer models capture the most salient features of the electronic structure of these molecular systems reasonably well and that the introduced structural simplification is acceptable. In particular, the agreement between the computed and experimentally observed effect of alkali-metal coordination on ¹⁵N NMR spectroscopic resonances supports the notion that the corresponding electronic structure changes are captured computationally in at least a plausible fashion. Thus, a detailed analysis of the bonding is justified and it promises to reveal relevant aspects about how nearby alkali-metal ions influence the bonding and spectroscopic properties of the Ti=N functionality.



Figure 1.10. Equilibrium geometries for $[(PN)_2Ti\equiv N]^-$, $[K(18\text{-}crown-6)][(PN)_2Ti\equiv N]$ and **1.3** together with the most important structural metrics computed and determined by single crystal X-ray diffraction (grey). Also given are the computed and measured ¹⁵N NMR chemical shifts of the nitride centers as well as Mulliken charges

of titanium, q(Ti), and the nitride center, q(N) together with the Mayer bond order (BO) index of the Ti \equiv N interaction.

As noted in our earlier communication,⁵³ various computed electronic structure descriptors imply that the main difference in the Ti–N_{nitride} bonding is the different covalent/ionic character of the bond in the monomeric species [K(18-crown-6)][(PN)₂Ti \equiv N] and [(PN)₂Ti \equiv N]⁻. Namely, the Ti \equiv N bond in [(PN)₂Ti \equiv N]⁻ exhibits a greater degree of covalent character than in $[K(18 - \text{crown-6})][(PN)_2\text{Ti} \equiv N]$. In the case of the latter, the proximity of the K⁺ ion encapsulated in crown ether electrostatically stabilizes the highly charged nitride center and, concomitantly, induces a density shift from the Ti center towards the Nnitride. This electron density shift induced by the proximity of K⁺ renders the titanium-nitride bond more ionic in [K(18-crown-6)][(PN)₂Ti=N] than in [(PN)₂Ti=N]⁻. As a matter of fact, the different ionic ionic character can be clearly witnessed in the computed atomic charges of Ti (0.53 *e* in $[(PN)_2Ti\equiv N]^-$ and 0.87 *e* in $[K(18-crown-6)][(PN)_2Ti\equiv N])$ and N (-0.63 *e* in $[(PN)_2Ti\equiv N]^-$ vs. -0.88 e in [K(18-crown-6)][(PN)_2Ti\equiv N]) (Figure 1.10). The reduced bond order in [K(18-crown-6)][(PN)₂Ti \equiv N] (2.36 vs. 2.54 in [(PN)₂Ti \equiv N]⁻) also conforms to a lower degree of covalent character of the $Ti \equiv N$ bond in this structure. These pronounced differences in Ti–N_{nitride} bonding are further enhanced with the presence of two potassium ions in **1.3**. In particular, atomic charges (q(Ti) = 1.02 eand q(N) = -0.975 e) as well as the reduced bond order of 2.27 indicate the higher ionic and lower covalent character of the Ti≡N bond in **1.3** to either [K(18-crown-6)][(PN)₂Ti \equiv N] or hypothetical [(PN)₂Ti \equiv N]⁻.

More thorough insights into the electronic structure changes induced by the alkali-metal ion are gained through a close inspection of the molecular orbitals (MOs) that describe the bonding of the titanium-nitride functionality. A conceptual MO-diagram that highlights the most relevant molecular orbitals of the metal–nitride interactions has been given in Figure 1.3, implying one σ - and two π -bonds and a lone pair at N_{nitride}. Instead of the expected four MOs representing these functions, however, Figure 1.11 depicts six occupied orbitals for each Ti \equiv N functionality merely 25

because the σ -bond as well as one of the Ti–N π -bonds can be defined by two MOs. In detail, the Ti–N_{nitride} σ -interaction of each Ti≡N functionality in Figure 1.11 is represented by two MOs, σ^{b} and σ^{a} , which evolve due to the formation of a bonding (b) and an anti-bonding (a) combination with a π -type orbital of the PN⁻ ligand(s). Similarly, orbitals π_{1}^{b} and π_{1}^{a} , which appear again as a bonding/anti-bonding pair with a PN⁻ ligand orbital, together characterize one of the Ti–N_{nitride} π -interactions. In addition, π_{2} represents the other π -type interaction which lies about in the P–Ti–P plane whereas, as hypothesized in Figure 1.3, the lone pair at N_{nitride} has a strong component of s atomic orbital character and it is of low energy.

Although the crown ether-encapsulated K⁺ breaks the symmetry in [K(18-crown-6][(PN)₂Ti \equiv N] as well as it alters the ordering of the orbitals, the computed MOs characterize the same Ti-N_{nitride} interactions as for [(PN)₂Ti \equiv N]⁻. Moreover, the analogous MOs can also be intuitively recognized for the dimer species **1.3** (Figure 1.11), for which only the symmetric combinations are illustrated for clarity. The side-by-side comparison of the corresponding MOs reveal that the σ -interaction, mostly σ^a , as well as π_1^a experiences a significant change in character when being affected by counter alkali metal ion(s); the atomic contribution of Ti decreases whereas that of N_{nitride} increases in these MOs as going from [(PN)₂Ti \equiv N]⁻ to [K(18-crown-6)][(PN)₂Ti \equiv N] or **1.3**. This difference in corresponding MOs conforms to the additional polarization of the Ti-N_{nitride} bond that was discussed above which was supported with charge distribution measures and bond descriptors. Finally, the stabilization effect of the nearby cation on the electron rich N_{nitride} can be clearly witnessed in the computed orbital energies, which are much more negative in **1.3** and in [K(18-crown-6)][(PN)₂Ti \equiv N] than in [(PN)₂Ti \equiv N]⁻.

The observed and computed ¹⁵N NMR chemical shift of $N_{nitride}$ is not only useful for precisely determining the identity of these species in solution, but can also be utilized as a diagnostic tool that gives direct information on the chemical environment about $N_{nitride}$ and, as such, on the Ti– $N_{nitride}$ interaction. In particular, the gradual upfield shift of 50–30 ppm when going from $[(PN)_2Ti\equiv N]^-$ to [K(18-crown6)][(PN)₂Ti \equiv N] and **1.3** suggests a subtle change in the electronic structure due to the nearby cation(s). In order to put this trend of ¹⁵N_{nitride} chemical shift into context with the underlying electronic structures it is critical to realize that magnetic shielding of heavy nuclei does not directly correlate to the electron density at the nucleus. Rather, heavy nuclei, such as ¹⁵N, have access to low-energy molecular orbitals of p and d-type atomic contributions that make the electron density around these nuclei very dynamic in the sense that local fluctuations of the electron cloud become more prevalent in an external magnetic field. The magnetic shielding that results from these electron density fluctuations is conventionally referred to as paramagnetic shielding, σ^p , and is typically more sensitive to the changes in chemical bonding than the diamagnetic shielding, σ^{d} , which originates from tightly-bound electron density at the nucleus. In a recent study from our lab, the basic relationships of such density fluctuations with MOs, shielding tensors and chemical shifts was discussed and, by scrutinizing vanadium- and molybdenum-cyclo-P₃ complexes, it was shown how a thorough analysis of shielding tensors of heavy nuclei can lead to a conceptual understanding of the bonding characteristics of unusual transition metalligand interactions.⁹⁷

To understand what makes the N_{nitride} nucleus more shielded in the case of K⁺ ligated species, Balazs computed and analyzed the ¹⁵N magnetic shielding tensors of the above-described slightly truncated versions of the complexes [(PN)₂Ti≡N]⁻, [K(18-crown-6)][(PN)₂Ti≡N] and **1.3**. In general, the magnetic shielding at a NMR-active nucleus and the resulting chemical shift can be calculated from first principles to a reasonable degree of accuracy^{90,98-100} and, accordingly, the computed values shown in Figure 1.10 also agree well with measured solution-state ¹⁵N NMR spectroscopic resonances. In addition, the above-discussed large chemical shift anisotropy (CSA) is reproduced computationally (~1500 ppm *vs.* 1470 ppm) for [(PN)₂Ti≡N]⁻ as well as the corresponding principal components of the shielding tensor ($\delta_{11} = 1562.2$ ppm, $\delta_{22} = 1285.0$ ppm and $\delta_{33} = 61.9$ ppm) are in line with the experimentally determined components in solid state ($\delta_{11} \approx \delta_{22} = 1392 \pm 50$ ppm and $\delta_{33} = -78 \pm 50$ ppm for [K(2,2,2-Kryptofix)][(PN)₂Ti≡N]. Due to omitting the K(2,2,2-27)

Kryptofix)⁺ counter ion and other condensed phase effects in the simulations, however, a difference of about 280 ppm between δ_{11} and δ_{22} appears in silico, which manifests in an underestimated axial symmetry component ($\kappa = 0.63$ vs. app. 1) for the computationally considered model system, $[(PN)_2Ti\equiv N]^-$. As expected, the diamagnetic term displays a narrow range of shielding contributions with computed σ^d values of 339.7, 341.3 and 347.7 ppm for ${}^{15}N_{nitride}$ in $[(PN)_2Ti\equiv N]^-$, $[K(18\text{-crown-6})][(PN)_2Ti\equiv N]$ and **1.3**, respectively. The paramagnetic contribution, on the other hand, differs significantly with computed shielding parameters of -1050.3, -996.3 and -967.3 ppm, respectively. These values illustrate the general concept mentioned above that σ^p dominates the overall shielding of heavy nuclei and, thus, determines the chemical shift δ_{avg} against a reference.

As demonstrated recently,⁹⁷ the thoroughly analysis of the paramagnetic contribution to the shielding can be challenging, because one has to decompose the sum of a great number of individual magnetic fields originating from occupiedunoccupied orbital pair couplings that actually couple through the angular momentum operator. In addition, the magnetic fields generated by what is most spontaneously understood as electron density fluctuations are hard to visualize or imagine. Finding a few numbers of distinguishing orbital-pairs that make a decisive contribution and that are characteristic for the certain species under investigation is the key to understanding such paramagnetic shielding. Nevertheless, one occupied orbital could be pinpointed, σ^a , whose contribution to shielding changes notably in the presence of a nearby K⁺. For example, the total paramagnetic shielding contribution of σ^a is -504.6 ppm in [(PN)₂Ti \equiv N]⁻ whereas it drops to -128.0 ppm in [K(18-crown-6)][(PN)₂Ti \equiv N] and even becomes shielding (157.6 ppm) in **1.3**. This σ^a MO couples most intensively with the vacant π^* orbitals corresponding to the antibonding combinations of Ti– $N_{nitride}$ π -bonds, e.g. π_1^* illustrated in Figure 1.11. In this context it is worth noting that Morokuma, Schrock, Griffin and Cummins reported very similar findings for the unusual ³¹P NMR chemical shielding tensors of terminal phosphide (M≡P) complexes of molybdenum and tungsten.⁹⁰ Namely, in the latter

systems the $\sigma(M \equiv P)$ and $\pi^*(M \equiv P)$ MO mixing makes the primary contribution to the ³¹P paramagnetic shielding due to the components of the applied magnetic field which are oriented perpendicular to the M≡P bond. Figure 1.11 also illustrates how the paramagnetic shielding contribution of $\sigma^a \leftrightarrow \pi_1^*$ mixing varies for each nitride species. Most importantly, the coupling of these orbitals in an external magnetic field induces a density flow that has a deshielding effect in $[(PN)_2Ti\equiv N]^-$, whereas it generates a shielding effect in [K(18-crown-6)][(PN)₂Ti≡N] and **1.3**, where the K⁺ affects the bonding characteristics. The energy gap (ΔE) between interacting orbitals is also given in Figure 1.11, as the coupling efficiency is inversely proportional to the energy difference between the interacting orbitals.⁹⁸ For example, the ³¹P NMR chemical shift of triple bonded phosphorous has been found to correlate very well with the σ - π^* energy gap, also the significance of energy gap of coupling orbitals was shown in determining the chemical shielding of phosphorous nuclei in metal-cyclo-P₃ complexes.⁹⁷ The very small differences in energy gaps (ΔE in Figure 1.11), however, cannot account for the qualitatively different paramagnetic shielding effects of σ - π^* coupling in the studied systems. Rather, the qualitative difference of paramagnetic contributions, i.e. deshielding in $[(PN)_2Ti\equiv N]^-$ and shielding in K⁺-ligated systems, implies that the spatial distribution of these molecular orbitals alters upon K⁺ coordination. Accordingly, the localization of σ^a on the nitride center as well as the localization of π_1^* on Ti in K⁺-ligated systems results in a constructive orbital overlap when these orbitals couple through the angular momentum operator, in contrast to the destructive overlap (deshielding effect) in naked [(PN)₂Ti≡N]⁻. Hence, the upfield shift of ¹⁵N_{nitride} resonance is linked to the K⁺ induced electronic structure change of the titanium-nitride functionality as demonstrated through a quantum chemical analysis of the corresponding shielding tensors.

Finally, our calculations reveal, in line with the N···K distances larger than 2.7 Å, that the $Ti\equiv N$ ···K⁺ interaction is merely electrostatic in nature without any sign of covalent or weak non-covalent contribution. This electrostatic interaction, beyond inducing the above-scrutinized change of the Ti \equiv N functionality, represents the main

source of thermodynamic stabilization and driving force for forming well-structured complex molecular ensembles such as $[K(18\text{-}crown\text{-}6)][(PN)_2Ti\equiv N]$ and the dimer **1.3**. The genuine kinetic stabilization effect that originates from the resulting integrity and compactness of these complex arrangements is substantial as the reactive Ti \equiv N functionality is completely hindered from incoming reactants.



Figure 1.11. Most relevant occupied MOs for $[(PN)_2Ti\equiv N]^-$, $[K(18\text{-crown-6})][(PN)_2Ti\equiv N]$ and **1.3** describing the electronic structure of the Ti \equiv N functionality. One of the unoccupied orbitals, π_1^* , which is critical for the paramagnetic shielding of N_{nitride} is also depicted.

Conclusion.

In these initial studies, it was demonstrated that the titanium nitride is a powerful nucleophile, able to do substitution chemistry for various R groups in order to synthesize unique imide scaffolds. Particularly of interest to us is the parent imide complex, given that this could provide a model for reduction of nitrogen to ammonia. Moreover, in the absence of light this imide could be isolated and kept in a bottle, unusual for an unsubstituted parent imide species.

With a thorough study of the reactivity of the titanium nitride with electrophiles, including complete N-atom transfer, this called into question whether the nitride was restricted to this behavior, or if this paradigm could be reversed. That is, is this titanium nitride only a classical nucleophile or could nitride reactivity be tuned to instead react as a nitridyl, or perhaps even electrophilic? In the next chapter, the divergent reactivity of this nitride species under differing reaction conditions will be discussed. Further, in Chapter 3 it will be shown how nitride synthesis can be extended down group 4 metal complexes.

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Experimental Details

General Procedures

Unless otherwise stated, all operations were performed in a M. Braun Lab Master double-dry box under an atmosphere of purified dinitrogen or using high vacuum standard Schlenk techniques under an argon atmosphere. NMR spectra were recorded on a Bruker AV-II 500 MHz spectrometer for ¹³C spectra, and a Bruker AVIII 400 MHz spectrometer for ¹H and ³¹P{¹H} spectra. ¹H NMR spectra are reported with reference to residual proteo solvent resonances of benzene- d_6 at 7.16 ppm. ¹³C{¹H} NMR spectra were referenced to solvent resonances of benzene-d₆ at 128.06 ppm. $^{31}P{^1H}$ NMR spectra were referenced to external H_3PO_4 (0 ppm). Pentane, hexanes, benzene, and toluene were purchased from Fisher Scientific and stabilizer-free diethylether (Et₂O) and tetrahydrofuran (THF) were purchased from Sigma Aldrich. Solvents were sparged with argon for 20 minutes and dried using a two-column solvent purification system where columns designated for pentane, hexanes, benzene, and toluene were packed with Q5 and alumina respectively, and columns designated for Et₂O and THF were packed with alumina. Deuterated benzene and deuterated toluene were purchased from Cambridge Isotope Laboratories (CIL) and were dried over 4 Å sieves, and degassed by freeze-pump-thaw cycles. All solvents were transferred into a dry box and were stored over 4 Å sieves. All sieves were heated to 200 °C under vacuum overnight prior to use. Celite used for filtrations was also heated to 200 °C under vacuum overnight prior to use. Compounds 1.1, 1.2, 1.3, **1.3**-¹⁵N, and [K(2,2,2-Kryptofix)][(PN)₂Ti=¹⁵N] were prepared following published procedures.⁵³ The UV-Vis absorption spectra were obtained in a J-young valve 1 cm quartz cell on a Cary 5000 UV-Vis-NIR. Elemental analyses were performed on a FLASH EA 1112 Series CHN analyzer (Thermo Finnigan).

[(PN)₂Ti=N]₂ (1.4): In a 20 mL scintillation vial, (PN)₂TiCl (**1.1**) (700 mg, 0.916 mmol, 1 equiv.) was dissolved in 5 mL toluene as a dark brown solution. To this 33

solution was added a 5 mL slurry of KC₈ (123.8 mg, 0.916 mmol, 1 equiv.) while stirring with a glass coated metal stirbar. The mixture was stirred overnight at room temperature, during which time it became a deep red color. This solution was filtered over a thick pad of celite. The product is highly insoluble, so the celite pad was washed with 80 mL of toluene in order to extract the product free of alkali. The filtrate solution was concentrated to 50 mL, and then layered with 20 mL of hexane. Storage at -35 °C overnight resulted in the formation of a magenta powder, which was isolated over a frit, followed by washing with 10 mL cold toluene. (673 mg, 0.458 mmol, 49%). Single crystals suitable for X-ray diffraction could be grown from a concentrated benzene solution after one week at room temperature. ¹H NMR (400 **MHz, 298 K, benzene-d₆**): δ 7.04 (br, $\Delta v_{1/2}$ = 8 Hz, 2H, meta-ArH_{Mesityl}), 6.85 (dd, ³J_H- $_{\rm H}$ = 4.12 Hz, 1H, meta-ArH_{Tolyl}), 6.73 (s, 1H, meta-ArH_{Tolyl}), 5.85 (dd, ³J_{H-H} = 4.10 Hz, 1H, ortho-ArH_{Tolyl}), 2.87 (s, 3H, CH_{3Tolyl}), 2.73 (br, 1H, P-CH-CH₃), 2.23 (s, 3H, ortho-CH_{3Mesityl}), 1.87 (s, 3H, para-CH_{3Mesityl}), 1.40 (d, ³J_{H-H} = 4.16 Hz, 3H, P-CH-CH₃), 0.54 (br, 3H, P-CH-CH₃), 0.29 (sept, ³J_{H-H} = 4.13 Hz, 1H, P-CH-CH₃). ³¹P{¹H} NMR (162 MHz, **298 K, benzene-d₆**): δ 18.98 (s, 2P, PN). Unfortunately, the poor solubility of this complex prevented us from obtaining reliable ¹³C NMR spectra. Anal. calcd for C₉₄H₁₃₀N₆P₄Ti₂ (including 1 benzene per dinuclear complex): C: 72.20 H: 8.38 N: 5.37 Found: C: 73.18 H: 9.19 N: 3.96 The N2 of the bridging dinitrogen complex was not detected based on the analysis found.

(PN)₂Ti≡NMe (1.5): In a 20 mL scintillation vial, compound 1.3 (200 mg, 0.105 mmol, 1 equiv.) was dissolved in 5 mL toluene. To this light orange solution was added methyl iodide dropwise by microsyringe (13.3 µL, 0.210 mmol, 2 equiv.) while stirring at room temperature. The color of the solution changed during addition of methyl iodide from light orange to dark red. The solution was stirred at room temperature for 15 minutes. Volatiles were removed under vacuum, resulting in a dark red residue. The residue was triturated three times with five mL of pentane. The resulting powder was dissolved in 5 mL pentane and filtered through celite to remove alkali. Crystallization from the 5 mL filtrate solution overnight at −35 °C resulted in $\frac{34}{100}$

the isolation of red crystals (149.9 mg, 0.198 mmol, 94.6%), which were suitable for X-ray diffraction studies. ¹H NMR (400 MHz, 298 K, benzene-d₆): δ 6.91 (br, 2H, *meta*-ArH_{Mesityl}), 6.78(s, 1H, *meta*-ArH_{Tolyl}), 6.89 (br, $\Delta v_{1/2} = 4$ Hz, 1H, *meta*-ArH_{Tolyl}), 5.84 (dd, ³J_{H-H} = 4.10 Hz, 1H, *ortho*-ArH_{Tolyl}), 2.63 (s, 3H, N-CH₃), 2.69 (br, $\Delta v_{1/2} = 20$ Hz, 3H, P-CH-CH₃), 2.23 (s, 3H CH_{3Tolyl}), 2.17 (s, 3H, *para*-CH_{3Mesityl}), 2.47, (br, 3H, P-CH-CH₃), 0.81, (br, 3H, P-CH-CH₃), 0.34 (br, 1H, P-CH-CH₃) ³¹P{¹H} NMR (162 MHz, 25 °C, benzene-d₆): δ 12.48 (s, 2P, PN). ¹³C{¹H} NMR (125.8 MHz, 298 K, benzene-d₆): δ 161.8 (Ar-*C*), 147.3, (Ar-*C*), 133.4 (Ar-*C*), 131.9 (Ar-*C*), 123.8 (Ar-*C*), 112.9 (Ar-*C*), 112.8 (Ar-*C*), 57.44 (NCH₃), 20.9 (PCH(CH₃)₂), 20.7 (PCH(CH₃)₂), 18.4 (Ar-CH₃), 16.0 (Ar-*C*H₃).

(PN)₂Ti=NTMS (1.6): In a 20 mL scintillation vial, compound 1.3 (166 mg, 0.088 mmol, 1 equiv.) was dissolved in 3 mL toluene as a light orange solution. To this solution was added trimethylsilylazide dropwise via a microsyringe (23 µL, 0.175 mmol, 2 equiv.) while stirring. The solution rapidly turned to a deep red, along with precipitation of a solid that deposited on the walls of the vial. The volatiles were taken to dryness after 5 minutes of stirring, and the resulting red residue was triturated with 5 mL pentane resulting in a dark red powder. This powder was dissolved in 5 mL pentane, filtered through celite, and concentrated to 3 mL pentane. Cooling to -35°C overnight resulted in the isolation of dark red crystals suitable for X-ray diffraction (128.1 mg, 0.157 mmol, 90.2%). ¹H NMR (400 MHz, 298 K, benzene-d₆): δ 7.00 (s, 1H, meta-Ar H_{Tolvl}), 6.89 (br, $\Delta v_{1/2}$ = 8 Hz, 2H, meta-Ar $H_{Mesitvl}$), 6.80 (dd, ³J_{H-H} = 4.12 Hz, 2H, meta-ArH_{Mesityl}), 5.81 (dd, ³J_{H-H} = 4.56 Hz, 1H, ortho-ArH_{Tolyl}), 2.53 (br, 3H, P-CH-CH₃), 2.23 (s, 3H, CH_{3Tolyl}), 2.14 (s, 3H, para-CH_{3Mesityl}), 1.02 (s, 6H, ortho-CH_{3mesityl}), 0.217 (s, 9H, NSiMe₃). ³¹P{¹H} NMR (162 MHz, 298 K, benzene-d₆): δ 13.33 (s, 2P, PN). ¹³C{¹H} NMR (125.8 MHz, 298 K, benzene-d₆): δ 161.7 (Ar-C), 147.6 (Ar-C),133.9 (Ar-C), 133.6 (Ar-C), 133.3 (Ar-C), 124.2 (Ar-C), 113.4 (Ar-C), 20.9 (PCH(CH₃)₂), 20.6 (PCH(CH₃)₂), 5.3 (TMS-CH₃).

(PN)₂Ti=NPⁱPr₂ (1.7): In a 20 mL scintillation vial, compound 1.3 (213 mg, 0.112 mmol, 1 equiv.) was dissolved in 5 mL toluene as a light orange solution in a 20 mL vial and cooled to $-35 \text{ }^{\circ}\text{C}$. After cooling for 20 minutes, to this solution was added chlorodiisopropylphosphine dropwise via microsyringe (34.5 µL, 0.225 mmol, 2 equiv.) while stirring. The solution rapidly turned dark green, and colorless alkali deposited on the walls of the vial. The volatiles were taken to dryness after five minutes, and the resulting red residue was triturated with 5 mL pentane to give a dark green powder. This powder was dissolved in 5 mL pentane, filtered over celite, and concentrated to 3 mL pentane. Cooling to -35 °C overnight resulted in the isolation of large dark green hexagonal crystals suitable for X-ray diffraction (182.2 mg, 0.212 mmol, 94.1%). ¹H NMR (400 MHz, 298 K, benzene-d₆): δ 7.05 (s, 2H, meta-Ar H_{Tolyl}), 6.95 (br, $\Delta v_{1/2}$ = 20 Hz, 2H, meta-Ar H_{Tolyl}), 6.82 (br s, 2H, meta-Ar H_{Mesityl}), 5.86 (br, $\Delta v_{1/2}$ = 20 Hz, 1H, ortho-Ar H_{Tolyl}), 2.95 (br, 3H, P-CH-CH₃), 2.86 (s, 3H, CH_{3Tolvl}), 2.21 (s, 3H, CH_{3Tol}), 2.16 (s, 3H, para-CH_{3Mesitvl}), 2.12 (s, 6H, ortho-CH_{3mesitvl}), 1.96 (sept, ³J_{H-H} = 4.31 Hz, 1H, N PCH(CH₃)₂), 1.61, 1.49 (br, 3H, NPCH(CH₃)₂) 0.30 (br, $\Delta v_{1/2}$ = 28 Hz, 1H, P-CH-CH₃). ³¹P{¹H} NMR (162 MHz, 298 K, **benzene-d**₆): δ 152.33 (br, $\Delta v_{1/2}$ = 16 Hz, 1P, NP^{*i*}Pr₂), 13.65 (br, $\Delta v_{1/2}$ = 30 Hz, 2P, PN). ¹³C{¹H} NMR (125.8 MHz, 298 K, benzene-d₆): δ 137.8 (Ar-C), 133.6 (Ar-C), 130.2 (Ar-C), 127.5 (Ar-C), 124.7 (Ar-C), 113.2 (Ar-C), 22.1 (NPCH(CH₃)₂), 20.9 (NPCH(*C*H₃)₂), 20.7 (P*C*H(CH₃)₂), 20.6 (PCH(*C*H₃)₂), 18.5 (Ar-*C*H₃), 14.4 (Ar-*C*H₃).

(PN)₂Ti=NBCat (1.8): In a 20 mL scintillation vial, compound 1.3 (297.5 mg, 0.157 mmol, 1 equiv.) was dissolved 5 mL toluene. To this light orange solution was added a 5 mL colorless toluene solution of chlorocatecholborane at room temperature (48.4 mg, 0.314 mmol, 2 equiv.). The solution immediately turned a deep green in color. After stirring at room temperature for 15 minutes, a colorless solid was observed on the walls of the vial, and all volatiles were removed under vacuum. The green residue was triturated once with 7 mL pentane, and then dissolved in 10 mL pentane. The solution was filtrated through celite, and then the filtrate solution concentrated to 5

mL. Large green block crystals formed after cooling the solution overnight to $-35 \,^{\circ}$ C (239.5 mg, 0.278 mmol, 88.5%). Suitable crystals for single crystal X-ray diffraction studies were grown from the saturated hexane solution at $-35 \,^{\circ}$ C. ¹H NMR (400 MHz, **198 K, benzene-d_6):** δ 7.05 (dd, ³J_{H-H} = 4.10 Hz, 1H, *meta*-Ar*H*_{Tolyl}), 6.92 (br, $\Delta v_{1/2}$ = 8 Hz, 2H, *meta*-Ar*H*_{Mesityl}), 6.84 (s, 1H, *meta*-Ar*H*_{Tolyl}), 6.82 (s, 2H, Ar-*H*_{catechol}), 6.75 (m, ³J_{H-H} = 8.10 Hz, 2H, Ar-*H*_{catechol}), 5.87 (dd, ³J_{H-H} = 8.21 Hz, 1H, *ortho*-Ar*H*_{Tolyl}), 2.96 (s, 3H, *CH*_{3Tolyl}), 2.35 (sept, ³J_{H-H} = 4.55 Hz, 1H, P-CH-CH₃), 2.26 (s, 3H, *ortho*-CH_{3Mesityl}), 2.13 (s, 3H, *para*-CH_{3Mesityl}), 1.40 (br, 3H, P-CH-CH₃), 0.80 (br, 3H, P-CH-CH₃), 0.23 (sept, ³J_{H-H} = 4.00 Hz, 1H , P-CH-CH₃). ³¹P{¹H} NMR (162 MHz, 298 K, benzene-d_6): δ 17.19 (s, 2P, *P*N). ¹³C{¹H} NMR (125.8 MHz, 298 K, benzene-d_6): δ 161.4 (Ar-*C*), 148.8 (Cat-*C*), 145.6 (Ar-*C*), 138.5 (Ar-*C*), 134.5 (Ar-*C*), 133.6 (Ar-*C*), 131.8 (Ar-*C*), 21.5 (PCH(CH₃)₂), 21.3 (PCH(CH₃)₂), 20.9 (PCH(CH₃)₂), 20.6 (PCH(CH₃)₂), 20.0 (PCH(CH₃)₂), 17.9 (Ar-CH₃), 15.9 (Ar-CH₃). No ¹¹B resonances were observed.

(PN)₂Ti≡NH (1.9): Experimental note: Synthesis of 1.9 must be conducted in the absence of light; further chemical transformations proceed in ambient light. Compound 1.3 (300 mg, 0.16 mmol, 1 equiv.) was dissolved in 6 mL toluene in a 20 mL vial. To this light orange solution was added a 5 mL colorless toluene solution of hexamethyldisilazane (66.3 µL, 0.32 mmol, 2 equiv.) at room temperature. Immediate color change to a magenta color was observed, and the solution was stirred for 15 minutes at ambient temperature. The solution was taken to dryness and the deep red oil was triturated with 5 mL of pentane three times. This red powder was then dissolved in 7 mL pentane, filtered over celite, and concentrated to 4 mL. Cooling overnight to −35 °C resulted in the formation of dark red microcrystals (198 mg, 0.267 mmol, 83.6%). Crystals suitable for X-ray diffraction were grown from a dilute solution of 1.9 in THF/pentane after 2 nights at −35 °C. ¹H NMR (400 MHz, 298 K, benzene-d₆): δ 7.01 (dd, ³J_{H-H} = 4.53 Hz, 1H, *meta*-ArH_{Tolyl}), 6.88 (br, 2H, *meta*-

Ar H_{Mesityl}), 6.80 (s, 1H, *meta*-Ar H_{Tolyl}), 5.81 (dd, J_{H-H} = 4.14 Hz, 1H, *ortho*-Ar H_{Tolyl}), 5.07 (s, 1 H, Ti=NH), 2.41 (sept, ³J_{H-H} = 16.0 Hz, 1H, P-CH-CH₃), 2.26 (s, 3H, C $H_{3\text{Tolyl}}$), 2.22 (s, 3H, *ortho*-C $H_{3\text{Mesityl}}$), 2.15 (s, 3H, *para*-C $H_{3\text{Mesityl}}$), 0.79 (br, 3H, P-CH-CH₃), 0.29 (sept, ³J_{H-H} = 8.11 Hz, 1H, P-CH-CH₃). ³¹P{¹H} NMR (162 MHz, 298 K, benzene-d₆): δ 15.66 (s, 2P, *P*N). ¹³C{¹H} NMR (125.8 MHz, 298 K, benzene-d₆): δ 161.6 (Ar-*C*), 146.4 (Ar-*C*), 137.6 (Ar-*C*), 133.7 (Ar-*C*), 133.4 (Ar-*C*), 131.6 (Ar-*C*), 130.4 (Ar-*C*), 129.9 (Ar-*C*), 128.4 (Ar-*C*), 124.2 (Ar-*C*), 22.6 (PCH(CH₃)₂), 21.3 (PCH(CH₃)₂), 21.0 (PCH(CH₃)₂), 20.8 (PCH(CH₃)₂), 20.7 (PCH(CH₃)₂), 18.2 (Ar-*C*H₃), 15.9 (Ar-*C*H₃).

(PN)₂Ti=O (1.10): Compound 1.3 (203.3 mg, 0.107 mmol, 1 equiv.) was dissolved in 3 mL toluene in a 20 mL vial. To this light orange solution was added pivaloyl chloride (26.4 µL, 0.214 mmol, 2 equiv.) by microsyringe at room temperature. The solution immediately turned a bright purple color, and a white solid precipitated. The solution was stirred for 15 minutes, and then all volatiles were removed under vacuum. The residue was extracted into 10 mL ether, and filtered over celite to remove alkali. The solution was concentrated to 7 mL. Cooling overnight to -35 °C resulted in the deposition of large purple crystalline plates on the walls of the vial (152 mg, 0.205 mmol, 95.9%) some of which were suitable for X-ray diffraction. NC^tBu was formed as a side product of the reaction, in the same ration as **1.10**, measured by integration with ¹H NMR. Compound **1.10** can alternatively be synthesized by the same experimental procedure as reported above when **1.3** (200 mg, 0.105 mmol, 1 equiv.) was treated in the same conditions with diphenylketene (20.5 μ L, 0.210 mmol, 2 equiv.). The same work-up procedure is conducted to isolate 1.10 from the KNCCPh₂ side product (118.9 mg, 0.16 mmol, 76%). ¹H NMR (400 MHz, 298 K, benzene-d₆): δ 6.88 (br, $\Delta v_{1/2}$ = 10 Hz, 2H, para-ArH_{Mesityl}), 6.86, (s, 1H, meta-ArH_{Tolyl}), 6.81 (dd, ³]_{H-} $_{\rm H}$ = 4.12 Hz, 1H, meta-ArH_{Tolvl}), 5.82 (dd, 3]_{H-H} = 4.14 Hz, 1H, meta-ArH_{Tolvl}), 2.79 (br, 3H, P-CH-CH₃), 2.26, (s, 3H, CH_{3Tolyl}) 2.19 (s, 3H, para-CH_{3Mesityl}), 1.54, (s, 3H, P-CH-CH₃), 1.26 (s, 3H, P-CH-CH₃), 0.89, (s, 3H, ortho-CH_{3mesityl}), 0.78 (s, 3H, ortho-CH_{3mesityl}), 0.29 (sept, ³J_{H-H} = 8.23 Hz, 1H, P-CH-CH₃). ³¹P{¹H} NMR (162 MHz, 298 K, benzene**d**₆**)**: δ 13.33 (s, 2P, *P*N). ¹³C{¹H} NMR (125.8 MHz, 298 K, benzene-d₆): δ 161.9 (Ar-*C*), 145.3 (Ar-*C*), 138.3 (Ar-*C*), 134.2 (Ar-*C*), 133.7 (Ar-*C*), 131.7 (Ar-*C*), 130.5 (Ar-*C*), 124.7 (Ar-*C*), 113.1 (Ar-*C*), 20.9 (P*C*H(CH₃)₂), 19.6 (PCH(*C*H₃)₂), 15.6 (Ar-*C*H₃), 15.9 (Ar-*C*H₃).

Crystallographic Experimental Details

Crystallographic data are summarized Tables 1.2 and 1.3. Suitable crystals for X-ray analysis of 1.4-1.10 were placed on the end of a Cryoloop coated in NVH oil. Data for single crystal structure determination of **1.4-1.10** were taken on a Bruker ApexII with a CCD area detector employing graphite-monochromated Mo-Kα radiation $(\lambda = 0.71073 \text{ Å})$ at a temperature of 100(1) K. Rotation frames were integrated using SAINT,¹⁰¹ producing a listing of non-averaged F^2 and $\sigma(F^2)$ values which were then passed to the SHELXTL¹⁰² program package for further processing and structure solution. The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS.¹⁰³ The initial structures of **1.4-1.10** were solved by Patterson and Fourier transform methods - SHELXS.¹⁰⁴ Refinement was by fullmatrix least squares based on F² using SHELXL.¹⁰⁵ All reflections were used during refinement. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using riding models with exception for **1.9**. For **1.6**, two crystallographically independent, but chemically equivalent molecules are present in the asymmetric unit. For **1.7**, ⁱPr groups of NPⁱPr₂ were disordered over two on the crystallographically special position. The thermal ellipsoids were fixed by SHELXL restraint commands, DELU and SIMU. Disordered pentane molecule was located with 0.5 occupancies and a negative PART number, and refined with a rigid group model. For **1.8**, one site occupied by hexane was identified in the asymmetric unit. This site was considerably disordered and was treated by SQUEEZE as a diffuse contribution.^{106, 107} In the resulting void space, a contribution of 134 e⁻ per unit cell was found and taken to represent one hexane in the asymmetric unit, giving one pentane molecule for each Ti complex. For 1.9, one site occupied by THF was 39

identified in the asymmetric unit. This site was also treated by SQUEEZE as a diffuse contribution, resulting in a contribution of 186 e⁻ per unit cell to give one THF molecule for each Ti complex. This data was treated as a two-component crystal data. One component with 0.8 occupancies was refined as a terminally bound parent imide complex **1.9**. The hydrogen atom of the imide ligand was located from the difference map and refined isotropically. The second component was considerably an insertion product in which the imide ligand has inserted into the arm of the PN ligand. The phosphorus atom and corresponding 'Pr groups were refined with 0.2 occupancies, but the hydrogen atom corresponding to the parent imide hydrogen in **1.9** could not be located from the difference map due to its low occupancy. These results were checked using the IUCR's CheckCIF routine. The alerts in the output are related to the disordered groups and crystal solvents.

Compound	1.4 · 2(C ₆ H ₆)	1.5 · C ₅ H ₁₂	
Molecular formula	C ₈₈ H ₁₂₄ N ₆ P ₄ Ti ₂ , 2(C ₆ H ₆)	$C_{45}H_{65}N_3P_2T_4$ (C_5H_{12})	
Formula weight	1641.82	829.98	
Temperature (K)	100(1)	100(1)	
Crystal system	Monoclinic	Orthorhombic	
Space group	C 1 2/c 1 P 2 ₁ 2 ₁ 2		
Cell constants:			
a (Å)	30.5846(16)	12.7371(6)	
b (Å)	15.6055(8)	14.7015(7)	

Table 1.2. Crystallographic Data of compounds 1.4-1.5.

c (Å)	25.1965(13)	26.1005(12)
Alpha Agle	90	90
Beta Angle	129.980(2)	90
Gamma Angle	90	90
Volume (Å ³)	9215.1(9)	4887.4(4)
Z	4	4
Density (calcd mg/m3)	1.183	1.128
Abs coeff (mm-1)	0.291	0.275
F(000)	3528	1800
Wavelength	0.71073	0.71073
θ range for data collection (°)	2.43 to 27.35	2.63 to 27.51
h, k, l ranges collected	$-39 \le h \le 39$	$-16 \le h \le 16$
	$-20 \le k \le 20$	$-19 \le k \le 18$
	$-32 \le l \le 32$	$-33 \le l \le 33$
# Reflns collected	10690	11259
Refinement method	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²
R_1^{a}	0.0646	0.0589
$wR_{2^{b}}$	0.1376	0.1456
Goodness-of-fit on F2 ^c	1.055	1.142

Table 1.3. Crystallographic Data of compounds 1.6-1.7.

Compound	1.6	2(1.7) · C ₅ H ₁₂

Molecular formula	$C_{47}H_{71}N_3P_2SiTi$	2(C ₅₀ H ₇₆ N ₃ P ₃ Ti), (C ₅ H ₁₂)
Formula weight	815.99	1864.18
Temperature (K)	100(1)	100(1)
Crystal system	Monoclinic	Monoclinic
Space group	P 1 2 ₁ /c 1 I 1 2/a 1	
Cell constants:		
a (Å)	30.336(2)	18.5929(8)
b (Å)	12.1037(10)	12.9042(5)
c (Å) Alpha Agle Beta Angle Gamma Angle	29.271(2) 90 118.588(4) 90	22.7421(14) 90 98.499(2) 90
Volume (ų)	9437.3(12)	5396.5(5)
Z	8	2
Density (calcd mg/m3)	1.149	1.147
Abs coeff (mm-1)	0.308	0.284
F(000)	3520	2024
Wavelength	0.71073	0.71073
θ range for data collection (°)	2.88 to 27.48	2.22 to 27.51
<i>h, k, l</i> ranges collected	$-39 \le h \le 39$ $-15 \le k \le 15$ $-38 \le l \le 35$	$-24 \le h \le 24$ $-16 \le k \le 16$ $-29 \le l \le 28$

21655	6146
Full-matrix least- squares on F ²	Full-matrix least- squares on F ²
0.0506	0.0662
0.1214	0.1786
1.127	1.058
	21655 Full-matrix least- squares on F ² 0.0506 0.1214 1.127

Table 1.4. Crystallographic Data of compounds 1.8-1.10.

Compound	1.8	1.9	1.10
Molecular formula	$C_{50}H_{66}BN_{3}O_{2}P_{2}Ti$	$C_{44}H_{62}N_3P_2T_1$	$C_{44}H_{62}N_2OP_2Ti$
Formula weight	947.88	817.73	744.79
Temperature (K)	100(1)	100(1)	100(1)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P 1	P 1 2 ₁ /c 1	P 1 2 ₁ /c 1
Cell constants:			
a (Å)	10.3049(6)	15.3708(10)	13.5295(4)
b (Å)	15.2566(9)	12.8618(8)	19.5970(6)
c (Å) Alpha Agle Beta Angle Gamma Angle	18.1286(10) 81.295(3) 79.167(3) 84.702(3)	23.2563(15) 90 92.737(4) 90	16.8163(5) 90 111.694(2) 90
Volume (Å ³)	2761.1(3)	4592.4(5)	4142.8(2)
Z	2	4	4

Density (calcd mg/m3)	1.140	1.183	1.194
Abs coeff (mm-1)	0.254	0.293	0.318
F(000)	1020	1767	1600
Wavelength	0.71073	0.71073	0.71073
θ range for data collection (°)	2.50 to 27.52	2.36 to 27.52	2.45 to 26.73
<i>h, k, l</i> ranges collected	$-13 \le h \le 13$ $-19 \le k \le 19$ $0 \le l \le 23$	$-19 \le h \le 18$ $-16 \le k \le 16$ $-30 \le l \le 30$	$-17 \le h \le 16$ $0 \le k \le 25$ $0 \le l \le 21$
# Reflns collected	12599	10568	9527
Refinement method	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²
R_1^{a}	0.0410	0.0418	0.0582
$wR_{2^{b}}$	0.1065	0.0951	0.1332
Goodness-of-fit on F2 ^c	1.018	1.037	1.036

a R1 = (|Fo| - |Fc|) / |Fo|. b wR2 = [[w(Fo2 - Fc2)2] / [w(Fo2)2]]1/2. c Goodness-of-fit = [[w(Fo2 - Fc2)2]/Nobservns Nparams)]1/2, all data.

Solid state ¹⁵N NMR Details

Solid-state ¹⁵N NMR spectra were recorded under the cross polarization (CP) magicangle spinning (MAS) condition on a Bruker Avance-600 NMR spectrometer (14.1 T) operating at the ¹H and ¹⁵N Larmor frequencies of 600.17 and 60.81 MHz, respectively. The Hartmann-Hahn matching condition was established with a solid ¹⁵NH₄NO₃ sample. High-power ¹H decoupling (70 kHz) was applied during data acquisition. A 4-mm Bruker MAS probe was used with sample spinning frequencies between 5.0 and 14.5 kHz. A relaxation delay of 2 s and a contact time of 2 ms for CP were used. Powder samples were packed into a ZrO_2 rotor (4-mm o.d.) in a glove box. All ¹⁵N chemical shifts were referenced to that of NH₃(liq) ($\delta = 0$ ppm) by using solid ¹⁵NH₄NO₃ as a secondary ¹⁵N chemical shift reference ($\delta = 23.8$ ppm). Spectral simulations were performed using DMFit.¹⁰⁸

Computational Details

All calculations were carried out using DFT as implemented in the ORCA program package.¹⁰⁹ Final geometry optimizations were performed using the BLYP^{110,111} functional and the all-electron def2-TZVP(-f)-ZORA¹¹² basis set in combination with the auxiliary basis set def2-TZV/J.¹¹³ To accelerate geometry optimizations we used the resolution of the identity, R,¹¹⁴ approximation. For these optimizations a tight convergence of the wavefuntion was demanded on grid quality of Grid4 (also using SlowConv). The scalar relativistic zero'th order regular approximation (ZORA)¹¹⁵ was employed to take into account relativistic effects whereas to dispersion was considered using Grimme's D3 method in all ORCA calculations. Our experience with the optimizations of the investigated extended molecules (~ 200 atoms) is that the convergence to the equilibrium structure is much faster when optimizing in Cartesian coordinates (COPT). Finally, the above-described final geometry optimizations were started from pre-optimized structures obtained *via* a lower level of theory (BLYP/def2-SV(P), def2-SVP/J, ZORA, RI, d3, LooseSCF, Grid3).

We used the NMR module of ADF2013¹¹⁶ code to compute ¹⁵N NMR chemical shifts on the equilibrium structures obtained *via* the protocol described above. The functional employed consisted of the local density approximation of Vosko, Wilk, and Nusair (LDA VWN)¹¹⁷ augmented with the nonlocal gradient correction PW91 from Perdew and Wang.¹¹⁸ This functional has been shown to provide reliable chemical shift values even for heavy atom containing transition metal complexes.¹¹⁹ The full electron basis set TZVP was utilized in these calculations and relativistic corrections were applied using ZORA. The computed isotropic shielding values of complexes were referenced to that of ammonia modeled in the same way.

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Chapter 2:

Titanium Nitrides: Reactivity Spanning from the Generation of Nitridyl Radicals to Electrophilic Behavior

Introduction. Unlike the ubiquitous oxygen centered radical that plays vital roles in life sustaining processes such as respiration,¹ the formation of biological reagents, and the biodegradation of toxic elements in the body (cytochromes), 2,3 nitrogen centered radicals are just now beginning to enter the stage.⁴ These less studied radicals are also vital given their roles in dinitrogen splitting (and its microscopic reverse step, N-N bond formation),⁵⁻²⁵ radical-ejection or atom-abstraction processes,²⁶⁻³³ as well as C-H insertion reactivities.³⁴⁻⁴² More recently, the role of nitrogen centered radicals in catalytic reactions involving aminyl (radical on a -NR₂ or -NHR) or imidyl (radical on a NR²⁻) are just now beginning to take advantage of their reactive nature for the construction of amine or N-based heterocycles.35 Whereas amidyl and imidyl metal species take advantage of the more secluded and delocalized nature of the radical, nitridyl species are far more scant given the more exposed nitrogen centered radical and hence their propensity to undergo reductive coupling, bridging or oligomerization to delocalize the unpaired electron, or undergo atom-abstraction reactions. To date, there are only a few examples of a metastable mononuclear nitridyl complexes that have been detected spectroscopically, namely the radical cation $[(PNP)Ir(N\bullet)][PF_6]$ or its neutral derivative $(PNP)Ir(N\bullet)$ (PNP = ${^tBu_2P}_2(CHCH)_2N^-$ which are stable at room temperature for several minutes (Scheme 2.1).⁴³ Another nitridyl species is the bridging dirhodium complex $[(PNN)Rh]_2(\mu_2-N)$ (PNN = 6-di-(*tert*-butyl)phosphino-CH-2,2'-bipyridine) shown in Scheme 2.1, which allows the unpaired electron to delocalize across the topologically linear Rh=N=Rh linkage.⁴⁴ However, other likely nitridyl candidates that merit mentioning based on computational predictions are tetragonal Fe(IV) species of the type [(cyclam)Fe(N)]²⁺ (cyclam = 1,4,8,11-tetrazacyclotetradecane) which are stable under frozen matrix condition,^{45,46} or the tetranuclear Fe nitride complex $[K]_2[Fe_4N_2(nacnac)_4Cl_2]$ (nacnac = $[ArNC(CH_3)]_2C(CH_3)$, Ar = 2,6-Me_2C_6H_3) derived from reductive N₂ splitting the latter which also provides a medium to delocalize the radical on nitrogen.⁴⁷



Scheme 2.1. Examples of spectroscopically characterized iridium nitridyl complexes (2012) and the spectroscopically and structurally characterized dirhodium nitridyl (2014) by the de Bruin and Schneider groups.

In 2012, our group referred for the first time the term nitridyl, *via* the likely intermediate $(nacnac)Ti(\equiv N \cdot)(Ntol_2)$ $(nacnac^- = [ArNC(CH_3)]_2CH$, Ar = 2,6-'Pr₂C₆H₃, tol = 4-CH₃C₆H₄)²⁹ formed enroute to the parent imido $(nacnac)Ti(\equiv NH)(Ntol_2)$, the later which was isolated and fully characterized. Although transition metal nitridyl species are generally produced *via* N₂ extrusion from an azide precursor L_nMⁿ(N₃) to afford the two-electron metal oxidized radical species L_nMⁿ⁺²(N),⁴⁸ our approach using early-transition metals takes advantage of the fact that the radical being generated is intuitively expected to be 100% nitrogen centered (with very little, if any delocalization into pi-bonds or metal d orbitals). Such a goal can be accomplished since the metal ion having the azido ligand can only be oxidized by one-electron, namely L_nMⁿ⁺¹(N•) since it has already reached its highest oxidation state. As a result, this transient moiety is expected to be quite reactive thus resulting in immediate radical reactions such as H-atom abstraction to produce the parent imide.²⁹⁻³¹

In Chapter 1 the synthesis and subsequent S_N2 reactions of a terminal molecular titanium nitride anion $[(PN)_2Ti\equiv N(\mu_2-K(OEt_2)]_{2,49,50}$ supported by two PN⁻ ligands, $(PN^- = (N-(2-P^iPr_2-4-methylphenyl)-2,4,6-Me_3C_6H_2)$ were discussed. Since two PN ligands chelate to the metal center, the system can interchange with minimal energy between geometries such as trigonal bipyramidal and square pyramidal, while taking advantage of the pseudo tetragonal scaffold ideal for metal-nitrogen multiple bonding with the nitride. Given the powerful nucleophilicity of the nitrido moiety,^{49,50} and its ability to make metal-ligand multiple bonds, we inquired if it would be possible to oxidize the nitride anion to independently generate a titanium nitridyl of the type $(PN)_2Ti(\equiv N\bullet)$. The study described in this chapter aims at understanding how the elusive titanium nitridyl, $(PN)_2Ti(\equiv N\bullet)$, is produced by two independent reactions and how these processes lead to divergent reactivity - N₂ extrusion of a Ti(III) azide precursor, $(PN)_2Ti(N_3)$, and one-electron oxidation of a titanium nitride anion $[(PN)_2Ti\equiv N]^-$ using weak inner-sphere oxidants such as I₂ and ClCPh₃. The following continuation of the nitride story details how a nucleophilic nitride of an early-transition metal can be converted to an radical intermediate by virtue of a one-electron oxidation reaction and the reactivity and spectroscopy used to elucidate the nature and reactivity of the putative nitridyl $(PN)_2Ti(\equiv N\bullet)$ (**2A**), generated from two independent routes.

As discussed in Chapter 1, as presupposed based on the disparity in electronegativity across the titanium-nitrogen bond of the nitride ligand, one would expect this terminal nitride to be a nucleophilic species. Indeed, this is what was observed in the reactivity detailed *vide supra*. Can the reactivity of a such a polarized moiety, with a large delta minus residing at the nitrogen atom ever be described as electrophilic? In recent years, it has been shown that a bridging hafnocene nitride efficiently carbonylated to form a cyanato ligands from Chirik and coworkers,⁵¹ and in other terminal vanadium and molybdenum complexes reactivity with carbon monoxide and isocyanides has also been observed.⁵²⁻⁵⁵ However, for titanium, with the exception of a proposed electrophilic titanium nitride intermediate,⁵⁶ in no instances of isolated titanium nitrides has electrophilic behavior been reported to the best of our knowledge. In the latter half of this chapter, the reactivity of the titanium nitride complex with isocyanides and the surprising results stemming from these reactions will be discussed. The synthesis and crystallographic characterization of these stable Ti(II) complexes will be presented.

Results and Discussion

A Titanium Nitridyl Generated from Nitride One-Electron Oxidation.

When the previously reported titanium nitride complex, $[(PN)_2Ti\equiv N\{\mu_2-K(OEt_2)\}]_2$ (1.3) was treated with a toluene solution containing two equiv. of I₂, an immediate color change from orange to deep red was observed. Stirring the reaction at room temperature for an additional 12 hours and after workup and crystallization of the reaction mixture, a ³¹P NMR spectrum of a sample revealed the presence of two inequivalent resonances at 14.7 ppm along with a more downfield resonance at 34.9 ppm, implying that the original C_{2v} symmetry in the nitride dimer **1.3** was no longer retained. The reaction was not complete however, and the method to push this reaction to completion will be discussed later in this chapter. Interestingly, vacuum transfer of the volatiles from the reaction mixture revealed H_2 formation (¹H NMR: 4.5 ppm) in addition to free Et_2O (stemming from complex 1.3). To elucidate the bonding in the complex formed from I₂ oxidation, a single crystal X-ray diffraction study was performed on isolated single crystals obtained from *n*-hexane at -35 °C. (Figure 2.1, left). Upon inspection of the solid-state structure, it is clear that the former nitride has inserted into one of the phosphorus arm of the PN⁻ ligand, altering this scaffold into the asymmetric ligand NPN' that now contains a phosphinimide moiety, namely compound (NPN')(PN)Ti(I) (2.1) (NPN' = N-(2-NP'Pr₂-4methylphenyl)-2,4,6-Me₃C₆H₂²⁻). Complex **2.1** can be isolated in 48% yield from the reaction mixture (Scheme 2.2). Structural information thus corroborated the two inequivalent phosphorus environments observed in the ³¹P NMR spectrum; one resonance for the unaltered PN⁻ ligand along with the more downfield resonance attributable to the phosphinimide arm of the ligand.



Scheme 2.2. Reaction of **1.3** with the weak and inner-sphere oxidants I₂ and ClCPh₃ to yield phosphinimide complexes **2.1** and **2.2**, respectively.

While our previously reported 5-coordinate complexes with two PN⁻ ligands have been closer to trigonal bipyramidal in geometry with τ_5^{57} values ~0.7-0.8, the nitrogen inserted product **2.1** has a value instead confined between the two geometries ($\tau_5 = 0.52$) for one of the crystallographically inequivalent (chemically equivalent) molecules confined in the asymmetric unit with N1–Ti1–P2 = 168.25(7)° and N2–Ti1–I1 = 137.08(6)°. Interestingly, the second independent molecule had a more distorted $\tau_5 = 0.35$ due to the differing angles of N1'–Ti1'–P2' = 162.52(7)° and N2'–Ti1'–I1' =141.78(7)°, indicating that both molecules are quite distorted, but on average, complex **2.1** most likely favor a square pyramidal geometry.

Alternatively, when complex **1.3** was treated with 2 equiv. of ClCPh₃, an oxidant with a similar oxidation potential to I₂ (-0.11 versus -0.14 V, respectively vs. SCE), an immediate color change from orange to dark red was also observed. However, it was established that four equiv. of ClCPh₃ were needed in order to achieve full consumption of the starting material. After work-up and crystallization of the mixture from hexane at -35 °C, the chloride analogue of **2.1**, (NPN')(PN)TiCl (**2.2**) was isolated

in 49% yield (Scheme 2.2) based on its spectroscopic similarity to **2.1** (³¹P NMR spectrum showed two singlet resonances at 12.7 ppm and 35.0 ppm), as well as connectivity confirmed by single crystal X-ray diffraction studies. Interestingly, examination of the reaction mixture by ¹H NMR spectroscopy also revealed the formation of HCPh₃ and Gomberg's dimer, Ph₃CC₆H₅CPh₂ (Scheme 2.2). As shown in Figure 2.1, complex **2.2** instead favors an even more square pyramidal geometry (t₅ = 0.16),⁵⁷ likely due to less steric hindrance in the axial position of a chloride versus the softer iodide (N2–Ti1–P1 = 153.68(6)° and N1–Ti1–Cl1 = 144.21(6)°). The insertion of the formal nitrido ligand into the phosphine group of the PN ligand tantalizingly suggests that a nitridyl moiety is generated upon oxidation of **1.3**. The oxidation of a phosphine by a nitride ligand is consistent with this moiety being electrophilic in nature, akin to those observed in Fe(IV) nitrides.⁵⁸⁻⁶³

To establish the source of the hydrogen atom (or hydride) that resulted in formation of HCPh₃ the parent imido complex, $(PN)_2Ti\equiv NH$ (1.9), provided mechanistic insight. As aforementioned in Chapter 1, the rare example of parent imido complex **1.9** could be prepared *via* treatment of **1.3** with HMDS (HN{SiMe₃}), as well as phenol as the proton source to afford 1.9 in greater yields given the insolubility of KOPh (Scheme 2.3). Surprisingly, it was found that complex **1.9** would gradually transform to a new previously unidentifiable major species proposed to be (NPN')(PN)Ti(H) (2.3) (Scheme 2.3). Akin to 2.1 and 2.2, the ³¹P NMR spectrum of this new material indicated the presence of two chemically inequivalent phosphorus ligand environments at 7.5 and 22.4 ppm. It was established that 1.9 sluggishly converts to 2.3 in benzene under photochemical conditions (several days in room light). This conversion is arrested if the sample is isolated and stored in the dark. To determine if the new species could indeed be an insertion product such as a titanium hydride, 2.3, based on similar reactivity observed in the oxidation reactions shown in Scheme 2.2 (vide supra), pure samples of **1.9** were subjected to photolysis using a xenon lamp source. Accordingly, the ³¹P NMR spectrum of this mixture showed complete conversion of 1.9 to 2.3 after 15 min of irradiation. In solution, complex 2.3 shows all the features expected for a Ti(IV) complex based on ³¹P and ¹H NMR spectra, 58

although there are no salient features in the ¹H NMR spectra to assign to this complex, other than the distinctly inequivalent two resonances in the ³¹P NMR spectrum. Surprisingly, it was not possible to spectroscopically observe the hydride resonance in **2.3**. Crystallization of the rather soluble complex from a saturated pentane solution at -35 °C overnight resulted in the deposition of trace dark red single crystals of the N-inserted product **2.3**. Due to poor resolution it was not possible to locate a hydride ligand in the difference map (Figure 2.1).



Figure 2.1. Solid-state structures of complexes **2.1** (left), **2.2** (right), and **2.3**, (lower) displaying thermal ellipsoids at the 50% probability level. H-atoms, a molecule of *n*-
hexane in **2.1**, half molecule of residual *n*-hexane in **2.2**, and 2 molecules of **2.3** have been omitted for clarity. Only one of the crystallographically independent molecules of **2.1** has been pictured. Selected distances (Å) for **2.1**: Ti1–N1, 2.041(2); Ti1–N2, 2.009(2); Ti1–N3, 1.786(2); Ti1–P1, 2.6616(8); Ti1–I1, 2.7920(5); for **2.2**: Ti1–N1, 2.043(2); Ti1–N2, 2.033(2); Ti1–N3, 1.787(2); Ti1–P, 1 2.6513(8); Ti1–Cl1, 2.3802(7); for **2.3**: Ti1–N1, 2.004(3); Ti1–N2, 2.044(5); Ti1–N3, 1.760(4); Ti1–P, 1 2.644(2).

Attempts were made *via* deuterium labeling studies to unequivocally assign this hydride ligand. **1.3** was treated with phenol- d_6 , immediately forming the parent deuteride complex (PN)₂Ti \equiv ND (**1.9**)- d_1 , which was confirmed by ³¹P NMR spectroscopy. Notably, the ²H NMR spectrum of **1.9**-*d*1 clearly shows the anticipated N-D resonance at 5.0 ppm, and a spectroscopic feature observed in the ¹H NMR spectrum for unlabeled **1.9**. The isotopologue analogue of **1.9**-*d*1, was then photolyzed to cleanly convert to (NPN')(PN)Ti(D) (2.3)- d_1 , confirmed by ³¹P NMR spectroscopy. However, ²H NMR spectral data of $2.3 - d_1$, was ambiguous and did not clearly reveal a characteristic Ti-H resonance at 8 ppm,⁶⁴⁻⁶⁷ that have been reported for a few examples of titanium hydrides. However, it cannot be ruled out that such a hydride resonance might be broadened due to ³¹P and ¹⁴N coupling. In the IR spectrum of **1.9**, an N-H stretch is clearly observed at 3398.0 cm⁻¹, with a corresponding decrease in energy as should be expected when this is deuterated to **1.9**- d_1 , displaying a stretch for the N-D at 2519.5 cm⁻¹. Unfortunately for **2.3**, there are no distinct features in the IR for a hydride or a deuteride in $2.3-d_1$, respectively. However, experimentally were able to show the presence of a hydrido ligand by addition of a stoichiometric quantity of $ClCPh_3$ to a solution of 2.3 in C_6D_6 . Examination of this reaction mixture by ¹H NMR spectroscopy demonstrated the quantitative formation of **2.2** and HCPh₃, providing evidence for the former hydride moiety.

A Titanium Nitridyl Produced by Incomplete Azide Reduction.

Intrigued by the insertion of the nitridyl nitrogen of a species such as **2A** into the phosphorous arm of the ligand, we inquired if this motif could be accessed via other routes to better understand their mode of reactivity and mechanism of formation. The nitrogen atoms in the ubiquitous azide ligand, N₃⁻, carry each a formal oxidation state of $-\frac{1}{3}$. Upon reduction by two electrons, the azide ligand disproportionates to N₂ and N^{3-} , the latter which carries a formal oxidation state of -3 (Eq. 2.1a). However, if one reduces an azide by one-electron while promoting N₂ extrusion, one could in principle produce a nitridyl nitrogen with a formal oxidation state of -2 (Eq. 2.1b). Previously, our group reported the synthesis of a stable Ti(III) azide complex, $(PN)_2$ Ti (N_3) (1.2),⁴⁹ which upon reduction by one electron (e.g. KC₈) produced nitride complex **1.3**, *vide* supra, in accordance with the simplified reaction shown in Eq. 2.1a. In such a transformation the Ti(III) supplied one electron while the KC₈ provided the second one. However, when a sample of **1.2** (in the absence of exogenous reductant) was dissolved in deuterated benzene as a dilute solution (10-15 mM) and was irradiated with a xenon lamp source for a period of five minutes in a J-Young NMR tube, the ³¹P and ¹H NMR spectra of the reaction mixture experiment allowed for identification of the parent imido and insertion complexes, respectively, **1.9** and **2.3** along with other side-products we have been unable to identify (Scheme 2.3). Complete conversion of **1.9** to **2.3** can be achieved if the mixture is photolyzed for an additional 10 min, in accordance with what we previously observed when independently prepared samples of pure **1.9** are photolyzed for the same period of time, *vide supra* (Scheme 2.3).

$$N_{3}^{-} + 2e^{-} \rightarrow N_{2} + N^{3-}$$
 (nitride) Eq. 2.1a

 $N_3^- + 1e^- \rightarrow N_2 + N^{2-}$ (nitridyl) Eq. 2.1b



Scheme 2.3. Synthesis of a mixture of parent imido 1.9 and the N-inserted hydride2.3 from the photolysis of the Ti(III) azide precursor 1.2.

Reactivity Studies to Understand Formation of 2.1 and 2.2 From Nitride 1.3 and oxidants I₂ and ClCPh₃.

Insertion of the formal nitrido nitrogen into the phosphine arm of one of the PNligands suggests that an electron deficient nitride is likely formed in the course of these reactions. Since I₂ and ClCPh₃ can serve as oxidants and radical traps, the reactions were monitored in order to observe intermediates or side products deriving from the putative nitridyl **2A**. Accordingly, treatment of **1.3** with I₂ resulted in immediate formation of **2.1** and **1.9**, along with the hydride **2.3**, the latter which over time was observed to convert to **2.1**. It was determined that the reaction 62 required approximately 2 equiv. of I_2 per equiv of **1.3** in order to proceed to completion. Notably, examination of volatiles revealed formation of H₂ (¹H NMR: 4.47 ppm) as one of the side products from this reaction. It was also found that conducting the reaction in the dark also led to formation of less than 50% 2.1, with the rest of the mixture being attributable to 1.9. Under these conditions only traces of 2.3 were spectroscopically detected by ¹H and ³¹P NMR spectroscopy suggesting that **2.3** most likely derives from the photochemical conversion of **1.9**. Indeed, control experiments using independently prepared **1.9** reveal that reaction with I_2 produces H_2 and **2.1**, when exposed to light. If instead in this control this mixture of 1.9 with H₂ is left in the absence of light, no reaction precedes. Based on this premise the hypothesis is that the formation of **2.1** from I₂ oxidation of **1.3** occurs via two plausible paths labeled as A and B in Scheme 2.4. In the first step, one electron oxidation of each nitride ligand in **1.3** with 1 equiv. of I₂ results in formation of KI and the nitridyl **2A**, which can either abstract H atom to form the parent imide **1.9** (path B) or undergo insertion into the phosphine arm to produce the Ti(III) phosphinimide radical (NPN')(PN)Ti (2B) (path A). In the presence of additional I₂, species 2B would rapidly get oxidized to 2.1. Meantime, photochemical conversion of complex 1.9 to 2.3 would allow any I_2 to oxidize the hydride by producing **2.1** and $\frac{1}{2}$ equiv. of H_2 . Since I_2 can be a troublesome oxidant to handle, we resorted to using a different oxidant that could allow us to observe the formation of a radical but also qualitatively react with the hydride in 2.3. As a result, the one-electron oxidant and hydride abstractor ClCPh₃ was selected since this reagent is a stable solid that can be easily weighed and scaled to small experiments for NMR spectroscopic measurements, but can also allow for identification of its radical, via formation of Gomberg's dimer.68 Accordingly, treatment of **1.3** with 4 equiv. of $ClCPh_3$ in C_6D_6 over 15 min and in the presence of light resulted in the formation of a half equivalent of Gomberg's dimer, 2.2, and HCPh₃ which were detected by a combination of ¹H and ³¹P NMR spectroscopy. Conducting the same experiment in the absence of light resulted also in formation of Gomberg's dimer, **2.2**, and the imide **1.9** therefore suggesting that HCPh₃ derives from hydride abstraction of **2.3** with ClCPh₃. This again demonstrates the presence of a hydride 63

ligand in **2.3** despite inconclusive spectroscopic measurement by NMR spectroscopy and X-ray diffraction. Indeed, addition of ClCPh₃ to a benzene-d₆ solution of independently prepared **1.9** in the presence of light cleanly results in formation of **2.3** and HCPh₃. As a result, our proposed pathway in Scheme 2.4 shows how paths A and B both result in formation of **2.1** and **2.2** by the addition of oxidants I₂ or ClCPh₃ to nitride **1.3**. Path A and B share in common the nitridyl intermediate **2A**, which can either oxidize a proximal phosphine P of the PN⁻ ligand (Path A) or abstract an Hatom (Path B). As it will be demonstrated, frozen matrix conditions can allow us to avoid the H-atom abstraction pathway, and spectroscopically identify the formation of a species such as **2B**.



Scheme 2.4. Proposed pathways (path A and path B) involving the oxidation of nitride **1.3** to the phosphinimide complexes **2.1** and **2.2**, with I_2 and ClCPh₃ respectively.

Attempts to Spectroscopically Observe Intermediate 2A and Formation of the Parent Imido 1.9.

Since intermediate **2A** is expected to be quite reactive, frozen matrix X-band EPR studies of 1.2 were performed under photolytic conditions. These measurements and simulations were conducted by Christophe Rebreyrand (student in Prof. Bas de Bruin's Group at the University of Amsterdam). Unfortunately, the direct photolysis of **1.2** at 20K using a strong UV lamp (270-600 nm range, glass fiber technology) is not completely clean, giving rise to two new signals. Hence, warming-up the sample after the photolysis, followed by rapidly freezing the sample led to a fairly clean spectrum shown in Figure 2.2 and Table 2.1. The major species observed under this condition was also observed at 20 K during photolysis. Despite simulation not being perfect, the trace looks quite reasonable, and reveals this signal to be the result of only one species. The spectrum shown in Figure 2.2 shows rhombic symmetry with g-tensors ($g_x = 1.9860$; $g_y = 1.9676$; $g_z = 1.9270$) and with hyperfine interactions clearly visible. This is also slightly different than the g-tensors found for the azido precursor **1.2** ($q_x = 1.835$; $q_y = 1.942$; $q_z = 1.975$). Simulation of the spectrum of the photolysis product reveals hyperfine interactions with an I = 1/2 nucleus (phosphorus; $A_x = NR$; $A_y = 50.00$ MHz; $A_z = 50.0$ MHz) and an I = 1 nucleus (nitrogen; A_x = 50 MHz; A_y = 50.00 MHz; A_z = NR). The g-values cannot be attributed to nitridyl complex **2A** (Scheme 2.5), as Christophe calculated with the help of DFT. However, the data are more likely attributed to the metal based radical insertion product 2B (Schemes 2.4-2.5), with g-values that can be reproduced by DFT (Table 2.2). The species observed with EPR show hyperfine coupling with one nucleus with $S = \frac{1}{2}$, presumably phosphorus (as supported by DFT calculation of **2B**). The obtained EPR data suggest that when species 2A is present at 20K and H atom transfer is inhibited at this low temperature, so the nitrogen atom instead undergoes insertion into the Ti–P bond.



Figure 2.2. Experimental and simulated EPR spectrum of species **2B** obtained after photolysis of **1.2**. Experimental parameters: Temperature 20 K, solvent toluene, microwave frequency = 9.362333 GHz, microwave power = 0.632 mW, mod. ampl. = 4 G. Parameters used in in the simulation are shown in Table 2.1.



Scheme 2.5. Photolysis of azido species **1.2** at 20 K, forming nitridyl species **2A**, after which the N atom inserts into the Ti-P in an apparently barrierless transformation.

g values	g	<i>A</i> ₁ (MHz) (I = 0.5)	A1 (MHz) (I = 1.0)
x	1.987	-	50.0
У	1.968	50.0	50.0
Z	1.927	50.0	-

Table 2.1. Experimental EPR Data obtained after photolysis of species **1.2** at 20K.

Table 2.2. Experimental *g*-values of obtained after photolysis of species **1.2** at 20K, compared with the DFT calculated values of nitridyl species **2A** and insertion product **2B**.

g values	Experimental	Species 2A (DFT)	Species 2B (DFT)
Х	1.987	2.010	1.998
у	1.968	2.005	1.965
Z	1.927	2.002	1.929

The lack of any spectroscopic evidence for formation of **2A** from the photolysis of **1.2** implies that under matrix frozen conditions, N-atom insertion involving pathway B (Scheme 2.4, *vide supra*) is plausible. Unfortunately, spectroscopic data under these conditions does not suggest **2A** to be present which is not too surprising given the fact that formation of the nitridyl is likely rate-determining in addition to 2A being a very high energy species. It is quite possible, however, that under the latter conditions an intramolecular N-atom rearrangement pathway becomes preferred over H-atom abstraction reactions. This could be more prominent in solution phase and that Hatom abstraction involves a thermal pathway as opposed to a photochemical process. To address the source of the H-atom resulting in formation of **1.9**, several control and isotopically labelled experiments were conducted. It was found that conducting photolytic reactions of **1.2** in deuterated solvent (toluene- d_8 or benzene- d_6) did not result in any detectable amount of the isotopomer 1.9- d_1 therefore ruling out solvent as the source of hydrogen. Likewise, NMR spectroscopic samples of photolyzed 1.2 using an internal standard of triphenylphosphine resulting in the quantification of 1.9 in 48% yield, thus providing a compelling argument that the source of the H-atom in question was indeed from the ligand cannibalization. Furthermore, experiments with H-atom sources such as 1,4-dihydroanthracene or 1,3-cyclohexadiene (in large excess) showed no improvement in the yield whereas conducting the same reaction 67

in concentrated or dilute conditions also did not improve the yield of **1.9**. Lastly, no evidence for formation of of diphenyl or dibenzyl stemming from homocoupling reactions when such reactions are conducted in either benzene or toluene, respectively was observed. As a result, we propose that the source of the H-atom in **1.9** is stemming from the more vulnerable benzylic groups of the PN ligand scaffold in an intramolecular fashion, most likely followed by a second intermolecular H-atom transfer, or vice versa in accordance with Scheme 2.6. To further understand the source of the H-atom, a reaction mixture of the products resulting from the photolysis of **1.2** were quenched with methanol-d₄. However, ²H NMR spectroscopic studies of the reaction mixture showed no resonances attributable to the HPN ligand or any of its isotopomers. Likewise, it has not been possible to isolate and characterize the side products formed after isolation of **1.9** from the reaction mixture involving the photolysis of **1.2**.



Scheme 2.6. Proposed intermediates stemming from an intramolecular HAT abstraction in **2A**, followed by a second HAT step resulting in **1.9** and most likely a decomposed Ti side product.

Although it was not possible to directly detect **2A** thru EPR studies, it is logical that this should not have the same result as solution studies. However, these studies still support our proposed mechanism in Scheme 2.4. Theoretical studies to support our mechanism are ongoing.

A Transition to Ti(II) Molecular Chemistry: Introduction

While some well-defined Ti(II) complexes have been reported, literature in this area is still not extensive given the lack of stability of these species. More commonly, these complexes are active intermediates or precursors used in organic syntheses⁶⁹⁻⁸¹ or are ill-defined.^{72,82-88} Wilson and Girolami reported the complex (dmpe)₂TiX₂ (dmpe = bis(dimethylphosphino)ethane, X⁻ = Cl.⁸⁹ Other reported Ti(II) complexes include (TMEDA)₂TiCl₂ (TMEDA = tetramethylethylene- diamine),⁸⁷ TiCl₂(py)₄ (py = pyridine),^{87,90} (porphyrin)Ti(L)₂ (L = THF, 4-picoline, OP(octyl)₃),⁹¹⁻⁹³ (κ_3 -Tp)₂Ti (Tp⁻ = tris(3,5-dimethylpyrazolyl)hydroborate),⁹⁴ and titanocene complexes Ti(Cp)₂ (Cp ligands are sterically hindered for these Ti(II) complexes).⁹⁵⁻¹⁰²



Scheme 2.7. Reactivity studies of complex **2.4** with a variety of unsaturated substrates to form complexes **2.5-2.8**.

With regard to these well-defined Ti(II) complexes, our group recently collaborated with multiple investigators including Gayan Wijeratne, Eva Zolnhofer, Chun-Hsing Chen, Prof. Karsten Meyer, Dr. J. Krzystek, Dr. Andrew Ozarowski, Prof. Timothy A. Jackson, and Prof. Joshua Telser to explore the magnetic susceptibility, 69 magnetic circular dichroism, and high-frequency and -field electron paramagnetic resonance spectroscopies, as well as theoretical studies, on $TiCl_2(py)_{4,103}$ Although this was largely a spectroscopic endeavor on part of other groups, from our lab Prof. Skye Fortier conducted synthetic studies, and I concluded some characterization of the reactivity of these complexes after Skye's departure. In this work a modified preparation for $TiCl_2(py)_4$ (2.4) is reported from $TiCl_3(THF)_3$ in THF, treated with excess KC₈ and pyridine. The reactivity studies, summarized in Scheme 2.6, show that this reagent is a potent reductant, and when treated with alkynes reduces these moieties to form *trans*- $[Ti(\eta^2-PhCCPh)(Cl)_2(py)_3]$ (2.5) (Figure 2.4), which is formally Ti(IV) in character and demonstrates an elongation of the alkyne C-C bond to 1.2966(19) Å. Alternatively, a dinuclear species was afforded when treated with diazoalkane. Treatement of (2.4) with N₂CPh₂ resulted in the formation of $(py)_2(Cl)_2Ti(\mu_2:\eta_2-N_2CPh_2)_2Ti(Cl)_2$ (2.6) (Scheme 2.7). As can be seen in the solid state structure (Figure 2.4), the η^2 -coordination of two diazoalkane ligands is occurring in only one metal ion, resulting in a highly asymmetric dinulcear species. The formation of **2.6** suggests that two diazoalkane molecules react rapidly with **2.4** to form the transient $TiCl_2(N_2CPh_2)_2(py)_2$ species, which then combines with starting material by displacing two equatorial pyridine ligands. When 2.4 was instead treated with 0.5 equiv. of PhN=NPh, four electron reduction occurred to afford the phenyl imido complex trans- $[Ti=NPh(Cl)_2(py)_3]$ (2.7) (Scheme 2.7), which was previously reported by Mountford and coworkers.^{104,105}



Figure 2.4. Solid-state structures of complexes **2.5** (upper left), **2.6** (upper right) displaying, and **2.8** (lower) with thermal ellipsoids at the 50% probability level. H-atoms, and three equivalents of pyridine have been excluded from **2.6** have been excluded for clarity.

Finally, reacting **2.4** with cyclooctatetraene (COT) results in the isolation of the Ti(III) complex Ti(η^{8} -COT)Cl(py)₂ (**2.8**) (Figure 2.4, Scheme 2.7). Since this is Ti(III), and the reaction is sluggish, the proposed mechanism is that Ti^{IV}(η^{8} -COT)(Cl)₂(py) reacts with **2.4** to form **2.8** and *mer*-[Ti^{III}Cl₃(py)₃], which was also identified in the reaction mixture. As it can be seen from all these reactions, in which the extremely reactive nature of complex **2.4** as a reductant towards unsaturated substrates results in fast decomposition, often resulting in a mixture of decomposition products contaminating the desired product. This, coupled with the paucity of well-defined or 71

stable Ti(II) complexes in the literature, in addition to those that actually have Ti(II) character (not Ti(IV)), led us to question if the titanium nitride complex **1.3** could be used as a synthon to stable Ti(II) complexes. With this, we could demonstate that by the use of our sterically protecting PN⁻ ligand, stable Ti(II) complexes capable of characterization could be used to expand upon what is known electronically and structurally for Ti(II) complexes given the relative scarcity of Ti(II) complexes in the literature that are both stable and that have Ti(II) character.

Electrophilic Reactivity of Titanium Nitride Complex with Isocyanides.

As aforementioned, electrophilic reactivity of titanium nitride complexes has not been demonstrated. In an effort to determine if the titanium nitride could behave in an electrophilic fashion, **1.3** was treated with a variety of isocyanides. In particular, adamantyl and *tert*-butyl isocyanide were used in these studies. Upon treating **1.3** with the respective isocyanide, a paramagnetic complex was observed in a ¹H NMR spectroscopic experiment. Upon obtaining single crystals of the reaction with *tert*butyl isocyanide and performing a single crystal X-ray spectroscopic experiment, it was elucidated that the isocyanide had reduced the Ti(IV) nitrido complex to a Ti(II) complex [(PN)₂Ti(NCN^tBu)][K(dme)₃] (**2.9**) (Figure 2.5, Scheme 2.8). Since Ti(II) complexes are quite unstable (vide supra), isolation of a Ti(II) from a reaction conducted at room temperature was indeed unexpected. As can be seen from the molecular structure of **2.9** (Figure 2.5), the Ti1–N3 bond (2.086(1) Å) has been elongated to the order of a single bond. Within the NCN^tBu moiety itself, the N3-C45 bond (1.195(2) Å) is indicative of triple bond character whereas the C45–N4 bond (1.276(2) Å) is on the order of a single bond. This is paired with the near linear angle within the N3–C45–N4 ligand 173.8(2)^o and the rather bent angle of the *tert*-butyl with respect to the NCN moiety C45-N4-C46 117.8(2)°, with N4 having a direct interaction (N4 distance to K1 of 3.036(2) Å) with potassium, which is coordinated with three molecules of DME. All these metrics considered, the resonance as drawn in Scheme 2.8, in which the anionic charge is centered at the terminal nitrogen 72

derived from the isocyanide is the most likely. With regards to overall molecular geometry a ($\tau_5 = 0.6$) demonstrates that this complex is confined between a squarepyramid and trigonal bipyramid. Indeed, not only could this complex be isolated for crystallographic characterization, but even in solution this compound was robust enough to last for hours at room temperature in C₆D₆ in a J-Young NMR tube prior to decomposing to an unidentifiable mixture of diamagnetic and paramagnetic compounds.



Scheme 2.8. Reactivity studies of complex 1.3 with isocyanides to form complexes2.9 and 2.10. Oxidation of 2.10 results in 2.12. Proposed alkylation of 2.10 by electrophiles to alkylate at the terminal nitrogen 2.11.

Analogously, when treated with adamantyl isocyanide, the isostructural complex [(PN)₂Ti(NCNAd)][K(2,2,2-Kryptofix)] (**2.10**) was isolated (Figure 2.5, Scheme 2.8).

While nearly all metrical parameters are identical with a Ti1–N3 bond (2.073(2) Å), a N3-C45 bond of (1.186(3) Å), a C45-N4 bond distance of (1.258(3) Å), a N3-C45-N4 angle of 172.1(3)°, a C45-N4-C46 angle of 119.6(2)°, and a ($\tau_5 = 0.68$), the one marked difference is that by encapsulation of the potassium ion with 2.2.2-Cryptand, the distance between N4 and K1 was increased to 6.495 Å. Without stabilization of the charge on nitrogen by the counter cation, it would be expected that this charge-separated species would be much more nucleophilic in character. To test this hypothesis, **2.10** was treated with a stochiometric amount of methyl iodide (Scheme 2.8). Although no color change occurred, (both Ti (II) precursors are brown), a change was observed the ¹H NMR spectrum, with all paramagnetic resonances attributable to **2.10** no longer observable and new paramagnetic resonances for a different species appearing. While multiple attempts to characterize this species were undertaken, ultimately the extremely soluble nature of this complex made for lack of structural characterization of this complex. However, due to the structure of the precursor **2.10**, the most logical proposition is alkylation of the terminal nitrogen **2.11** as proposed in Scheme 2.8. This unusual ligand would be of interest to isolate as an organic complex (a dialkyliminonitrile).



Figure 2.5. Solid-state structures of complexes **2.9** (upper left), **2.10** (upper right) displaying, and **2.12** (bottom) with thermal ellipsoids at the 50% probability level. H-atoms, disorder of one DME group of **2.9**, and disorder of the adamantyl group in **2.12** have been excluded for clarity.

Using these titanium complexes that are extremely nucleophilic at nitrogen might present a way to access these organic compounds if cleanly oxidizing them from the metal precursor is possible. From a solution of complex **2.10** stored over periods of time in the glove box freezer, a color change to a lighter brown was noted over time, and the formation of some plate shaped crystals on the wall of the vial. Examination of this material by single crystal X-ray diffraction revealed that the complex had been oxidized to a Ti(III) (PN)₂Ti(NCNAd) (**2.12)** (Figure 2.5, Scheme 2.8). While few metrical parameters have changed, some slight changes include a minor decrease is observed of the Ti1–N3 bond (1.948(2) Å). A slight increase in the N3–C45 bond (1.227(4) Å) coupled with a slight decrease in the C45–N4 bond (1.229(34) Å) results in more double bond character in both of these bonding interactions. The N3–C45–N4 angle is essentially unchanged at 174.8(4)° while more importantly the C45–N4–C46 angle of 129.5(4)° is slightly less bent, likely as a result of the elimination of anionic charge residing on this terminal nitrogen. The other marked difference is that this structure is closer to a trigonal bipyramid in character ($\tau_5 = 0.82$) Although unfortunately this complex was in poor yield and likely just a side product of eventual oxidation in the glove box atmosphere overtime, this demonstrated that oxidation to Ti(III) could be achieved. The reproduction of this complex by intentional chemical oxidation has unfortunately not yet been accessible, but if possible in future studies, this complex would provide a nice electronic comparison of the Ti(II) vs. Ti(III) complex constrained to the same ligand environment.

Conclusion.

This chapter has revealed the completely unexpected reactivity of a titanium nitride to be a source of nitridyl radicals. Since little is know of these extremely reactive radicals, this study provides the first detailed mechanistic study of the behavior of early transition metal nitridyl radicals in solution, as well as a glass in matrix EPR studies. It has also been shown that this titanium nitride can be electrophilic in character in reactivity with various isocyanides. Given the novelty of all reactivity discussed in this chapter, and our continued interest to develop the scope of reactivity in early transition metal nitride chemistry, we questioned if we could design zirconium nitride complexes.

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Experimental Details

General Procedures

Unless otherwise stated, all operations were performed in a M. Braun Lab Master double-dry box under an atmosphere of purified dinitrogen or using high vacuum standard Schlenk techniques under an argon or dinitrogen atmosphere. Hexanes, pentane, tetrahydrofuran (THF) and toluene were purchased from Fisher Scientific and Et₂O was purchased from Sigma Aldrich. Solvents were sparged with argon for 20 minutes and dried using a two-column solvent purification system where columns designated for hexanes and toluene were packed with Q5 and alumina respectively, and columns designated for Et₂O and THF were packed with alumina. Deuterated benzene was purchased from Cambridge Isotope Laboratories (CIL) and was sparged with nitrogen for 20 minutes, then was dried over a potassium mirror, vacuum transferred to a collection flask, and degassed by freeze-pump-thaw cycles. All solvents were transferred into a dry box and were stored over 4 Å sieves. Tritylchloride and iodine were purchased and used without further purification. mer-[TiCl₃(THF)₃]¹⁰⁶ and N₂CPh₂¹⁰⁷ were prepared according to literature procedures. **1.3** and **1.9** were prepared according to published literature procedures.^{49,50} NaN₃ was dried by evacuating in a schlenk flask overnight, followed by stirring overnight in THF after bringing into the glovebox. This solution was decanted, and then suspended and stirred in toluene overnight. Finally, after decanting this solution, it was suspended in pentane, stirred overnight, and then this was taken to dryness for use. KC₈ was prepared with by mixing carb

on with potassium and heating over a week at 150 °C in a well-sealed, high pressure flask, with good stirring with a metal stirbar. Each night, the reaction vessel was brought back into the glovebox to manually mix the two reagents to ensure good mixing. All sieves were heated to 200 °C under vacuum overnight prior to use. Celite used for filtrations was heated to 200 °C under vacuum overnight prior to use. ¹H NMR spectra were recorded on a Bruker AVIII 400, AVII 500 MHz spectrometer, DMX

300 MHz spectrometer, or a Bruker DMX 360 MHz spectrometer. ¹³C spectra were recorded on a Bruker AVII 500 MHz spectrometer, ${}^{31}P{}^{1}H}$ spectra were recorded on a Bruker AVIII 400 spectrometer, and ⁷Li NMR spectra were recorded on a Bruker AVIII 400 spectrometer, and ¹⁵N NMR spectra were recorded on a Bruker AVIII 400 spectrometer. ¹H NMR spectra are reported with reference to residual proteo solvent resonances of C₆D₆ at 7.16 ppm. ³¹P{}¹H} NMR spectra were referenced to external H₃PO₄ (0.0 ppm). Elemental analyses were measured by Midwest Microlab for all PN ligand chemistry and in the inorganic chemistry department at the Friedrich-Alexander University Erlangen-Nürnberg, Germany, and also by Robertson Microlit Laboratories, Ledgewood, NJ, USA for the Ti(II) reactivity studies from **2.4**.

Synthesis of (NPN')(PN)Til (2.1)

To a 10 mL orange solution of **1.3** (201 mg, 0.106 mmol, 1 equiv.) in toluene in a 20 mL vial was added 5 mL solution I₂, (253.8 mg, 0.212 mmol, 2 equiv.). The reaction was allowed to stir at room temperature overnight at room temperature. The reaction can then be driven to complexiton by one of the following methods: the solution can be placed into a 25 mL Schlenk flask and photolyzed for fifteen minutes, or alternatively (though not recommended, the reaction will also go if left stirring in ambient light for three days). After completion, all volatiles were removed *in vacuo*. The deep red residue was extracted into toluene and filtered over Celite. The toluene was taken to a minimum (less than 2 mL) in a 20 mL vial and layered with 5 mL hexane. This vial was stored at -35 °C overnight, resulting in the deposition of red crystals suitable for XRD (184 mg, 0.101 mmol, 48% yield). Due to the nature of the proposed mechanism, involving both parent imide and hydride complexes en route to **2.2**, there is inevitably always a small amount (5-10% contamination) of these species in isolated samples. Between this contamination, and the assymetry of the resulting complex, specific resonances are nearly impossible to assign due to overlapping peaks. Reliable / values cannot be determined for most resonances for this reason. ¹H **NMR (400 MHz, 298 K, benzene-d₆):** δ 7.14-6.65 (6H, C-*H*, Ar), 6.55 (d, J = 10.7 Hz,

2H, C-*H*, Ar), 6.17 (dd, *J* = 8.6, 3.5 Hz, 1H, C-*H*, Ar), 5.66 (dd, *J* = 8.6, 3.7 Hz, 1H, C-*H*, Ar), 3.27 (sept, ${}^{3}J_{\text{H-H}}$ = 6.9 Hz, 2H, P-C*H*Me₂), 2.95 (sept, *J* value not possible to measure, 1H, P-C*H*Me₂), 3.63 (s, $\Delta v_{1/2}$ = 4.0 Hz, 6H, C*H*₃, mesityl Ar), 2.67 (s, $\Delta v_{1/2}$ = 3.8 Hz, 6H, C*H*₃, mesityl Ar), 2.3-0.79 (multiple overlapping peaks from P-CH*Me*₂ and Ar-*Me*, 36 H). ${}^{31}P{}^{1}H{}$ NMR (162 MHz, 298 K, benzene-d₆): δ 34.9 (1P, NPN'), 14.7 (1P, PN). Multiple attempts to obtain satisfactory elemental analysis were unsuccessful.

Synthesis of (NPN')(PN)TiCl (2.2)

To a 10 mL orange solution of **1.3** (10 mg, 0.005 mmol, 1 equiv.) in C_6D_6 in a 20 mL vial was added 5 mL solution ClCPh₃, (5.88 mg, 0.02 mmol, 4 equiv.). Triphenylphosphine was added to monitor yield by ³¹P NMR (2.77 mg, 0.01 mmol, 2 equiv.). The reaction was allowed to stir at room temperature overnight at room temperature. The reaction can then be driven to complexiton by one of the following methods: the solution can be photolyzed for fifteen minutes with a Xenon lamp, or alternatively (though not recommended, the reaction will also go if left stirring in ambient light for three days). This NMR reaction was used to determine best yield with the internal standard. This reaction can be scaled up to \sim 200-300 mg of **1.3**, with slightly lowere yields than in the NMR reaction due to increased solubility of 2.2. If conducted on a larger scale, the same procedure is followed, with the exception of the use of toluene as a solvent. After completion, all volatiles were removed in vacuo. The red residue was extracted into toluene and filtered over Celite. The toluene was taken to a minimum (less than 2 mL) in a 20 mL vial and layered with 5 mL hexane. This vial was stored at -35 °C overnight, resulting in the deposition of red crystals suitable for XRD (4 mg, 0.005 mmol, 49% yield). Due to the nature of the proposed mechanism, involving both parent imide and hydride complexes *en route* to **2.2**, there is inevitably always a small amount (5-10% contamination) of these species in isolated samples. Between this contamination, and the assymetry of the resulting complex, specific resonances are nearly impossible to assign due to overlapping peaks. Reliable / values cannot be determined for most resonances for this reason. ¹H NMR (400 MHz, 298 **K, benzene-d₆**): δ 7.10-6.73 (6H, C-*H*, Ar), 6.68 (d, *J* = 7.6 Hz, 2H, C-*H*, Ar), 6.44 (dd, *J* 79

= 10.2, 2.0 Hz, 1H, C-*H*, Ar), 5.92 (dd, *J* = 10.3.6, 3.7 Hz, 1H, C-*H*, Ar), 2.8-0.82 (multiple overlapping peaks from P-CH*Me*₂ and Ar-*Me*). ³¹P{¹H} NMR (162 MHz, 298 K, **benzene-d**₆): δ 35.0 (1P, NPN'), 12.7 (1P, PN). Multiple attempts to obtain satisfactory elemental analysis were unsuccessful.

Synthesis of (NPN')(PN)TiH (2.3)

A 5 mL orange solution of **1.2** in C₆D₆ (10 mg, 0.012 mmol, 1 eq.) was photolyzed by a Xenon lamp for 15 minutes in a J-Young NMR tube and conversion was monitored by ³¹P NMR. The solution turns slightly darker. After completion, all volatiles were removed *in vacuo* and the reaction mixture was filtered over Celite. While stability and increased solubility of this complex prevents bulk characterization, cooling a solution of **2.3** in 1 mL *n*-hexane at -35 °C overnight resulted in the deposition of reddish brown crystals of **2.3** suitable for single crystal XRD. While yield from crystallization was not reliable, monitoring the solution with added triphenyl phosphine (2.6 mg, 0. 012 mmol, 1 eq.) determined the yield to be just less than 49%, as expected given the determined degradation of 50% of the ligand scaffold (4.5 mg, 0.006 mmol, ~50%), However, since bulk isolation of this complex free from starting materials has not been possible, characterization by ¹H NMR has not been possible. ³¹P{¹H} NMR (162 MHz, 298 K, benzene-d₆): δ 22.3 (1P, NPN'), 7.4 (1P, PN).

Experiments to Convert 2.3 to 2.2

A solution of **2.3** (10 mg, 0.013, 1 equiv.) in benzene- d_6 in a J-Young NMR tube was treated with tritylchloride (3.8 mg, 0.12 mmol, 1 equiv.). Immediately ¹H and ³¹P NMR spectra showed clean and quantitative formation of tritylmethane and **2.2**.

Modified Protocol to Prepare *trans*-[(py)₄TiCl₂] (2.4)

In a 250 mL round-bottom flask, 1.000 g (2.70 mmol) of *mer*-[TiCl₃(THF)₃], prepared as described by Jones et al.¹⁰² was dissolved in 100 mL of THF, giving a pale blue solution. With vigorous stirring, 1.1 mL (13.5 mmol) of pyridine was added, turning 80

the solution dark green instantaneously. A sample of 0.5472 g (4.049 mmol) of KC₈ was then added to the flask. The reaction mixture was stirred for 15 min and then filtered through a medium porosity frit layered with a bed of Celite. The Celite was washed with 10 mL of THF, and the combined dark blue filtrate was concentrated in vacuo to ~20 mL. The supernatant was decanted off, and the dark blue product **2.4** was dried in vacuo (yield: 880 mg, 75%, one crop). Attempts to isolate more compound from the filtrate did not produce pure material. Elemental analysis (%), calc for C₁₂H₃₂Cl₂N₄Ti (MW = 351.18 g/mol): C, 55.20; N, 12.87; H, 4.63. Found: C, 47.27; N, 10.51; H, 4.04. The lower carbon content (as well as H and N) is most likely due to pyridine loss (and possible replacement by oxygen and/or water during handling) and the overall thermally unstable nature of this species.

Synthesis of *trans*-[Ti(η²-PhCCPh)(Cl)₂(py)₃] (2.5)

In a 20 mL vial containing a 1/2-in.-long Teflon-coated magnetic stir bar, toluene (4 mL) was added to trans-[(py)₄TiCl₂] (107 mg, 246 µmol), producing a dark blue slurry. In a separate 20 mL vial, toluene (1 mL) was added to PhCCPh (44 mg, 246 μ mol), producing a colorless solution. Both vials were left in a freezer at -35 °C for 30 min. The vials were removed from the freezer, and the PhCCPh solution was added dropwise over 5 min to the stirred **2.4** slurry, producing a dark, amber-colored slurry, which was stirred for 1 h at ambient temperature before filtering through a plug of Celite in a pipet, resulting in separation of a small amount of dark green solid from the amber-colored filtrate. The solvent volume was reduced to \sim 2 mL in vacuo and npentane (10 mL) was added, resulting in the precipitation of a light-green solid. The supernatant was decanted, and the solid was dried in vacuo and isolated as an olivegreen microcrystalline powder (99 mg, 75% yield). ¹H NMR (300 MHz, 298 K, **benzene-d**₆): δ 9.28 ($\nu_{1/2}$ = 34 Hz, 6H, *o*-H_{DV}), 7.48 (d, ³]_{HH} = 8 Hz, 4H, *o*-HPh), 7.13–7.02 (5H, H_{tol}) 7.01 (pseudo-t, ${}^{3}I_{HH}$ = 8 Hz, 4H, m-H_{Ph}), 6.89 (t, ${}^{3}I_{HH}$ = 7 Hz, 2H, p-HPh), 6.69 ($v_{1/2}$ = 44 Hz, 3H, *p*-H_{py}), 6.42 ($v_{1/2}$ = 32 Hz, 6H, *m*-Hpy), 2.11 (s, 3H, H_{tol}). ¹³C{¹H} NMR (**75 MHz, 298 K, benzene-d₆**): δ 152.0 ($\nu_{1/2}$ = 58 Hz), 141.5 ($\nu_{1/2}$ = 1 81

Hz), 136.8 ($\nu_{1/2}$ = 41 Hz), 131.9 ($\nu_{1/2}$ = 1 Hz), 128.1 ($\nu_{1/2}$ = 1 Hz), 127.6 ($\nu_{1/2}$ = 1 Hz), 126.5 ($\nu_{1/2}$ = 2 Hz), 123.4 ($\nu_{1/2}$ = 19 Hz). Crystals suited for X-ray diffraction (XRD) analysis were obtained by layering a saturated solution in toluene with *n*-pentane. Multiple attempts to obtain satisfactory elemental analysis were unsuccessful.

Synthesis of Complex (py)₂(Cl)₂Ti(µ₂:η₂-N₂CPh₂)₂Ti(Cl)₂ (2.6)

In a 20 mL vial containing a 1/2-in.-long Teflon-coated magnetic stir bar, toluene (4 mL) was added to 2.4 (135 mg, 310 µmol), producing a dark blue slurry. In a separate 20 mL vial, toluene (2 mL) was added to N_2CPh_2 (60 mg, 310 μ mol), producing a fuchsia-colored solution. The N₂CPh₂ solution was added dropwise to the slurry of **2.4** over 2 min, resulting in a color change to orange-red. The mixture was stirred for 15 h and then filtered to remove a small amount of a dark green precipitate, presumably a Ti(III) disproportionation product. The reaction mixture was concentrated to approximately 2 mL in vacuo. To this solution n-pentane (10 mL) was added, resulting in the generation of a precipitate. The supernatant was decanted and the solid was dried in vacuo. The solid was triturated in n-pentane (5 mL) and the supernatant was decanted. The solid was dried in vacuo and isolated as a dark, red residue (76 mg, 21% yield). ¹H NMR **(300 MHz, 298 K, benzene-d₆):** δ 9.38 (s/br, 6H, o-H_{Pv}), 8.20 (d/br, 4H, o-H_{Ph}), 7.71 (s/br, 4H, H_{Ph}), 7.14–6.78 (12H, H_{Ph}), 6.72–6.41 (9H, m, p-H_{Pv}). ¹³C{¹H} NMR (75 MHz, 298 K, benzene-d₆): δ 136.4, 136.1, 131.6, 131.2, 131.1, 131.0, 129.8, 129.5, 129.1, 128.9, 128.8, 126.8, some resonances for the py and phenyl ligands could not be located. Multiple attempts to obtain satisfactory elemental analysis were unsuccessful.

Synthesis of trans-[Ti=NPh(Cl)₂(py)₃] (2.7)

2.4 (50.4 mg, 0.116 mmol) was suspended in ~3 mL of toluene. To this suspension,
PhN=NPh (14.8 mg, 0.081 mmol) was added as a solid, changing rapidly the color from blue to brown-red with precipitation of a brown solid. The brown solid was
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filtered, washed with pentane, and then dried under reduced pressure. ¹H NMR spectroscopy of the solid in CDCl₃ confirmed quantitative formation of complex **2.7** by comparison with the literature report.⁹⁹

Synthesis of Ti(η^{8} -COT)Cl(py)₂ (2.8) Contaminated with *mer*-[(py)₃TiCl₃].

An excess of COT (10–15 equiv.) was added at room temperature to a stirring suspension of **2.4** (100 mg, 0.230 mmol) in toluene (5 mL) resulting in formation of an insoluble brown powder, which was dissolved in a minimum of pyridine (0.1–0.5 mL). The solution was then layered with Et_2O and cooled to –35 °C to afford palecolored crystals of **2.8** contaminated with pale blue-green crystals of the known complex *mer*-[(py)₃TiCl₃].¹⁰¹ Multiple attempts to purify **2.8** by fractional crystallization failed due to its similar solubility to that of *mer*-[(py)₃TiCl₃]. A few crystals of **2.8** could be separated manually and were used for XRD studies.

Synthesis of [(PN)₂Ti(NCN^tBu)][K(dme)₃] (2.9)

To a 10 mL orange solution of **1.3** (305.8 mg, 0.161 mmol, 1 equiv.) in toluene in a 20 mL vial was added 5 mL solution $CN^{t}Bu$, (36.5 μ L, 0.323 mmol, 2 equiv.). The reaction was allowed to stir overnight at room temperature. At this point the reaction was an orange brown color. All volatiles were removed *in vacuo*. The sticky residue was extracted into toluene and filtered over Celite. The toluene was taken to dryness and the residue was dissolved in a minimum (less than 2 mL of DME). This vial was stored at -35 °C overnight, resulting in the deposition of brown crystals suitable for XRD (105 mg, 0.09 mmol, 28% yield).

Synthesis of [(PN)₂Ti(NCNAd)][K(2,2,2-Kryptofix)] (2.10)

To a 10 mL orange solution of **1.3** (98.4 mg, 0.052 mmol, 1 equiv.) in toluene in a 20 mL vial was added 5 mL solution CNAd, (19.3 mg, 0.119 mmol, 2 equiv.) and a toluene 83

solution of 2,2,2-Kryptofix (39 mg, 0.104 mmol, 1 equiv.). The reaction was allowed to stir at room temperature overnight. At this point the reaction was an orange brown color. All volatiles were removed *in vacuo*. The sticky residue was extracted into toluene and filtered over Celite. The toluene was taken to dryness and the residue was dissolved in a minimum (less than 2 mL of Et₂O). This vial was stored at -35 °C overnight, resulting in the deposition of orange brown crystals suitable for XRD (30 mg, 0.02 mmol, 19.1% yield).

Crystallographic Experimental Details

Crystallographic data are summarized Tables 2.3-2.4. Suitable crystals for X-ray analysis of **2.1-2.3**, **2.9-2.11**, and **2.12** were placed on the end of a Cryoloop coated in NVH oil. Data for single crystal structure determination of **2.1-2.3**, **2.9-2.11** and **2.12** were taken on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-Kα radiation (λ =0.71073 Å) at a temperature of 100(1) K. Suitable crystals for X-ray analysis of **2.4-2.6** and **2.8** were placed onto the tip of MiTeGen loop coated in NVH oil and mounted on an Apex Kappa Duo diffractometer. Rotation frames were integrated using SAINT,¹⁰⁸ producing a listing of non-averaged F^2 and s(F^2) values The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS.¹⁰⁹ The initial structures were solved by dual methods – SHELXT.¹¹⁰ Refinement was by full-matrix least squares based on F² using SHELXL.¹¹¹ All reflections were used during refinement.

Table 2.3. Crystallographic Data of compounds **2.1-2.3**.

Compound	2.1 · 0.5(C ₆ H ₁₄)	2.2 · 0.5(C ₆ H ₁₄)	2.3
Molecular formula	$C_{93}H_{136}I_2N_6P_4Ti_2$	C ₄₄ H ₆₂ ClN ₃ P ₂ Ti, 0.5(C ₆ H ₁₄)	$C_{44}H_{62}N_3P_2T_1$
Formula weight	1811.56	821.34	742.81

Temperature (K)	100(2)	100(2)	100(2)
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P -1	P -1	C 2/c
Cell constants:			
a (Å)	13.8717(7)	11.3590(4)	47.9344(11)
b (Å)	14.6574(7)	12.5559(5)	11.7870(3)
c (Å) Alpha Agle Beta Angle Gamma Angle	23.5957(12) 82.944(2) 84.692(2) 83.895(2)	17.5731(6) 70.559(2) 82.073(2) 68.708(2)	42.7402(9) 90 120.6210(10) 90
Volume (ų)	4718.8(4)	2201.68(14)	20781.0(8)
Z	2	2	20
Density (calcd mg/m3)	1.275	1.239	1.187
Abs coeff (mm-1)	0.936	0.363	0.316
F(000)	1892	882	7980
Wavelength	0.71073	0.71073	0.71073
θ range for data collection (°)	1.41 to 27.63	2.83 to 27.54	0.99 to 27.51
<i>h, k, l</i> ranges collected	$-18 \le h \le 18$ $-19 \le k \le 19$ $-30 \le l \le 30$	$-14 \le h \le 14$ $-16 \le k \le 16$ $-22 \le l \le 22$	$-62 \le h \le 62$ $-15 \le k \le 15$ $-55 \le l \le 55$
# Reflns collected	21720	7721	23896
Refinement method	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²
R_1^{a}	0.0381	0.0521	0.0966

$wR_{2^{b}}$	0.0880	0.1384	0.2473
Goodness-of-fit on <i>F2^c</i>	1.058	1.032	1.029

Table 2.4. Crystallographic Data of compounds **2.9-2.10** and **2.12**.

Compound	2.9	2.10	2.12
Molecular formula	$C_{61}H_{101}KN_4O_6P_2Ti$	$C_{73}H_{113}KN_6O_6P_2Ti$	$C_{55}H_{77}N_4P_2T_1$
Formula weight	1135.40	1319.63	904.04
Temperature (K)	100(2)	100(2)	100(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P -1	P 1 2 ₁ /c 1	P 1 2 ₁ /c 1
Cell constants:			
a (Å)	12.6755(10)	12.8677(7)	14.1176(3)
b (Å)	15.8383(13)	27.2098(15)	27.0441(7)
c (Å) Alpha Agle Beta Angle Gamma Angle	$18.5406(15) \\70.607(4) \\73.508(4) \\69.841(4)$	20.9332(12) 90 99.951(2) 90	13.2120(3) 90 91.6870(10) 90
Volume (ų)	3235.0(5)	7219.0(7)	5042.1(2)
Z	2	4	4
Density (calcd mg/m3)	1.166	1.214	1.191
Abs coeff (mm-1)	0.295	0.274	0.273
F(000)	1228	2848	1948
Wavelength	0.71073	0.71073	0.71073

θ range for data collection (°)	1.59 to 27.55	1.497 to 27.535	0.99 to 27.51
<i>h, k, l</i> ranges collected	$-16 \le h \le 16$ $-20 \le k \le 20$ $-24 \le l \le 24$	$-16 \le h \le 16$ $-35 \le k \le 35$ $-26 \le l \le 27$	$-18 \le h \le 18$ $-35 \le k \le 35$ $-17 \le l \le 17$
# Reflns collected	14731	16454	11622
Refinement method	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²
$R_{1^{\mathrm{a}}}$	0.0441	0.0510	0.0512
$wR_{2^{b}}$	0.1065	0.1216	0.1278
Goodness-of-fit on <i>F2^c</i>	1.020	1.063	1.046

 $\overline{a R1} = (|Fo| - |Fc|) / |Fo|. b wR2 = [[w(Fo2 - Fc2)2] / [w(Fo2)2]]1/2. c Goodness-of-fit = [[w(Fo2 - Fc2)2]/Nobservns Nparams)]1/2, all data.$

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Chapter 3:

Extending Reactivity: Synthesis of A Molecular Zirconium Nitrido Superbase and A Transient Uranium Nitrido

Introduction. As discussed in Chapter 1, group 4 transition metal nitrides represent an important category of materials due to their inherent properties such as extraordinary hardness, anticorrosiveness, and heat-resistance which make them useful for coating or protective purposes.¹⁻³ Molecularly, group 4 metal nitrides have been proposed inasmuch as isolated from the reductive splitting of atmospheric nitrogen,⁴⁻¹³ as well as in the ring-opening, denitrogenation and hydrodenitrogenation of pyridines and quinolines.¹⁴ Precursors for mononuclear molecular zirconium nitrides, a class of compounds which can allow us to understand the bonding and structure for this ligand, have remained elusive. The challenge in accessing a multiply bonded zirconium nitride moiety is attributed to both the propensity of titanium and zirconium nitrides to bridge and oligomerize,¹⁵⁻²¹ and also the lack of suitable N-atom transfer reagents that deliver a single N-atom selectively. This is in stark contrast to the aforementioned preparation through titanium parent imido species or azido ligands.²²⁻²⁵ Although one class of reagent that fits such criteria for the preparation of new Zr nitrides is the ubiquitous azido ligand, the lack of L_nZr(II) precursors that can promote metal oxidation with concurrent disproportionation of N_3^- to N_2 and N^{3-} make this approach more of an encumbrance. Realizing coordinatively unsaturated Zr(III) precursors are unstable (Figure 3.1),^{26,27} and a parent imide should be a synthon to a nitride, we hypothesized that a Zr(IV) azide precursor could be instead reduced to a radical species. As depicted in Figure 3.1 are non-metallocene Zr(III) complexes reported by Eisen and coworkers and also our group. Eisen reported the allyl complex $L_2M(\mu-Cl)_2Li(TMEDA)$ (L = $(^{t}BuMe_{2}SiCH)_{2}CH$, M = Ti, Zr). While these complexes were crystallographically characterized and competent at olefin polymerization, they were easily oxidized by oxygen (and during the polymerization process dry to L₂MCl₂ and (^tBuMe₂SiCH=CHCH(SiMe₂^tBu)CH(SiMe₂^tBu)CH=CH(SiMe₂^tBu).²⁷ The complex (PN)₂ZrCl, which is also depicted in Figure 3.1, will be discussed in greater detail in Chapter 5. Given the success of the PN⁻ ligand with Ti nitrides, we continued with the use of this ligand since it supports an ideal geometry for metal-ligand multiple bonding, while providing flexibility and robustness.^{23,24,26,28,29}



Figure 3.1. Non-metallocene M(III) complexes, M = Ti, Zr. $L_2M(\mu$ -Cl)₂Li(TMEDA) L = (^tBuMe₂SiCH)₂CH reported by Eisen and coworkers (left). (PN)₂MCl M = Ti, Zr, Hf, reported by our group and will be discussed in Chapter 5 (right).

Using an alternate route to that of titanium, we were able to synthesize the first mononuclear example of a zirconium parent imide, namely $(PN)_2Zr\equiv NH$ (3.3). Using a strong base, complex 3.3 can be deprotonated to afford a molecular monoanionic nitride complex { $(PN)_2Zr\equiv N[\mu_2-Li(THF)]$ } (3.4). Utilizing 50% α -N enriched ¹⁵N₃⁻, the NMR and IR spectroscopic data for the isotopologues of 3.2-3.4 will be discussed. The super basicity of the nitride ligand in 3.4 is estimated, and theoretical studies conducted by Prof. Balazs Pinter for this new class of moiety in zirconium coordination chemistry.

In addition to Zr nitrides, looking down group (IV), we show how other platforms using the PN⁻ ligand can potentially be capable of stabilizing a nitrido ligand of hafnium or cerium. The synthesis and characterization of a uranium nitride supported by the PN ligand done in collaboration with the Schelter and Baik groups is also presented.
Results and Discussion

Synthesis of a Zirconium Nitride.

As will be further discussed in Chapter 5, trivalent complexes (PN)₂MCl can be prepared from one electron reduction of (PN)₂MCl₂ (M = Zr (**3.1**), Hf),²⁶ but these compounds are metastable and readily undergo disproportionation in solution especially with NaN₃. Intuitively, a cleaner and more convenient entry to **3.2** involved vigorous stirring of **3.1** with excess (4 equiv.) NaN₃ in 1,4-dioxane over 72 hours at 75 °C (Scheme 3.1). A notable feature is the characteristic N₃⁻ vibration at 2094 cm⁻¹ in the IR spectrum which has been identified unambiguously through the isotopologue (PN)₂Zr(¹⁵N₃)₂ (**3.2**)-¹⁵N, red-shifted to 2081 cm⁻¹. The ¹⁵N NMR spectrum of **3.2**-¹⁵N also revealed two resonances at 154.6 and 114.0 ppm, akin to two resonances observed for the reported ¹⁵N-enriched bisazide *trans,trans,trans*-[Pt(N₃)₂(OH)₂(py)₂].³⁰ A single-crystal X-ray diffraction (XRD) study of **3.2** confirmed the presence of two azido ligands, oriented *trans* to each other with the two PN ligands occupying the basal plane (Figure 3.2).



Scheme 3.1. Synthesis of precursor **3.2**, parent imide **3.3**, nitride **3.4**, and protonation back to **3.3**.

Having the azido ligand on zirconium(IV), complex 3.2 was treated with an excess of KC_8 (2.2 equiv.) in Et_2O (or THF), in hopes of producing the nitride salt $\{(PN)_2 Zr \equiv N[\mu_2 - K(solvent)_x]\}_2$ like that found for the titanium congener **1.3**.^{23,24} As detailed in the introduction, since Zr(III) precursors aren't easily stabilized, and (PN)₂ZrCl rapidly disproportionates (see Chapter 5), a Zr(IV) precursor is used as opposed to Ti(III) used to access **1.3**. Upon work-up of the reaction mixture, the monomeric zirconium parent imide, **3.3**, was instead isolated in 42% yield (Scheme 3.1). Mononuclear parent imides are unknown for zirconium and examples of bridging imides are exceptionally rare.^{19-21,31,32} Complex **3.3** displays a singlet resonance ($\Delta v_{1/2}$ = 9.0 Hz) in the ¹H NMR spectrum corresponding to the parent imido ZrNH residue at 5.11 ppm (Figure 3.3, top left). The latter spectroscopic feature resolved into a doublet accompanied with \sim 50% of the signal for unlabeled **3.3** with a ${}^{1}I_{NH}$ = 63.5 Hz for the isotopologue (PN)₂Zr \equiv ¹⁵NH, (**3.3**)-¹⁵N (Figure 3.3, top right). A weak v(NH) stretch in IR spectrum at 3392 cm⁻¹ could be assigned, which redshifted to 3385 cm⁻¹ for **3.3**-¹⁵N. With 50% enriched **3.3**-¹⁵N, the presence of the parent imido moiety at 351.4 ppm (referenced to liquid ammonia at 0.0 ppm, Figure 3.3, bottom left) using INEPT ¹⁵N NMR spectroscopic experiment (conducted with the assistance of Dr. Jun Gu) was confirmed. Without signal enhancement, this resonance was too broad to conclusively assign, due to 91 Zr (*I* = 5/2, 11.22%) in addition to 50% loss of enriched ¹⁵N as a result of the reduction. There are scarce examples of terminal parent imides of titanium reported in the literature, 22,24,25,33 and their 1 /_{NH} values (1 /_{NH} = 64.0 Hz) are coincident with those observed for 3.3 or $3.3^{-15}N^{22,25}$ A bridging $Zr_2(\mu_2-NH)$ moiety also has a nearly identical ¹*J*_{NH} value to **3.3** or **3.3**⁻¹⁵N when prepared with enriched ¹⁵N, which demonstrates that these indeed have characteristic coupling constants even though this was a Zr amido/imido/nitrido cluster complex.¹⁹ The XRD of **3.3** established a C_2 symmetric complex (Figure 3.2, right) with the phosphine and anilide moiety pairs in a *trans* orientation and with the 97

metal ion being confined between square pyramidal and trigonal bipyramidal geometries ($\tau_5 = 0.69$).³⁴ The imido H-atom was located on a difference map and refined isotropically with an N–H distance of 0.86(3) Å. However, the most salient metrical parameter for compound **3.3** is the very short Zr–N_{imide} distance of 1.830(3) Å (Figure 3.2).



Figure 3.2. Molecular structures of **3.2** (left), **3.3** (middle), and **3.4** (right) with ellipsoids shown at the 50% probability level. H-atoms and residual pentane from **3.3** and toluene from **3.4** have been omitted for clarity.

Formation of **3.3** from precursor **3.2** most likely traverses through a putative Zr(III) azide (PN)₂ $Zr(N_3)$ (**3A**) species, followed by N₂ extrusion to form a nitridyl (PN)₂ $Zr \equiv N \cdot (3B)$, which then abstracts an H-atom to generate **3.3** (Scheme 3.2). As discussed in Chapter 2, these group 4 nitridyl species are incredibly rare, and this study presents an exciting opportunity to investigate the reactivity of these elusive radical intermediates. Performing the reduction in isotopically enriched solvent, THF- d_8 , did not result in any observable deuteration of the imido residue in **3.3**, thus confirming the PN ligand to be the source of the H-atom. The yield of <50% of **3.3** is in agreement with at least half the amount of the "(PN)₂Zr" scaffold being cannibalized.



Figure 3.3. ¹H NMR Spectrum of **3.3** in C₆D₆, featuring N-*H* (upper, left); ¹H NMR Spectrum of **3.3**-¹⁵N in C₆D₆, featuring N-*H* (upper, right); ¹⁵N INEPT NMR Spectrum of **3.3**-¹⁵N in C₆D₆ (bottom, left); ⁷Li NMR Spectrum of **3.4**-¹⁵N in C₆D₆.



Scheme 3.2. Synthesis of **3.3** from precursor **3.2** through a putative Zr(III) azide $(PN)_2Zr(N_3)$ (**3A**) species. Loss of N₂ forms a transient nitridyl $(PN)_2Zr\equiv N \bullet$ (**3B**), which abstracts an H-atom to generate **3.3**.

Studies to Quantify Basicity of the Zirconium Nitrido Moiety.

Having successfully obtained **3.3**, strong bases were used to attempt deprotonation of this rare functional group. While benzyl potassium resulted in no reaction (p K_a of toluene is ~43@25 °C in DMSO),³⁵ treatment of **3.3** with LiCH₂SiMe₃ in toluene³⁶ rapidly formed TMS along with a new material. Work-up of the reaction resulted in the formation of yellow colored crystals in 45% yield, which were identified to be the nitride {(PN)₂Zr \equiv N[μ_2 -Li(THF)]}₂ (**3.4**) (Scheme 3.1). ¹H and ³¹P NMR spectra of **3.4** are in accordance with a C_2 symmetric system, but now in absence of the broad feature at 5.11 ppm (¹H NMR, *vide supra*) for the formal ZrN*H* moiety in **3.3**. Surprisingly, attempts to observe a ¹⁵N NMR spectroscopic feature for 50% labeled isotopomer { $(PN)_2Zr \equiv {}^{15}N[\mu_2-Li(THF)]$ }, (3.4)- ${}^{15}N$, were inconclusive. Computational studies conducted by Prof. Balazs Pinter suggest the NMR spectroscopic signal to reside quite downfield (745 ppm (B3LYP) and 684 ppm (TPSSh), as expected, whereas a $Zr \equiv N$ stretch in the IR was estimated to be at 884 cm⁻¹. Despite this, the ⁷Li NMR spectrum of **3.4**-¹⁵N shows a doublet (in addition to a broad shoulder) due to coupling with nitrogen, ${}^{1}/_{NLi}$ = 43.2 Hz (Figure 3.3, bottom right). This broad shoulder is expected based on the mixture of isotopologues (see discussion below), in which for 50% of the mixture both nitride nitrogens carry a ¹⁵N label, and then for 25% of the mixture only one nitrogen is labeled, so more than one signal is expected. Therefore, we are confident that coupling of the nitride with lithium (⁷Li, I = 3/2, 92.58%) leads to significant broadening of the ¹⁵N NMR spectroscopic signal. A ⁷Li NMR spectrum of unlabeled **3.4** indeed shows a singlet and further corroborates the nitrogen/lithium coupling. The observed doublet in the 7Li NMR spectrum of **3.4**-¹⁵N can be best explained when considering the mixture of isotopologues { $(PN)_2 Zr \equiv {}^{15}N[\mu_2-Li(THF)]_2 {}^{15}N \equiv Zr(PN)_2$ } (25%), { $(PN)_2 Zr \equiv {}^{14}N[\mu_2-Li(THF)]_2 {}^{15}N \equiv Zr(PN)_2$ } 100

Li(THF)]₂{¹⁴N≡Zr(PN)₂} (25%), and {(PN)₂Zr≡¹⁵N[μ_2 -Li(THF)]₂{¹⁴N≡Zr(PN)₂} (50%), with the latter species being the most prevalent. To unequivocally prove the presence of an N-atom coordinated to Zr in **3.4**, exceptionally weak acids were used. Diisopropylamine (p K_a = 36@25 °C in THF)³⁷ resulted in clean formation of **3.3** concurrently with LiN^{*i*}Pr₂ (Scheme 3.1). This feature contrasts the titanium nitride {(PN)₂Ti≡N[μ_2 -K(Et₂O)]}₂ which could not deprotonate diisopropylamine, hence rendering the zirconium nitride ten orders of magnitude more basic and in line with the IUPAC definition of a superbase. Since toluene does not protonate **3.4**, this complex is definitely an inorganic superbase in the –36 to –43 p K_b range.³⁸

A single crystal of **3.4** suitable for an XRD study allowed us to conclusively confirm not only the degree of aggregation of the nitride, but also the extent of bonding involving the Zr(IV) ion, N³⁻ and the counter cation Li⁺ (Figure 3.2). In contrast to the nitrides bridging the Zr(IV) ions, the Li⁺ counter cations bridge the nitride ligands with each Zr(IV) ion confined between square pyramidal and trigonal bipyramidal (τ_5 = 0.55). Overall, the solid-state structure of **3.4** parallels our reported titanium analogue {(PN)₂Ti=N[μ_2 -K(Et₂O)]}₂,^{23,24} with the notable feature being the presence of the shortest Zr=N bond distance recorded to date for a molecular zirconium nitride (1.822(2) Å).

Computational Studies Scrutinizing the Zirconium Nitride Functionality.

To gain further insight into the bonding of these unique $Zr\equiv NH$ and $Zr\equiv N^{-1}$ functionalities, Prof. Balazs Pinter modeled the structures of **3.3** and **3.4** without truncation using DFT methods (note that Prof. Pinter conducted all theoretical studies for this work). The lengths of the zirconium-nitrogen bonds are slightly overestimated (by about 0.02 Å) for both $Zr\equiv NH$ and $Zr\equiv N^{-1}$ functionalities in **3.3** and **3.4**, respectively, most likely due to condensed phase effects being omitted. Figure 3.4 shows the MO analysis of **3.4** with one σ - and two π -type orbitals expected for the $Zr\equiv N^{-1}$ moiety in the dimer. The fragment orbitals representing these interactions in each subunit from symmetry allowed bonding (+) combinations and antibonding (-) 101

combinations (Figure 3.4, right, Figure 3.7). When scrutinizing the electronic structure of molecular titanium nitrides,^{23,24} vide supra, we established that the redox inactive alkali metal ligation to the nitride center significantly alters the covalent/ionic nature of the terminal metal-nitride bonds. Proximity of the potassium ion electrostatically stabilizes the highly charged nitride center and induces a substantial density shift from the metal center towards the N_{nitride}, resulting in the Ti \equiv N bond becoming more ionic in [(PN)₂Ti \equiv N-K(18-crown-6)] than in the discrete salt [K(cryptand)][(PN)₂Ti \equiv N].



Figure 3.4. MOs representing the $Zr \equiv N$ bonding in **3.3** and **3.4**, shown at isovalue of \pm 0.04 and given together with their orbital energies in eV. Subscripts || and for \perp

characterize the orientation of the π orbitals; in-plane with or perpendicular to the N₂Li₂ plane, respectively.

To reveal if the lithium ions in **3.4** play a crucial effect in the $Zr \equiv N$ bonds the in silico investigation was extended to the hypothetical monomeric anion $[(PN)2Zr \equiv N]^{-}$, **3.5**. Electronic structure descriptors indeed show that the proximity of the Li⁺ ions render the $Zr \equiv N$ functionalities more ionic in **3.4**. Notably, the different ionic characters can be clearly witnessed in the computed atomic NBO charges of Zr (2.1 e in **3.4** and 1.34 e in **3.5**) and N_{nitride} (-1.81 e vs. -1.27 e, respectively). Likewise, the reduced Wiberg [Mayer] bond order index of 1.55 [2.79] for the Li/Zr≡N bond of **3.4** with respect to that of the $Zr \equiv N^-$ bond in **3.4** (2.28, [2.92]) further implies a lower degree of covalent bonding character for the former. Proximity of Li⁺ to the N_{nitride} lowers the energy of the nitrogen's atomic orbitals thus creating a large energy mismatch with the interacting zirconium orbitals. Due to this energy mismatch of interacting atomic orbitals, the polarized $Zr \equiv N$ bonding orbitals possess a higher degree of nitrogen character.^{23,24} It is also worth noting that, although the N...Li distances are barely larger than 2 Å, calculations reveal these to be mostly electrostatic in nature. Similar observations were made by Schwarz et al. based on an analysis on the stabilization and bond character altering effects of Li⁺ coordination to electron-rich multiple-bonded nitrogens in titanium complexes $[TiMe(NAr)_3[Li(py)]_3]$ and $[Ti(NAr)_2(NHAr)_2[Li(py)]_2]$ where $Ar = 2,6-C_6H_3^iPr_2^{.39}$ For comparison, calculations were performed on a nitride variant were potassium is exchanged for the lithium cation, $\{(PN)_2 Zr \equiv N[\mu_2 - Li(THF)]\}_2$ (3.6). For this derivative, the NBO charge of Zr is instead 1.83 e and $N_{nitride}$ is -1.47. Furthermore, the slight increase in Wiberg [Mayer] bond orders to 1.69 [2.83] relative to 3.4, along with the slightly larger N...K distance of 2.67 Å implies that in this proposed structure, **3.6** has $Zr \equiv N$ bond character in between that of **3.4** and **3.5**.

The molecular orbitals of the parent zirconium-imide complex **3.3** (Figure 3.4, left, Figure 3.8) reveal Zr–N interactions that are conceptually very similar to that of the above-discussed Zr \equiv N functionality for **3.4**. Namely, two π -bonds and one σ -bond can be clearly recognized for the terminal Zr \equiv NH group, while the lone pair on nitrogen 104

in **3.4** transforms into the N–H σ bond in **3.3**. The latter feature is in fact the main difference between the Zr \equiv N...Li⁺ and Zr \equiv NH functionalities. NBO charges of 1.74 e for Zr and -1.37 e for N indicate an ionic character for the Zr–N bond in **3.3** that is between that of **3.4** and **3.5**. Metrical parameters and Wiberg bond order indices (1.48 in **3.3** and 1.55 in **3.4**) actually indicate overall identical bonding topologies in these species.

Extending Studies to Uranium.

Continued research on the chemistry of U–N multiple bonds is motivated in part by their strikingly different behavior when compared to analogous U=O bonds. For example, while *cis*-uranyl complexes have remained elusive, *cis*-bis(imido)complexes are known.⁴⁰⁻⁴² Recent advances in the field of uranium nitrogen multiple bonds include isolation of the first examples of a terminal, molecular uranium-nitride,⁴³⁻⁴⁵ uranium tris- and tetrakis-imido moieties, and the complete scission and functionalization of N₂ with a molecular uranium cluster compound.⁴⁶⁻⁴⁹ The single example of a uranium complex with a terminal parent imido U=NH moiety, [K(15crown-5)₂][U^{IV}(Tren^{TIPS})(=NH)] (Tren^{TIPS} = N-(CH₂CH₂NSiⁱPr₃)₃), has been reported by Liddle and coworkers.⁵⁰

Extending these studies to the f-block, we were able to accomplish the synthesis of uranium halide complexes supported by PN⁻ ligands, $(PN)_2U^{III}I$ (**3.7**) and $(PN)_2U^{IV}Cl_2$ (**3.8**) in collaboration with the Schelter group, specifically student Kim Mullane. These compounds served as a new platform for exploring uranium–nitrogen multiple bond chemistry. Reaction of both **3.7** and **3.8** with sodium azide yielded the uranium(IV) product, $(PN)_2U^{IV}(N_3)_2$ (**3.9**). When treated with potassium graphite, complex **3.7** yielded a rare example of an f-block parent imido complex, $[K(THF)_3][(PN)U^{IV}(=NH)[^iPr_2P(C_6H_3Me)N-(C_6H_2Me_2CH_2)]]$ (**3.10**). We propose that this reaction proceeded through a transient uranium nitride intermediate, which added across the C–H bond of a proximate methyl group of the PN⁻ ligand, forming the parent imido metallacycle-ate product.

Synthesis of a Uranium Parent Imido Complex.

Treatment of UI₃(THF)₄ and UCl₄ with 2 equiv. K(PN) in THF solutions yielded **3.7** and **3.8**, respectively (Scheme 3.3). Note that **3.7** was previously synthesized by Prof. Daniel Mindiola with Humboldt Stifstung, and the crystal structure was obtained by him while he worked at the lab of Prof. Karsten Meyer and crystallographer Dr. Frank Heinemann. The salt metathesis reactions were completed in 2 h, and the products were isolated in crystalline yields of 48% and 62% for compounds **3.7** and **3.8**, respectively. In addition to ¹H NMR spectra, these compounds were characterized by single crystal X-ray diffraction (Figure 3.5). Notably, compounds **3.7** and **3.8** had differing coordination modes of the PN⁻ ligand, with transoid-(N,N) and cisoid-(N,N) geometries for **3.7** and **3.8**, respectively, which presumably coincide with their uranium(III) and uranium(IV) oxidation states. Similar isomerization processes have been observed in trivalent versus tetravalent group 4 transition metal complexes of the type (PN)₂M^{III}Cl or (PN)₂M^{IV}Cl₂ (M = Ti, Zr, and Hf).²⁶

Compound **3.7** was treated with 1–2 equiv. of sodium azide (NaN₃), and after 1.5 h the ¹H NMR spectrum revealed the formation of a uranium(IV) species, which corresponded to (PN)₂U^{IV}(N₃)₂ (**3.9**) on the basis of solid-state structural data (Figure 3.5, Scheme 3.3). Note that all synthetic work described in the synthesis of this and the following compounds was conducted by Kim Mullane in the Schelter group. The reaction mixture also contained free HPN presumably formed through the disproportionation of **3.7** or similarly through a disproportionation of the putative (PN)₂U^{III}(N₃) to **3.9** and elemental uranium. This type of reaction has been previously observed for uranium(III) compounds; for example, reaction of U^{III}[N(SiMe₃)₂]₃ with MeLi results in MeU^{IV}[N(SiMe₃)₂]₃.⁵¹ Given the low yield of **3.9** from **3.7** and NaN₃, a more rational route involved salt metathesis of **3.8** with 2 equiv. NaN₃, which resulted in clean conversion to **3.9** in 94% isolated yield.

Extruding N₂ and forming the U-nitrido moiety is formally an oxidative process involving an increase of the oxidation state of the metal cation by +2. Thus, if **3.9** were to eject N₂, the resulting nitrido ligand in a hypothetical complex (PN)₂U \equiv N(N₃) would 106 be bound formally to a U(VI) center. The mechanism of N₂ extrusion is reminiscent of previous work on Mo-azides.⁵² DFT-calculations done in collaboration with the Baik group (students Ho Ryu and Ji Young Park) estimate this process to be 24.1 kcal/mol downhill, due to the strong driving force provided by the liberation of N₂, but the barrier is estimated to be high at 30.3 kcal/mol. Unsurprisingly, there was no sign of such reaction from **3.9** experimentally. An obvious way of promoting N₂ extrusion is reducing the uranium center. Our DFT-calculations indicate that the reduction of the U(IV) center by a single electron to U(III) reduces the N₂ extrusion barrier by 9.3 kcal/mol to afford a ΔG + of 21.0 kcal/mol. Additional reduction to U(II) lowers the free energy barrier further by 20.6 to 0.4 kcal/mol, rendering it a barrierless process. These computed barriers illustrate the general trend that the oxidative release of N₂ from the uranium center in lower oxidation states is more feasible. Realistically, U(III) is most likely the active species, as the barrier of 21.0 kcal/mol is reasonable and should result in rapid N₂ extrusion, while maintaining structural integrity. The overreduction to U(II) is likely accompanied by degradation and decomposition of the metal-complex, initiated by loss of both azido ligands.



Scheme 3.3. Synthesis of **3.7** UI₃(THF)₃. Treatment of **3.7** with NaN₃ forms **3.9**. Treatment of **3.9** with excess KC₈ results in the formation of parent imido anion complex **3.10**. Note that **3.9** can also be formed from dichloride complex **3.8**, which can be synthesized from UCl₄.

To test the simple notion that N₂ extrusion from a uranium center should become easier as the metal ion is reduced and made more electron-rich, Kim treated **3.9** with an excess of potassium graphite (KC₈) in a THF solution as shown in Scheme 3.3. The reaction mixture changed color immediately from pale orange to dark green concurrent with gas evolution, and within seconds the solution became dark red. Following workup of the reaction mixture, red crystals of a uranium(IV) parent imido complex having a metallacycle, namely, [K-(THF)₃][(PN)U^{IV}(=NH)[^{*i*}Pr₂P(C₆H₃Me)N-(C₆H₂Me₂CH₂)]] (**3.10**), were isolated from a saturated hexanes solution in 15% crystalline yield. The ¹H NMR spectrum of **3.10** was consistent with a highly 108 desymmetrized system with multiple chemical environments ranging from 52.64 to -39.04 ppm. A ¹H NMR spectrum of the reaction mixture showed free HPN in addition to compound **3.10**, the latter of which was only stable at low temperatures for 48 h. Notably, reaction between KC₈, NaN₃, and **3.7** also formed **3.10** as detected in a ¹H NMR spectrum of the reaction mixture. However, isolation of **3.10** on a preparative scale returned higher yields from **3.9**, presumably due to deleterious side reactions on starting from **3.7** and NaN₃. An attempt to reduce **3.9** with (C₅Me₅)₂Co showed no reaction. Efforts to trap the putative nitride intermediate (vide infra) using low temperatures or B(C₆F₅)₃ were not successful. Finally, attempts to deprotonate **3.10** with KBn or MeLi led to decomposition.



Figure 3.5. Molecular structures of **3.7** (upper), **3.9** (lower left), and **3.10** (lower right) with ellipsoids shown at the 50% probability level. H-atoms with the exception of H3 in **3.10** and residual hexane from **3.10** and azide disorder from **3.9** have been omitted for clarity.

The U(IV) center in **3.10** is six-coordinate and shows the cyclometalated anilido fragment with a characteristic U(1)–C(42) bond length of 2.589(3) Å, which is 109

comparable other uranium metallacycle complexes, to such as $(C_5Me_5)_2U^{IV}[N(SiMe_3)SiMe_2CH_2]$ (U-C 2.52(2) Å).⁵³ The average U-Namide bond length in **3.10** (avg U– N_{amide} 2.431(2) Å) was long when compared with those of **3.8** and **3.9** (avg. U–N_{amide} 2.2793(17) and 2.283(3) Å, respectively). The parent imido bond length (U(1)–N(3) 1.997(2) Å) in **3.10** was notably shorter than what was previously seen in other known uranium(IV) imido compounds, such as [K(15crown-5)₂][U(Tren^{TIPS})(NH)], which had a U=N bond length of 2.034(3) Å.⁵⁰ The K⁺ countercation coordinated to the nucleophilic imido group exhibited a close contact to the alkyl moiety of 2.957(3) resulting from C–H activation.

Conclusion.

In conclusion, the first examples of a terminally bound molecular zirconium parent imide along with its nitride counterpart have provided a rare opportunity to characterize these zirconium-nitrogen multiple bonds using structural and spectroscopic data. Theoretical studies clearly reveal both **3.3** and **3.4** to possess *bona fide* $Zr\equiv N$ triple bonds. Our study has also allowed us to determine the basicity of a zirconium nitride. We predict the pK_a of the zirconium imide **3.3** to be between 36-43, far less acidic than that for the titanium analogue (pK_a was estimated to be between 26-36). This feature demonstrates that **3.4** is indeed a superbase, at least ten orders of magnitude stronger than the structurally similar titanium nitride. We have also shown the synthesis and characterization of a uranium parent imido complex, **3.10**.

Studies to extend the reach of these studies is already in progress including the synthesis of a complex analogous to **3.2**, (PN)₂Hf(N₃)₂. It should be noted that the Hf analogue was synthesized from the chloride precursor, (PN)₂HfCl₂. (PN)₂HfCl₂ will be discussed in further detail in Chapter 5. Given the increase by ten orders of magnitude in basicity in going from titanium to zirconium, it should be expected that by going to hafnium, this nitride should be even more powerfully basic. In fact, it may not even be possible to find a base strong enough to deprotonate a hafnium parent imido! In 110

other efforts, while a monoanionic nitride would not be achievable, looking to scandium, the azido complex (PN)₂ScN₃ (**A5**) was synthesized from (PN)₂ScCl (**A4**) when treated with NaN₃ (Figure 3.6, Scheme 3.4). (PN)₂ScCl was synthesized from ScCl₃(THF)₃ and two equivalents of LiPN. Of interest in this project would be to synthesize the dianionic, likely extremely reactive, nitride (PN)₂ScN²⁻ (**3.11**) (Scheme 3.4). This reaction has not yet been successful, but given the accessibility of nitride complexes in this platform, it is with hope that this will be achieved in the near future. Alternatively, consider the possibility of photochemical activation of the azido moiety to provide evidence of a scandium nitrene diradical that could then activate either C–H bonds of the ligand or solvent to form an amido complex (**3.12**) (Scheme 3.4).



Scheme 3.4. Synthesis of (PN)₂ScN₃ from (PN)₂ScCl. Note that (PN)₂ScCl could be synthesized from ScCl₃(THF)₃ and two equivalents of LiPN. Proposed is the reduction of (PN)₂ScN₃ with magnesium naphthalenide to form a dianionic scandium nitrido complex. Alternatively, photolysis produces an asymettric species which we propose is an amido ligand formed by activation of the PN ligand.

This would be similar to the aforementioned uranium nitride complex in that we might consider C-H activation at the ligand scaffold, although in this case C-H activation would only occur at the nitrogen radical moiety and not at the metal center. When placed under a xenon light source, a clean product, asymmetric product was observed by ³¹P NMR spectroscopy, but could not be isolated. Given the asymmetric nature of the ³¹P NMR spectrum, it can also be imagined that the nitrogen inserts into the Sc-P bond, oxidizing the phosphorous as observed in Chapter 2 (**3.13**) (Scheme 3.4). Extending down the group to cerium, we also proposed the idea that we could make a cerium nitride. After extensive attempts, it was possible to metallate the PN ligand one Ce to make (PN)₂Ce(OTf) (**A7**). However no further complexes were pursued. Crystal structures of the hafnium azide complex and scandium chloride and azide complexes, as well as the cerium triflate complex, can be found along with crystallographic tables in the Appendix of Molecules.⁵⁴



Figure 3.6. Molecular structures of **A4** (left) and **A5** (right) with ellipsoids shown at the 50% probability level. H-atoms and residual toluene from **A4** have been omitted for clarity.

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Experimental Details

General Procedures

Unless otherwise stated, all operations were performed in a M. Braun Lab Master double-dry box under an atmosphere of purified dinitrogen or using high vacuum standard Schlenk techniques under an argon or dinitrogen atmosphere. Hexanes, pentane, tetrahydrofuran (THF) and toluene were purchased from Fisher Scientific and Et₂O was purchased from Sigma Aldrich. Solvents were sparged with argon for 20 minutes and dried using a two-column solvent purification system where columns designated for hexanes and toluene were packed with Q5 and alumina respectively, and columns designated for Et₂O and THF were packed with alumina. 1,4-dioxane was purchased from Sigma Aldrich in 99.8% purity, anhydrous in a sure-seal bottle and was used as received without further drying. Deuterated benzene was purchased from Cambridge Isotope Laboratories (CIL) and was sparged with nitrogen for 20 minutes, then was dried over a potassium mirror, vacuum transferred to a collection flask, and degassed by freeze-pump-thaw cycles. All solvents with the exception of 1,4-dioxane were transferred into a dry box and were stored over 4 Å sieves. Diisopropylamine and bis(trimethylsilyl)amine were dried over 4 Å sieves prior to use, and degassed by freeze-pump-thaw cycles. All sieves were heated to 200 °C under vacuum overnight prior to use. Celite used for filtrations was heated to 200 °C under vacuum overnight prior to use. NaN₃ was dried by evacuating in a schlenk flask overnight, followed by stirring overnight in THF after bringing into the glovebox. This solution was decanted, and then suspended and stirred in toluene overnight. Finally, after decanting this solution, it was suspended in pentane, stirred overnight, and then

this was taken to dryness for use. KC_8 was prepared with by mixing carbon with potassium and heating over a week at 150 °C in a well-sealed, high pressure flask, with good stirring with a metal stirbar. Each night, the reaction vessel was brought back into the glovebox to manually mix the two reagents to ensure good mixing. ¹H NMR spectra were recorded on a Bruker AVIII 400 and AVII 500 MHz spectrometer, ¹³C spectra were recorded on a Bruker AVII 500 MHz spectrometer, ³¹P{¹H} spectra were recorded on a Bruker AVIII 500 MHz spectrometer, ³¹P{¹H} spectra were recorded on a Bruker AVIII 400 spectrometer, and ⁷Li NMR spectra were recorded on a Bruker AVIII 400 spectrometer, and ¹⁵N NMR spectra were recorded on a Bruker AVIII 400 spectrometer. ¹H NMR spectra are reported with reference to residual proteo solvent resonances of C₆D₆ at 7.16 ppm. ³¹P{¹H} NMR spectra were referenced to external H₃PO₄ (0.0 ppm). ¹⁵N NMR spectra were referenced to liquid ammonia (0.0 ppm). IR spectra were recorded on a JASCO FT/IR-4600LE Spectrometer using clear disks and mini KBr plates. (PN)₂ZrCl₂ was prepared according to published literature procedures.²⁶ Elemental analyses were measured by Midwest Microlab.

Synthesis of $(PN)_2 Zr(N_3)_2 (3.2)$

To a 10 mL orange solution of (PN)₂ZrCl₂ (**3.1**) (671 mg, 0.79 mmol, 1 equiv.) in 1,4dioxane charged in a 100 mL J-Young Tube was added a 15 mL slurry of NaN₃, excess, (207 mg, 3.19 mmol, 4 equiv.). This flask was heated to 75 °C for 3 days. After cooling to room temperature, all volatiles were removed *in vacuo*. The orange residue was extracted into toluene and filtered over Celite. The toluene was taken to a minimum (less than 1 mL) in a 20 mL vial and layered with 10 mL hexane. This vial was stored at -35 °C overnight, resulting in the deposition of an orange powder (392 mg, 0.46 mmol, 58% yield). Crystals suitable for single crystal XRD can be grown from a saturated solution (20 mg) in a minimum of toluene (1 mL) stored overnight at -35°C. Note that these crystals were grown from a reaction done in THF, which is not the ideal solvent for this reaction. However, as seen below, when performed in 1,4dioxane, residual solvent is seen in the NMR spectrum. **1H NMR (500 MHz, 298 K**, **benzene-d₆**): δ 6.96 (dd, *J* = 4.7, 6.2 Hz, 2H, C-*H*, Ar), 6.69 (d, *J* = 8.7 Hz, 2H, C-*H*, Ar), 6.56 (s, $\Delta v_{1/2}$ = 3.2 Hz, 4H, C-*H*, m-mesityl Ar), 5.50 (dd, *J* = 8.5, 3.4 Hz, 2H, C-*H*, Ar), 3.35 (s, 8H, C-*H*₂, 1,4-dioxane), 2.41 (sept, ³*J*_{H-H} = 7.1 Hz, 4H, P-C*H*Me₂), 2.27 (s, $\Delta v_{1/2}$ = 2.2 Hz, 12H, C*H*₃, *o*-mesityl Ar), 2.14 (s, $\Delta v_{1/2}$ = 2.4 Hz, 6H, C*H*₃, *p*-Ar), 2.09 (s, $\Delta v_{1/2}$ = 2.3 Hz, 6H, C*H*₃, *p*-Ar), 1.32 (d, ³*J*_{H-H} = 7.1 Hz, 6H, P-CH*Me*₂), 1.29 (2 overlapping doublets, ³*J*_{H-H} = 7.1 Hz, 12H, P-CH*Me*₂), 1.26 (d, ³*J*_{H-H} = 7.4 Hz, 6H, P-CH*Me*₂). ³¹P{¹H} **NMR (162 MHz, 298 K, benzene-d₆)**: δ 14.4 (2P, Zr-*P*). ¹³C{¹H} **NMR (125.8 MHz, 298 K, benzene-d₆**): δ 158.3 (2C, C-Ar), 139.72 (4C, C-Ar), 138.1 (2C, C-Ar), 136.7 (2C, *C*-Ar), 133.6 (2C, *C*-Ar), 67.2 (4C, *C*-H₂, 1-4-dioxane) 25.8 (d, *J*_{C-P} = 9.8 Hz, 4C, P-*C*HMe₂), 21.4 (2C, *C*H₃-Ar), 20.6 (2C, *C*H₃-Ar), 19.9 (2 overlapping doublets, ²*J*_{C-P} = 2.4 Hz, 8C, P-CH*Me*₂), 19.3 (2C, *C*H₃-Ar), 19.1 (2 *C*H₃-Ar). ¹⁵N{¹H} **NMR (from 3.2**-¹⁵N) **(40.5 MHz, 298 K, benzene-d₆)**: δ 154.6, 114.0 (4N, Zr-*N*₃). Anal. Calcd for C₄₄H₆₂N₈P₂Zr: C, 61.72; H, 7.30; N, 13.90. Found: C, 62.34; H, 7.80; N, 11.01.

Synthesis of (PN)₂Zr≡NH (3.3)

To a 10 mL yellow slurry of **3.2** in Et₂O (700 mg, 0.86 mmol, 1 equiv) was added a 5 mL slurry of KC₈ in Et₂O (255 mg, 1.89 mmol, 2.2 equiv.) dropwise at room temperature while stirring rapidly in a 20 mL vial. Upon adding the KC₈, a rapid effervescence was observed, in addition to consumption of the KC₈ (visibly turned to graphite). After stirring for five minutes at room temperature, the reaction mixture was filtered over Celite and taken to dryness. The yellow residue was suspended in 5 mL pentane, causing a light yellow powder to precipitate. Diethyl ether was added dropwise (less than 1 mL) until all material was dissolved as a homogenous yellow solution. This was cooled to $-35 \,^{\circ}$ C overnight, and yellow crystals were deposited on the walls of the vial suitable for single crystal XRD (310 mg, 0.36 mmol, 42% yield). ¹H NMR (400 MHz, 298 K, benzene-d₆): δ 6.95-6.77 (m, unable to resolve *J* coupling value, 8H, C-*H*, Ar), 5.87 (dd, *J* = 6.9, 5.5 Hz, 2H, C-*H*, Ar), 5.11 (s, $\Delta v_{1/2} = 9.0 \text{ Hz}, 1 \text{ H}, ZrNH)$, 2.69 (s, $\Delta v_{1/2} = 2.8 \text{ Hz}, 6\text{H}, CH_3, \text{p-Ar})$, 2.29 (sept, ³*J*_{H-H} = 6.8 Hz, 2H, P-CHMe₂), 2.27 (s, $\Delta v_{1/2} = 3.5 \text{ Hz}, 6\text{H}, CH_3, \text{p-Ar})$, 2.18 (s, $\Delta v_{1/2} = 3.1 \text{ Hz}, 6\text{H}, CH_3, \text{o-mesityl Ar})$, 115

2.15 (s, $\Delta v_{1/2} = 2.8$ Hz, 6H, *CH*₃, *o*-mesityl Ar), 1.46 (d, unable to resolve *J* coupling, 6H, P-CH*Me*₂), 1.20 (d, unable to resolve *J* coupling, 6H, P-CH*Me*₂), 0.89 (d, unable to resolve *J* coupling, 6H, P-CH*Me*₂), 0.82 (d, unable to resolve *J* coupling, 6H, P-CH*Me*₂), 0.52 (sept, ${}^{3}J_{\text{H-H}} = 6.8$ Hz, 2H, P-C*H*Me₂). ${}^{31}\text{P}{}^{1}\text{H}$ NMR (162 MHz, 298 K, benzened₆): δ 13.39 (2P, Zr-*P*). ${}^{13}\text{C}{}^{1}\text{H}$ NMR (125.8 MHz, 298 K, benzene-d₆): δ 161.7 (d, *J*_C. P = 20.9 Hz, 2C, *C*-Ar), 142.0 (2C, *C*-Ar), 139.0 (2C, *C*-Ar), 134.1 (2C, *C*-Ar), 133.6 (2C, *C*-Ar), 132.5 (2C, *C*-Ar), 130.6 (4C, *C*-Ar), 130.2 (4C, *C*-Ar), 123.7 (d, *J*_{C-P} = 4.0 Hz, 2C, *C*-Ar), 113.0 (d, *J*_{C-P} = 8.3 Hz, 2C, *C*-Ar), 21.7 (d, unable to resolve *J* coupling, 2C, P-CH*Me*₂), 21.2 (d, unable to resolve *J* coupling, 2C, P-CH*Me*₂), 21.1 (d, *J*_{C-P} = 5.7 Hz, 2C, P-*C*H*Me*₂), 20.9 (2C, *C*H₃-Ar), 20.6 (4C, *C*H₃-Ar), 19.8 (2C, *C*H₃-Ar), 19.1 (d, *J*_{C-P} = 5.7 Hz, 2C, P-*C*HMe₂), 18.3 (d, unable to resolve *J* coupling, 2C, P-CH*Me*₂). ${}^{15}\text{N}{}^{1}\text{H}$ NMR (from 3.3- ${}^{15}\text{N}$) (40.5 MHz, 298 K, benzene-d₆): δ 351.4 (1N, Zr-*N*). Anal. Calcd for C₄₄H₆₃N₃P₂Zr: C, 67.14; H, 8.07; N, 5.34. Found: C, 66.64; H, 8.24; N, 5.00.

Synthesis of $\{(PN)_2 Zr \equiv N[\mu_2 - Li(THF)]\}_2$ (3.4)

To a 5 mL yellow solution of **3.3** in toluene (105 mg, 0.122 mmol, 1 eq.) was added a 2 mL toluene solution of trimethylsilylmethyl lithium (11.5 mg, 0.122 mmol, 1 eq.) while stirring at room temperature in a 20 mL vial. No visible color change occurs although the reaction is done within five minutes of stirring at room temperature. The reaction mixture was filtered over Celite to ensure ideal crystallization although TMS is the only byproduct. The solution volume was reduced to 3 mL and several drops of THF were added. This was cooled to -35 °C overnight, resulting in the deposition of yellow crystals of 3.4 suitable for single crystal XRD (115 mg, 0.0549 mmol, 45% yield). ¹H NMR (400 MHz, 298 K, benzene-d₆): δ 7.15-6.75 (overlapping m, unable to resolve J coupling value, 16H, C-H, Ar), 5.87 (dd, J = 6.9, 5.4 Hz, 4H, C-H Ar), 3.34 (m, 8H, THF CH₂ (2,5)), 2.65 (s, $\Delta v_{1/2}$ = 5.4 Hz, 12H, CH₃, p-Ar), 2.36 (sept, ³/_{H-H} = 6.9 Hz, 4H, P-CHMe₂), 2.26 (s, $\Delta v_{1/2}$ = 4.0 Hz, 12H, CH₃ p-Ar), 2.20 (s, $\Delta v_{1/2}$ = 3.8 Hz, 12H, CH_{3} o-mesityl Ar), 2.13 (s, $\Delta v_{1/2} = 5.1$ Hz, 12H, CH_{3} o-mesityl Ar), 1.47 (d, unable to measure ³J_{H-H}, 12H, P-CHMe₂), 1.35 (m, 8H, THF CH₂ (3,4)), 1.08-0.86 (three overlapping, d, unable to measure ${}^{3}J_{H-H}$, 36H, P-CHMe₂), 0.77 (sept, unable to resolve 116

³*J*_{H-H}, 4H, P-C*H*Me₂), ¹³C{¹H} NMR (125.8 MHz, 298 K, benzene-d₆): δ 145.5 (4C, *C*-Ar), 142.0 (4C, *C*-Ar), 138.2 (4C, *C*-Ar), 133.3 (4C, *C*-Ar), 132.7 (4C, *C*-Ar), 132.4 (8C, *C*-Ar), 130.7 (8C, *C*-Ar), 130.0 (4C, *C*-Ar), 121.1 (2C, *C*-Ar), 113.7 (2C, *C*-Ar), 68.1 (4C, THF *C*H₂ (2,5)), 25.9 (4C, THF *C*H₂ (3,4)), 22.2 (d, unable to resolve *J* coupling, 4C, P-CH*Me*₂), 21.7 (d, unable to resolve *J* coupling, 4C, P-CH*Me*₂), 21.7 (d, unable to resolve *J* coupling, 4C, P-*C*HMe₂), 20.7 (8C, *C*H₃-Ar), 20.4 (4C, *C*H₃-Ar). ³¹P{¹H} NMR (162 MHz, 298 K, benzene-d₆): δ 12.15 (2P, Zr-*P*). ¹⁵N{¹H} NMR (from 3.4-¹⁵N) (40.5 MHz, 298 K, benzene-d₆): δ ~719 (br, inconclusive assignment, 2N, Zr-*N*). ⁷Li NMR (155.5 MHz, 21i). Anal. Calcd for C₉₆H₁₄₀Li₂N₆O₂P₄Zr₂: C, 66.63; H, 8.16; N, 4.86. Found: C, 69.19; H, 8.17; N, 4.50.

Protonation Experiments to Convert 3.4 to 3.3

For both reactions detailed, solutions of **3.4** (5 mg, 0.002 mmol, 1 equiv.) in benzened₆ in a J-Young NMR tube were treated with diisopropylamine (1 μ L, 0.004 mmol, 2 equiv.) or bis(trimethylsilyl)amine (1 μ L, 0.004 mmol, 2 equiv.), respectively, at room temperature. Immediately ¹H and ³¹P NMR spectra showed clean and quantitative protonation to form **3.3** and the corresponding lithium amide salt.

Crystallographic Experimental Details

Crystallographic data are summarized Table 3.1. Suitable crystals for X-ray analysis of **3.2-3.4** were placed on the end of a Cryoloop coated in NVH oil. Data for single crystal structure determination of **3.2-3.4** were taken on a Bruker D8 with CMOS area detector employing graphite-monochromated Mo-Kα radiation (λ =0.71073 Å) at a temperature of 100(1) K, while **3.4** was taken on a Bruker ApexII with a CCD. Rotation frames were integrated using SAINT,⁵⁵ producing a listing of non-averaged *F*² and s(*F*²) values The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS.⁵⁶ The initial structures of **3.2-3.4** were solved by 117 dual methods – SHELXT.⁵⁷ Refinement was by full-matrix least squares based on F² using SHELXL.⁵⁸ All reflections were used during refinement.

Compound	3.2	3.3	3.4 · 4(C ₇ H ₈)
Molecular formula	$C_{44}H_{62}N_8P_2Zr$	$C_{44}H_{63}N_3P_2Zr,\ C_5H_{12}$	$C_{96}H_{140}Li_2N_6O_2P_4Zr_2, 4(C_7H_8)$
Formula weight	856.17	859.28	2098.87
Temperature (K)	100(1)	100(1)	100(1)
Crystal system	Orthorhombic	Monoclinic	Tetragonal
Space group	P b c a	P 1 2 ₁ /c 1	P 4 ₂ 2 ₁ 2
Cell constants:			
a (Å)	17.0256(8)	16.199(4)	14.569(2)
b (Å)	15.8891(7)	13.062(3)	14.569(2)
c (Å) Alpha Agle Beta Angle Gamma Angle	32.2683(15) 90 90 90	23.636(6) 90 96.243(7) 90	27.444(4) 90 90 90
Volume (Å ³)	8729.3(7)	4972(2)	5825.1(2)
Z	8	4	2
Density (calcd mg/m3)	1.303	1.148	1.197
Abs coeff (mm-1)	0.366	0.319	0.285
F(000)	3616	1840	2240

Table 3.1. Crystallographic Data of compounds **3.2-3.4**.

Wavelength	0.71073	0.71073	0.71073
θ range for data collection (°)	2.899 to 27.543	2.972 to 27.858	2.63 to 27.49
<i>h, k, l</i> ranges collected	$-22 \le h \le 22$ $-20 \le k \le 19$ $-41 \le l \le 41$	$-21 \le h \le 21$ $-16 \le k \le 16$ $-30 \le l \le 29$	$-17 \le h \le 18$ $-18 \le k \le 18$ $-35 \le l \le 35$
# Reflns collected	10048	11253	6696
Refinement method	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²	Full-matrix least squares on F ²
R_1^{a}	0.0549	0.0477	0.0280
$wR_{2^{b}}$	0.1192	0.1415	0.0659
Goodness-of-fit on F2 ^c	1.032	1.081	1.066

a R1 = (|Fo| - |Fc|) / |Fo|. b wR2 = [[w(Fo2 - Fc2)2] / [w(Fo2)2]]1/2. c Goodness-of-fit = [[w(Fo2 - Fc2)2]/Nobservns Nparams)]1/2, all data.

Computational Details

All calculations were carried out using DFT as implemented in the Gaussian09 program package.⁵⁹ Geometry optimizations on the experimentally investigated structures, without any truncation, were performed using the hybrid-meta GGA TPSSh⁶⁰ functional in combination with the relativistic core potential containing cc-pVDZ-PP basis set for Nb⁶¹ whereas the cc-pVDZ basis set for light atoms.⁶² Analytical vibrational frequency calculations were carried out at the same level of theory to confirm that the optimized structures correspond to minima of the potential energy surface. Dispersion was taken into account in all calculations, including geometry optimizations, using Grimme's D3 method⁶³ with the original D3 damping function and with SR6 and S8 parameters of 1.660 and 1.105, respectively, originally recommended for TPSS. The energies and the wavefunction of the optimized

structures were reevaluated using the triple-z basis set cc-pVTZ(-PP) (-PP applies for Nb) using the former protocol for dispersion.⁶⁴ Accordingly, molecular orbitals, charges and bond indices analysed and discussed in the study were determined at the latter TPSSh/cc-pVTZ(-PP) level of theory. In all of these calculations an ultrafine grid has been used.



Figure 3.7. MOs of **3.4** describing the Zr–N bondings and lone pairs at the nitride centers. Bonding (+) and antibonding (-) combinations of fragment orbitals of the two subunits are shown on the right and left sides, respectively. Subscripts \perp and \parallel 121

indicate that the π orbital is perpendicular to or in-plane of the $N_2 Li_2$ plane, respectively.



Figure 3.8. MOs of **3.3** describing the Zr–N and N–H bonds.

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Chapter 4:

The (First)StructuralCharacterization of a TitaniumMethylidene

Introduction. In an entry in his notebook dated July 1974, Frederick Tebbe recorded for the first time the synthesis of the complex $Cp_2Ti(\mu_2-CH_2)(\mu_2-Cl)Al(CH_3)_2$ (Figure 4.1, Scheme 4.1).¹ The addition of excess amounts of AlMe₃ to Cp_2TiCl_2 gave a reagent² that has been instrumental in methylidene transfer reactions to carbonyl functionalities presumably *via* a transient [$Cp_2Ti=CH_2$] species. Appropriately called "Tebbe's reagent", this complex was also one of the first systems to exchange the methylidene group with olefins and to engage in olefin homologation.^{2–6}



Scheme 4.1. Synthesis of the Tebbe reagent, $Cp_2Ti(\mu_2-CH_2)(\mu_2-Cl)Al(CH_3)_2$. Abstraction of AlClMe₂ by Lewis Bases promotes the formation of the transient methylidene, $Cp_2Ti=CH_2$. This can also be synthesized *via* thermolysis of $Cp_2Ti(CH_3)_2$ *via* extrusion of methane, or from $Cp_2Ti[CH_2C(CH_3)_2CH_2]$. Phosphines can be used to trap the methylidene.

Since then, it was found that intermediate $[Cp_2Ti=CH_2]$ can be generated independently by either a thermolytic α -hydrogen abstraction from $Cp_2Ti(CH_3)_2$ or by a retro-cycloaddition reaction involving the metallacyclobutane species $Cp_2Ti[CH_2C(CH_3)_2CH_2]$ (Figure 4.1).⁷⁻¹⁰ The transient $[Cp_2Ti=CH_2]$ species can be intercepted in solution at low temperatures using various phosphines by forming $Cp_2Ti=CH_2(PR_3)$ (PR₃ = PMe₃, PMe_2Ph, PEt₃) (Figure 4.1).³ Unfortunately, the inherent reactivity of the Ti-methylidene fragment made it impossible thus far to directly characterize the structure of this important moiety.¹¹ In fact, among the class of Schrock-carbenes, a terminal methylidene with a 3d metal has never been isolated and structurally characterized.¹² Other than the recently reported crystal structure of the Tebbe reagent (Figure 4.1),⁵ no other reports have existed with regard to the long awaited structure of this elusive titanium methylidene, without stabilizing Lewis Acid groups.



Figure 4.1. Crystal Structure of the Tebbe reagent, $Cp_2Ti(\mu_2-CH_2)(\mu_2-Cl)Al(CH_3)_2$.⁵ The dichloride derivative, $Cp_2Ti(\mu_2-Cl)_2Al(CH_3)_2$ was also co-crystallized for this complex, but has been omitted for clairity.

Results and Discussion

Synthesis and Structural Characterization of the Titanium Methylidene.

In this chapter, we show how a tetragonal environment enforced by two phosphino-anilide ligands can stabilize a Lewis-acid free and terminally bound titanium methylidene, to an extent that it can be formed and thus interrogated spectroscopically and computationally.



Scheme 4.2. Two synthetic routes to a mononuclear titanium complex having a terminally bound methylidene.

In the previous three chapters, we have shown how the scaffold $[(PN)_2Ti]^{2+}$ (PN⁻ (N-(2-(diisopropylphosphino)-4-methylphenyl)-2,4,6-trimethylanilide)) can = stabilize terminal nitride and oxo functionalities.^{13,14} However, a methylidene ligand should make the Ti⁴⁺ center more electron deficient when compared to the isovalent oxo and nitride groups since it now has two less electrons in this scaffold compred to N^- or O, but it may be comparable to the borylimido complex (PN)₂Ti=N=Bcatechol (1.8) *vide supra*.¹³ Accordingly, we turned our attention to the same precursor as that which was used for the synthesis of the titanium nitride complex, $(PN)_2$ TiCl (1.1), since it could be smoothly methylated with LiCH₃ in Et₂O, which was added dropwise at -35 °C and the solution was slowly warmed to room temperature to form the Ti(III)-methyl complex (PN)₂Ti(CH₃) (4.1) in 95% yield as an green colored material (Scheme 4.2). Complex 4.1 displays magnetic features in accord with a d^1 species (μ_{eff} = 2.03 μ_B , 25 °C, Evans method) and the solid state structure confirms the presence of a distorted trigonal-bipyramidal ($\tau_5 = 0.738$)¹⁵ Ti(III) species bearing transphosphine groups (177.22(3)°) and a bound methyl group (Figure 4.2a). The most salient structural feature, however, is the Ti–C bond length of 2.129(3) Å, akin to what has been observed in other five-coordinate Ti(III) derivatives supported by two benzamidinate or β -diketiminate ligands (PhC(NSiMe_3)_2⁻) as (PhC(NSiMe_3)_2⁻)_2Ti(CH_3) and ([ArN(CCH_3)]_2, Ar = 2,6-iPr_2C_6H_3).¹⁶⁻¹⁸ However, unlike the Ti(III) methyl complex reported by Arnold and co-workers, which has a Ti–C–H angle of 105.1° and was reported to have an agostic interaction, we observe no apparent C–H interaction in **4.1.**¹⁶



Figure 4.2. Solid state structures of (a) complex **4.1** and (b) complex **4.3** with thermal ellipsoids at the 50% probability level. H-atoms with the exception of methyl/methylidene hydrogens are excluded for clarity.

Complex **4.1** can be readily oxidized with [FeCp₂][OTf]¹⁹ in Et₂O to produce the Ti(IV) methyl-triflate (PN)₂Ti(CH₃)(OTf) (**4.2**) in nearly quantitative yield as a bright red colored microcrystalline material (Scheme 4.2). Although we were unable to obtain solid state structural information for **4.2**, ¹H, ¹³C and ³¹P NMR spectra are consistent with this formulation. Notably, the methyl resonance could be readily located at 1.78 ppm in the ¹H NMR spectrum and correlated to a resonance at 55.1 ppm in the ¹³C NMR trace by an HMQC NMR spectroscopic experiment. The ¹⁹F NMR spectrum showed a resonance at –76.49 ppm in accord with the presence of a OTf⁻

group, but given the high solubility of **4.2** in non-polar solvents such as hexanes and arenes, we propose that this ligand is coordinated to the titanium(IV) ion to give a pseudo-octahedral coordination geometry.



Figure 4.3. Top left: NOESY NMR spectrum of **4.3** featuring interaction of $Ti=CH_2$ with N*Mes*; Top right: ¹H-¹H COSY NMR spectrum of **4.3** featuring coupling of $Ti=CH_2$ with N*Mes*; Bottom: ¹³C NMR spectroscopic data of **4.3**, coupled with both ¹H and ³¹P nuclei. The inset figure features the expanded region of the ¹³C{¹H} NMR spectrum of **4.3**.

Dissolving **4.2** in Et₂O and treating it with the ylide base $H_2CPPh_3^{20}$ at -35 °C rapidly produced a colorless precipitate, [H₃CPPh₃][OTf], which could be separated from the mixture to afford the titanium methylidene (PN)₂Ti=CH₂ (**3**) as orange crystals in 75% yield subsequent to crystallization from hexanes at -35 °C (Scheme 131)
4.2). Given its extremely reactive nature, formation of **4.3** is always accompanied by a small amount (~10%) of the methyl species **4.1**, which appears to form *via* H-atom abstraction by the methylidene ligand. Applying an HMQC NMR spectroscopic experiment we were able to correlate the downfield shifted signal at 11.82 ppm in the ¹H NMR spectrum to a highly downfield shifted ¹³C NMR resonance at 291.10 ppm, consistent with the existence of a terminal methylidene ligand. Notably, the methylidene carbon resonance clearly observed as a triplet of triplets due to ${}^{1}J_{CH}$ = 124 and ${}^{2}J_{CP}$ = 12 Hz (Figure 4.3), whereas the ${}^{13}C{}^{1}H$ NMR experiment collapsed this downfield multiplet resonance into a triplet due to coupling to the equivalent phosphines. In order to acquire this ¹³C{¹H} NMR spectrum, we had to use a signal enhanced cryo500 instrument due to the instability of 4.3 in solution. This data collection was assisted by the late Dr. George Furst. In fact, if left in a J-Young NMR tube for more than a half hour, it is possible to see the formation of large bubbles of methane in the NMR tube, and a corresponding degradation of all NMR spectral features. If monitored with care, it is possible to see the formation of **4.1** after several minutes in solution, and over longer periods of time unidentifiable products as well as a large resonance for methane. Interestingly, the methylidene resonance at 11.9 ppm in the ¹H NMR experienced multiplicity features that were shown to be due to long range interactions as well as coupling to two nearby benzylic hydrogens with the aid of a NOESY and ¹H-¹H COSY NMR experiments, respectively (Figure 4.3, top). The ³¹P NMR spectrum is consistent with two equivalent phosphino-anilido ligands in solution, thus, corroborating the triplet resonance observed in the ¹³C{¹H} NMR spectrum (vide supra). Given the observation of intramolecular H-atom abstraction from **4.3**, it seemed an interesting experiment to try an H-atom abstraction reaction with **4.1** to form **4.3**. Remarkably, it was found that complex **4.3** can be prepared directly in 48% yield via H-atom abstraction of **4.1** with the the aryl oxyl radical \cdot OMes^{*} (Mes^{*} = 2,4,6-^tBu₃C₆H₂).²¹ Based on the average bond dissociation enthalpies²² this reaction is feasible, but the sterically protected nature of the methylidene in **4.3** and the alcohol byproduct HOMes* prevents subsequent reactions

between the two. The reaction does take several hours to go to completion resulting in some decomposition of **4.3**.

Single crystals of **4.3** could be obtained from a concentrated hexanes solution cooled to $-35 \,^{\circ}$ C, and Figure 4.2b depicts the solid-state structure of the first terminal Schrock-type methylidene bound to a 3d metal. Akin to the oxo (PN)₂Ti=O and nitride salt [K(222-kryptofix)][(PN)₂Ti=N], complex **4.3** has a $\tau_5 = 0.517$, consistent with a geometry between square-pyramidal and trigonal bipyramidal.¹³ Remarkably, the hydrogen atoms could be located in the electron density map and refined isotropically revealing the π -bond to be oriented along the P–Ti–P plane. Short contacts between the ortho-methyl hydrogens on the mesityl and 'Pr methyl moieties of the PN ligand and the methylidene carbon could be observed (2.7(2) and 2.8(6) Å). The Ti=C bond length of 1.939(3) Å is significantly shorter than that observed for the Ti–CH₃ in **4.1** but is comparable to structurally characterized 5-coordinate titanium complexes having a substituted alkylidene ligand.^{17,18,23} Complex **4.3** gradually decomposes at room temperature to form some **4.1** along with a mixture of other products including CH₄.

Computational Studies Scrutinizing the Titanium Methylidene Functionality.

To better understand the electronic structure of the titanium methylidene complex density functional calculations were carried out on **4.3** by student Seihwan Ahn of the Baik group. The coordination geometry that is between square-pyramidal and trigonal bipyramidal motifs is reasonably well reproduced in our calculations with a $\tau_5 = 0.518^{15}$ and a computed Ti=C bond length of 1.868 Å, which is somewhat shorter than what is observed experimentally. Calculations confirm that there is no agostic interaction between the C-H and the Ti center. Several possible electronic states were considered: The most natural configuration for a classical Schrockcarbene is the closed-shell singlet state where a formally dianionic $[CH_2]^{2-}$ ligand interacts with a Ti(IV)- d^{0} center. Alternatively, a triplet state may be considered, where the two electrons in the π -orbital manifold are unpaired and distributed across 133 the metal-ligand fragment, in which a Ti(III)- d^1 center is connected to a formally mono-anionic, radical ligand moiety [•CH₂]⁻. There is no experimental evidence for such a non-classical electronic state. More importantly, the open-shell singlet analogue was considered, where the two electrons remain in different spatial orbitals, but are spin-paired utilizing a weak antiferromagnetic coupling.²⁴ Such a nontraditional singlet state is experimentally difficult to distinguish from the classical carbene complex. Over the last decade, there has



Figure 4.4. Qualitative MO-diagram of **4.3** displaying the molecular orbitals for the σ and π bonds (isodensity value: 0.05 a.u.).

been a growing realization that many small ligands become redox non-innocent and adopt such open-shell configurations.²⁵ Calculations show, however, that the triplet state of **4.3** is 14.3 kcal/mol higher in energy than the closed-shell singlet, and despite substantial efforts, we were unable to obtain the open-shell singlet state and concluded that it is not a reasonable minimum. Thus, the only stable configuration in the singlet spin state manifold is the classical closed-shell Schrock-carbene state. Consequently, a Wiberg²⁶ bond order between Ti and C was found to be 1.70, whereas 0.64 is found for the triplet state. Calculations also indicate a significant negative partial charge that remains on the α -carbon and the NBO²⁷ analysis assigned a natural charge of -0.74 to the α -carbon. The qualitative MO-diagram in Figure 4.4 illustrates five empty d-orbitals for the (PN)₂Ti(IV) fragment. When the dianionic [CH₂]²⁻ ligand is added to the axial position, two dominating electronic interactions exist. The first forms the Ti–C σ -bond, where the sp-hybridized donor orbital on the carbene ligand is paired with the $d(y^2-z^2)$ orbital to afford HOMO-11 at -0.254 eV, as illustrated in Figure 4.4 (note that the principle axis is along x). The second important interaction is a dative bond in the π -space from the p-orbital based lone pair on the carbene with a π -acidic d(yz) orbital to form a π -orbital HOMO-1 at -0.178 eV. This electronic structure leaves the t_{2g}-like orbitals empty, which establishes a physical oxidation state of Ti(IV)- d^0 , supporting formal classification mentioned above.

Conclusion.

In summation of this penultimate chapter considering reactivity of the PN ligand, we have prepared and fully characterized the first example of a titanium methylidene complex that serves as a structural analog of the historically important Tebbe's reagent. We speculate the stability of **4.3** to be a combination of its pseudo tetragonal structure as well as the long-range interactions of the methylidene ligand with benzylic hydrogens from the PN ligand. While solution stability of this complex made the scope of reaction studies limited, future modifications to the ligand architecture such as fluorination of C–H bonds of the ligand currently involved in degradation of 135 **4.3** *via* H-atom abstraction will hopefully prevent this process. In the next and final chapter of PN ligand reactivity, we will consider the ability of this scaffold to support unusual oxidation states of early transition metal complexes.

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Experimental Details

General Procedures

Unless otherwise stated, all operations were performed in a M. Braun Lab Master double-dry box under an atmosphere of purified dinitrogen or using high vacuum standard Schlenk techniques under an argon or dinitrogen atmosphere. Anhydrous solvents were purchased from Fisher Scientific or Aldrich. All anhydrous solvents were sparged with argon for 20 minutes and dried by passage through two columns of activated alumina and Q-5 drying agent in a Grubbs-type solvent system. Stabilizerfree Et₂O and THF were purchased from Fisher Scientific and dried by passage through two columns of activated alumina. Deuterated benzene and deuterated toluene were purchased from Cambridge Isotope Laboratories (CIL) and was sparged with argon for 20 minutes, then was dried over 4 Å sieves, and degassed by freezepump-thaw cycles. All solvents were transferred into a dry box and were stored over 4 Å sieves. All sieves were heated to 200 °C under vacuum overnight prior to use. Celite used for filtrations was also heated to 200 °C under vacuum overnight prior to use. Solution state magnetic susceptibility was measured by the Evans'²⁸ method in benzene-d₆/tetramethylsilane solution at 298 K. Corrections were applied for diamagnetism calculated for Pascal constants.²⁹ (PN)₂TiCl,¹⁴ the, aryl oxyl radical •OMes* (Mes* = 2,4,6-tBu₃C₆H₂),²¹ H₂CPPh₃,²⁰ and [FeCp₂][OTf]¹⁹ were prepared according to published literature procedures. NMR spectra were recorded on a 136

Bruker UNI 400 MHz spectrometer for ¹H and ³¹P{¹H} spectra. ¹³C NMR spectra were recorded on a cryo500. ¹H and ¹³C NMR chemical shifts are reported referenced to the internal residual proton or carbon resonances of C_6D_6 ($\delta = 7.16$ ppm or 128.06 ppm). ¹⁹F and ³¹P NMR chemical shifts are reported with respect to external CF₃CO₂H ($\delta = 7.8.5$ ppm) and H₃PO₄ ($\delta 0.0$ ppm).

Synthesis of (PN)₂Ti(CH₃) (4.1)

A dark brown solution of $(PN)_2$ TiCl (1.1) (294 mg, 0.38 mmol, 1 equiv.) in 5 mL of toluene was cooled to -35 °C for 30 mins in a 20 mL vial. To this solution was added an ethereal solution of 1.6 M LiCH₃ (0.24 mL, 0.38 mmol, 1 equiv.) dropwise, over a period of 3 minutes. An immediate color change to dark green was observed during this time. The reaction mixture was stirred at room temperature for 15 minutes, followed by removal of all volatiles. The green residue was then dissolved in 15 mL diethyl ether, filtered through Celite, and the filtrate concentrated to 5 mL. This concentrated solution was then layered with 10 mL n-hexanes and stored at -35 °C overnight, resulting in the deposition of a dark green powder. To isolate this material, the solution was rapidly filtered cold and the solid dried *in vacuo*. Total collected was 278 mg (0.37 mmol, 98% yield). In order to grow single crystals suitable for X-ray diffraction studies, half of the powder product from the isolated reaction mixture (140 mg) was dissolved in 10 mL ether, and stored at -35 °C overnight without further filtration to yield green single plates of complex 4.1. ¹H NMR (400 MHz, 298 K, **benzene-** d_6 **):** δ 11.98 (br, $\Delta v_{1/2}$ = 5.7 Hz, 2 H, meta-Ar H_{Tolvl}), 9.37 (s, 2 H, meta-Ar H_{Tolyl}), 8.23 (br, $\Delta v_{1/2}$ = 65.2 Hz, 2 H, ortho-Ar H_{Tolyl}), 8.14 (s, 4 H, meta-Ar $H_{Mesityl}$), 4.29 (s, 12 H, ortho-CH_{3Mesityl}), 3.31 (s, 6 H, para-CH_{3Tolyl}), 2.80 (s, 6 H para-CH_{3Mesityl}), 2.39 (br, $\Delta v_{1/2}$ = 33.2 Hz, 12 H, P-CH-CH₃), 1.37 (s, 3 H, Ti-CH₃) 0.49 (br, 4 H ea, P-CH-CH₃). Some residual solvents such as *n*-hexanes and *n*-pentane are present based on the ¹H NMR spectrum. μ_{eff} = 2.03 μ_{B} , 298 K, benzene- d_{6} , Evans' method.

Synthesis of (PN)₂Ti(CH₃)(OTf) (4.2)

To a dark green solution of **4.1** in 5 mL THF in a 20 mL vial (224.5 mg, 0.3 mmol, 1 equiv.) was added a 10 mL THF slurry of [FeCp₂][OTf] (101.5 mg, 0.3 mmol, 1 equiv.) at room temperature while stirring. A color change to dark red was observed, whereby all [FeCp₂][OTf] was consumed as it was added, instantaneously resulting in a homogeneous bright red solution. As monitored by ¹H NMR spectroscopy, complex **4.1** is converted quantitatively to complex **2**. Removal of volatiles after stirring at room temperature for 30 minutes provides a pure powder that can be used for NMR characterization. Complex **4.2** is cleanly formed along with FeCp₂ based on the ¹H NMR spectrum. Given the clean conversion of **4.1** to complex **4.2**, it is possible to conduct *in situ* experiments with the crude material without need for separation from the FeCp₂. The details below rely on the use of crude mixture for the synthesis of complex **4.3**. ¹H NMR (400 MHz, 298 K, benzene-d₆): δ 6.70 (s, 4H, meta-ArH_{Mesityl}), 6.55, (br, $\Delta v_{1/2}$ = 3.3 Hz, 2 H, meta-Ar H_{Tolyl}), 6.53 (s, 2 H, meta-Ar H_{Tolyl}), 5.48 (dd, ³J_{H-H} = 3.5 Hz, 2H, ortho-Ar H_{Tolyl}), 3.60 (s, 12 H, ortho-CH3Mesityl), 2.82 (sept, ${}^{3}J_{H-H}$ = 3.5 Hz, 2 H, P-CH-CH₃), 2.57 (sept, 3 J_{H-H} = 3.3 Hz, 2 H, P-CH-CH₃), 2.31 (s, 6 H, para-CH_{3Tolyl}), 2.19 (s, 6 H para-CH_{3Mesityl}), 1.69 (t, ³J_{H-H} = 9.1 Hz, 3 H, Ti-CH₃), 1.54 (m, 3 H, P-CH-CH₃, coupling constant not assignable due to overlapping resonances), 1.48 (m, 3 H, P-CH- CH_3 , coupling constant not assignable due to overlapping resonances), 1.26 (m, 3 H, P-CH-CH₃, coupling constant not assignable due to overlapping resonances). ³¹P{¹H} NMR (162 MHz, 298 K, benzene-d₆): δ 17.45 ppm. ¹⁹F NMR (282 MHz, 298 K, benzene-d₆): δ -76.49 ppm. ¹³C NMR (125.8 MHz, 298 K, benzene-d₆): δ 158.45 (Ar-C), 145.43 (Ar-C), 13, 8.41 (Ar-C), 136.47 (Ar-C), 136.10 (Ar-C), 133.67 (Ar-C), 132.40 (Ar-C), 130.63 (Ar-C), 130.04 (Ar-C), 129.27 (Ar-C), 113.90 (Ar-C), 55.22 (t, ¹J_C-_H= 8.1 Hz, Ti-CH₃), 28.01 (PCH(CH₃)₂, 27.17 (PCH(CH₃)₂), 21.61 (Ar-CH₃), 21.46 (PCH(*C*H₃)₂), 21.26 (PCH(*C*H₃)₂), 20.99 (Ar-*C*H₃), 20.66 (Ar-*C*H₃), 20.49 (Ar-*C*H₃).

Synthesis of (PN)₂Ti=CH₂ (4.3)

Route A:

To a dark green solution of complex **4.1** (224 mg, 0.3 mmol, 1 equiv.) in 5 mL of THF in a 20 mL vial was added a 5 mL slurry of [FeCp₂][OTf] (101.5mg, 0.3 mmol, 1 equiv.) 138

at room temperature while stirring. A color change to a bright red color was observed immediately upon addition. The solution was stirred for another hour at room temperature during which no further color change was observed. All volatiles were taken to dryness under reduced pressure, and the residue redissolved in 5 mL toluene. To this solution was added a stoichiometric amount of H₂CPPh₃ (83.3 mg, 0.3 mmol, 1 equiv.) as a 5 mL toluene solution at room temperature while stirring. A rapid color change from bright red to light orange was observed. The solution was stirred for 5 minutes, and then taken to dryness under reduced pressure, followed by two triturations with *n*-hexanes. The orange residue was then dissolved in 8 mL of *n*hexanes, and filtered over Celite to remove the colorless precipitate, presumably [H₃CPPh₃][OTf]. The filtrate was quickly stored at -35 °C overnight without further concentration, resulting in the deposition of light orange crystals of complex **4.3** suitable for x-ray diffraction (168 mg, 0.22 mmol, 75% yield). In solution complex **4.3** gradually decomposes so it is recommended that manipulation of such a species must be conducted rapidly while maintaining the solution cold.

Route B:

To a dark green stirred solution of complex **4.1** (75 mg, 0.1 mmol, 1 equiv.) in 5 mL of toluene in a 20 mL vial was added a 5 mL toluene solution of the aryl oxyl radical •OMes* (Mes* = 2,4,6^{-t}Bu₃C₆H₂), at room temperature. Within five minutes, the solution began to lighten to an orange color. The reaction does not fully convert to complex **4.3** as monitored by ¹H NMR spectroscopy. The optimized reaction time for conversion to **4.3** is 15 minutes at room temperature. After this time, the reaction mixture was then taken to dryness under reduced pressure, triturated with *n*-hexanes, and then redissolved in 10 mL *n*-hexanes. The solution was filtered over Celite and the filtrate stored at –35 °C overnight to yield orange crystals of complex **3** (35 mg, 0.05 mmol, 48% yield).¹H NMR (400 MHz, 298 K, benzene-d₆): δ 11.82 ppm (t, J_{H-H}=3.68 Hz, 2 H, Ti=CH₂), 7.04 (s, 4 H, *meta*-ArH_{Mesityl}), 6.85 (br, $\Delta v_{1/2}$ = 4.0 Hz, 2 H, *meta*-ArH_{Tolyl}), (br, $\Delta v_{1/2}$ = 4.0 Hz, 2 H, *meta*-ArH_{Tolyl}), 5.69 (dd, ³J_{H-H} = 4.1 Hz, 2 H, *ortho*-ArH_{Tolyl}), 2.62 (sept, ³J_{H-H} = 6.6 Hz, 2 H, P-CH-CH₃), 2.50 (s, 6 H, para-CH_{3Tolyl}), 2.20 (s, 6 H para-CH_{3Mesityl}), 2.08 (s, 12 H, ortho-CH_{3Mesityl}), 1.01 (m, 6 H, P-CH-CH₃, 139

coupling value not assignable), 0.79 (m, 6 H, P-CH-C H_3 , coupling value not assignable due to overlapping residual solvent residues), 0.53 (sept, ${}^{3}J_{H-H} = 6.4$ Hz, 2 H, P-C H_{-} CH₃). ${}^{31}P{}^{1}H{}$ NMR (162 MHz, 298 K, benzene-d₆): δ 23.60 ppm. ${}^{13}C$ NMR (125.8 MHz, 298 K, toluene-d₈): δ 291.10 (t, ${}^{1}J_{C-H}=123.5$ Hz, ${}^{2}J_{C-P}=12.5$ Hz, Ti= CH_2), 170.32 (Ar-C), 159.67 (t, Ar-C, ${}^{2}J_{CP}=$ 12.3 Hz), 158.17 (Ar-C), 145.46 (Ar-C), 136.85 (Ar-C), 133.78 (Ar-C), 133.60 (Ar-C), 131.82 (Ar-C), 130.27 (Ar-C), 129.89 (Ar-C), 112.78 (Ar-C), 112.12 (t, Ar-C, ${}^{2}J_{C-P}=$ 4.2 Hz), 22.47 (PCH(CH₃)₂, CP coupling constant not assignable due to overlapping resonances), 21.67 (PCH(CH₃)₂, 20.86 (PCH(CH_3)₂), 20.65 (PCH(CH_3)₂), 20.28 (Ar- CH_3), 19.97 (Ar- CH_3), 19.21 (Ar- CH_3).

Crystallographic Experimental Details

Crystallographic data for compounds **4.1** and **4.3** are summarized Table 4.1. Suitable single crystals for X-ray analysis of **4.1** and **4.3** were placed on the end of a Cryoloop coated in NVH oil. The X-ray intensity data collection was carried out on a Bruker APEXII CCD area detector using graphite-monochromated Mo-K radiation (l =0.71073 Å) at 100(1) K. Preliminary indexing was performed from a series of thirtysix 0.5° rotation frames with exposures of 10 seconds. Rotation frames were integrated using SAINT,³⁰ producing a listing of non-averaged F^2 and $s(F^2)$ values which were then passed to the SHELXTL³¹ program package for further processing and structure solution. The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS.³² All calculations were performed using SHELXS³³ and SHELXL.³⁴ The structures were solved by Patterson and Fourier transform methods. All reflections were used during refinement. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using riding models with exception for methylidene of **4.3**.

Table 4.1. Crystallographic Data of compounds **4.1** and **4.3**.

Compound	4.1	4.3
Molecular formula	$C_{100}H_{154}N_4P_4Ti_2\\$	$C_{45}H_{64}N_2P_2Ti$
Formula weight	815.98	742.82
Temperature (K)	100(2)	100(1)
Crystal system	Triclinic	Monoclinic
Space group	ΡĪ	C 1 2/c 1
Cell constants:		
a (Å)	12.3342(3)	15.3286(7)
b (Å)	14.2207(4)	12.3358(5)
c (Å) Alpha Agle Beta Angle Gamma Angle	28.9433(8) 79.409(2) 86.348(2) 6.348(2)	22.4869(11) 90 95.728(2) 90
Volume (Å ³)	4833.9(2)	4230.8(3)
Z	4	4
Density (calcd mg/m3)	1.121	1.166
Abs coeff (mm-1)	0.277	0.310
F(000)	1772	1600
Wavelength	0.71073	0.71073
heta range for data collection (°)	1.43 to 27.56	3.079 to 27.519
<i>h, k, l</i> ranges collected	$-15 \le h \le 16$ $-18 \le k \le 18$ $0 \le l \le 37$	$-19 \le h \le 19$ $-16 \le k \le 16$ $-29 \le l \le 29$

# Reflns collected	21616	4850
Refinement method	Full-matrix least- squares on F2	Full-matrix least- squares on F2
R_1^{a}	0.0575	0.0374
$wR_{2^{b}}$	0.1480	0.0891
Goodness-of-fit on <i>F2^c</i>	1.044	1.058

a R1 = (|Fo| - |Fc|) / |Fo|. b wR2 = [[w(Fo2 - Fc2)2] / [w(Fo2)2]]1/2. c Goodness-of-fit = [[w(Fo2 - Fc2)2]/Nobservns Nparams)]1/2, all data.

Computational Details

All calculation results were obtained using density functional theory³⁵ as implemented in the Jaguar 9.1 suite³⁶ of ab initio quantum chemistry programs. The geometry optimizations were carried out with B3LYP³⁷⁻⁴⁰ functional and 6-31G^{**} basis set. Titanium was represented using the Los Alamos LACVP basis set⁴¹⁻⁴³ that includes effective core potentials. The energies of the optimized structures were readdressed by single-point calculations using cc-pVTZ(-f)⁴⁴ basis set. Titanium used a modified version of LACVP denoted LACV3P. Vibrational frequency calculations were carried out at the B3LYP/6-31G^{**} level of theory. Standard approximation was used to obtain zero-point vibrational energy and entropy corrections. Solvation energies were evaluated by Self-Consistent Reaction field (SCRF)⁴⁵⁻⁴⁷ calculations with the dielectric constant $\varepsilon = 4.3$ (Ethyl Ether) using the optimized gas phase structures. The natural bond orbital (NBO) analysis was carried out using NBO 6.0 program⁴⁸⁻⁵⁰ in the Jaguar 9.1 suite. The Gibbs free energy in solution phase was computed as follows⁵¹:

$$G(Sol) = G(gas) + G^{solv}$$
(1)

$$G(gas) = H(gas) - TS(gas)$$
(2)

$$H(gas) = E(SCF) + ZPE$$
(3)

$$\Delta G(\text{Sol}) = \Sigma G(\text{Sol}) \text{ for products - } \Sigma G(\text{Sol}) \text{ for reactants}$$
(4)

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Chapter 5:

Stabilizing Unusual Oxidation States with the PN Ligand

Introduction. Structurally characterized examples of mononuclear, trivalent complexes of Zr¹⁻⁹ are generally confined to the more robust metallocene systems, which often limit the metal ion to a coordinatively saturated environment. Whereas trivalent and mononuclear Zr systems are relatively scarce, Hf systems are even more scant due to its greater propensity to dimerize, oligomerize, disproportionate, or promote radical-coupling given its greater ionic radius and inherent reducing ability. To date, the only mononuclear and trivalent Hf metallocene-like complexes that have been structurally characterized are $(\eta^5-Cp^{tBu2})_2$ HfCl $(Cp^{tBu2} = 1,3-di-tert$ butylcyclopentadienyl)¹⁰ and $Hf(\eta^5-Cp)_3$.¹¹ Taken that aside, and to our knowledge, the only example of a structurally characterized mononuclear Zr(III) complex that is not metallocene-based is the allyl-ate complex ${^{tBuMe_2SiCH}_2CH}_2T(\mu$ -Cl)₂Li(TMEDA) reported by Eisen and co-workers, for which the reactivity and decomposition was discussed in Chapter 3.¹² A second example of a formal Zr(III) complex was reported by Arnold and co-workers, namely $(OEP)Zr(CH_2SiMe_3)$ (OEP = octaethylporphyrin). However, for the latter case, OEP acts as a one-electron acceptor; thus, rendering the metal ion overall 4+ with a coordinated ligand-centered radical.13

In this chapter, we report the isolation of mononuclear and non-metallocene complexes (PN)₂MCl (M = Zr or Hf) *via* one-electron reduction of their respective precursors, (PN)₂MCl₂, with KC₈. With knowledge of how the PN⁻ ligand could support reactive nitride and methylidene moieties, it was a logical choice to attempt use of this ligand as a platform for the synthesis of Zr and Hf (III) complexes. Given the sterically protected nature of the methylidene as well as nitrido ligands by the isopropyl groups of the PN⁻ ligands, we proposed that this same protective pocket could also stabilize the complex from dimerization so we could isolate well-defined mononuclear complexes in these rare oxidation states. Crystals were isolated and characterized *via* X-ray diffraction analysis, as well as variable temperature X-band EPR spectroscopy in collaboration with Prof. Karsten Meyer and student Matthias Miehlich at FAU, Bavaria, Germany. The latter spectroscopic technique revealed the presence of a d^1 metal-centered radical with significant super hyperfine coupling to 146

two equivalent nitrogens from each chelating ligand. Using the known complex $(PN)_2TiCl^{14}$ (**1.1**) as a stable model, a comparison of structural studies and EPR spectral data for the triad $(PN)_2MCl$ (M = Ti, Zr, and Hf) is therefore reported.

Results and Discussion

Synthesis and Structural Characterization of Hf (III) and Zr (III) Complexes.

Addition of two equiv. of Li(PN) (PN⁻ = (N-(2-(diisopropylphosphino)-4methylphenyl)-2,4,6-trimethylanilide)¹⁵ to the precursors $[MCl_4(THF)_2]$ (M = Zr, or Hf) results in clean transmetallation to form (PN)₂MCl₂ in near quantitative yields for both metals (Scheme 5.1). Complexes 3.1 and 5.2 display characteristic ³¹P NMR spectroscopic features for the PN⁻ ligand at 11.4 and 8.8 ppm, respectively, while the ¹H NMR spectrum shows equivalent PN⁻ residues, such that in solution these complexes possess pseudo- C_{2v} symmetry. To conclusively establish the orientation of the PN ligands as well as the degree of aggregation, solid-state X-ray diffraction studies were conducted on a single crystal of 3.1 and 5.1, grown from a hexane/toluene mixture at -35 °C. Figure 5.2 displays the structural representations for **5.2** and **5.3**, revealing the two PN residues to occupy the equatorial sites, whereas the chlorides are distorted from a strict trans geometry (156.40(4)°, **3.1**; 158.01(4)°, **5.1**). Note that in the structures of both **3.1** and **5.1**, there are two crystallographically independent (but chemically equivalent) molecules in the asymmetric unit, but due to the similarities in bond and angle metrics, only one of these values is reported in Figure 5.2. The PN⁻ ligands are also oriented with the nitrogen and phosphorus atoms being cisoid (P-Zr-P, 96.11(3)° and N-Zr-N, 120.49(1)° for **3.1**; P-Hf-P, 95.50(3)° and N-Hf-N, 118.27(1)° for 5.1).



Scheme 5.1 Synthetic route to mononuclear, tetra and trivalent complexes of Zr (**3.1** and **5.2**) and Hf (**5.1** and **5.3**) along with disproportionation of **5.2** and **5.3**.



Figure 5.1. Sample of crystallized mixture of reaction between KC₈ and **3.1**. Circled in blue are orange needle crystals of **3.1**. Circled in green are red crystals of **5.2**.

When a slight excess of KC_8 (1.2 equiv.) was added as a slurry to a cold solution (-35 °C) of **3.1** in THF or **5.1** in Et₂O, a rapid color change from orange (**3.1**) or pale vellow (5.1) to dark red was observed. The reactions must be conducted on small scales of **3.1** or **5.1** (0.12 mmol), but also kept cold at a minimum of -78 °C to avoid rapid decomposition of the product by disproportionation in polar solvent. Notably, work-up of the mixture must be performed immediately after addition of the reductant (< 1 min). It is imperative that the temperature of the solution is kept at -78 °C (or lower; -196 °C is the preferred method) at all times, including the filtrate upon separation of carbon and excess reductant. The filtrate solution must be then rapidly taken to dryness, extracted into a minimum of hexane or toluene, and stored in the freezer to form a few red crystals (21.7 % for 5.2), which are then separated from some of the bulk material in the solution (typically orange and yellow microcrystalline powders for **3.1** and **5.1**, respectively) (Figure 5.1). The red crystals isolated from this reaction were found to be the trivalent complexes $(PN)_2MCI$ (M = Zr, **5.2**; M = Hf, **5.3**) (Scheme 5.1) on the basis of solid-state X-ray diffraction analysis and ¹H NMR spectroscopy (in the case of **5.2**). The bulk material (powder) was identified to be **3.1** and **5.1**, respectively, based on ¹H and ³¹P NMR spectroscopy. Ideally, these reduction reactions would be performed in a non-polar solvent, such as toluene, but under such conditions no reaction occurred.



Figure 5.2. Solid-state structures of complexes **3.1** (left) and **5.2** (right) displaying thermal ellipsoids at the 50% probability level. H-atoms and residual toluene in **5.2** have been omitted for clarity. Two molecules of hexane were also squeezed out of **3.1**. Selected distances (Å) for **3.1**: Zr1–Cl1, 2.4618(1); Zr1–Cl2, 2.4504(1); Zr1–N1, 2.122(3); Zr1–N2, 2.095(3); Zr1–P1, 2.8590(1); Zr1–P2, 2.9319(1). For **5.2**: Hf1–Cl1, 2.4380(1); Hf1–Cl2, 2.4304(1); Hf1–N1, 2.111(4); Hf1–N2, 2.095(3); Hf1–P1, 2.822(1); Hf1–P2, 2.8768(1).

The solid-state structures of the ruby red crystals **5.2** and **5.3**, obtained from their respective reactions, are shown in Figure 5.3. It can be seen how each trivalent metal center is coordinated in a nearly trigonal bipyramidal fashion, which is supported by the angular structural parameter, as defined by Addison and Reedijk, $\tau_5 = 0.84$ (M = Zr), 0.86 (M = Hf), with the two N atoms of the PN ligands occupying the equatorial positions.¹⁶ In contrast to **3.1** and **5.1**, the PN⁻ ligands have rearranged their positions with the phosphorus and nitrogen atoms being transoid to each other now. A similar orientation was also reported by us for the trivalent complexes (PN)₂TiCl¹⁴ (**1.1**) and our other reported five-coordinate complexes supported by two PN⁻ ligands.^{17,18} The Zr–Cl (2.4294(7) Å) and Hf–Cl (2.3964(6) Å) distances are slightly shorter with respect to **3.1** (2.4618(1), 2.4504(1) Å) and **5.1** (2.4380(1), 2.4304(1) Å), which is

likely due to a trans influence. Likewise, we were able to collect ¹H NMR spectra for crystalline samples of **5.2** and **5.3** in C_6D_6 . It was found that both isolated



Scheme 5.2. Reactivity of **3.1** under reducing conditions. When treated with KC₈ and Na(OCP)(dioxane)_{2.5} in THF, formation of (PN)₂Zr(OCP)₂ (**A8**) is observed, after disproportionation of the intermediate (PN)₂Zr(OCP) (**5A**). This same reaction type also observed when **3.1** is treated with NaN₃ in THF, going through (PN)₂ZrN₃ (**3A**) prior to disproportionation to **3.2**.

species are more stable in non-polar solvents (for several hours) revealing the presence of broad spectral features in the 14-11 ppm range corresponding to paramagnetic species **5.2** and **5.3**. Over hours, it was found that solutions of **5.2** or 5.3 in C₆D₆ gradually formed 3.1 and 5.1, respectively, along with species nonisolable from the mixture nor present in the NMR data. To further identify the product(s) formed from the reduction of **3.1** and **5.1**, crude samples of the reaction mixture were examined by ¹H and ³¹P NMR spectroscopy. In crude mixtures, the ¹H NMR spectral signals showed the presence of **3.1** with **5.2**, as well as **5.1** accompanied with **5.3**, respectively, along with the formation of unidentifiable diamagnetic products most likely resulting from disproportionation and/or decomposition via "M(PN)₂". Crystalline samples of both rapidly decompose in THF or Et₂O solution to **3.1** and **5.1** as well as products unidentifiable by NMR spectroscopy. Disproportionation of these species was also confirmed by *in situ* metathesis reactions that were made more facile by use of the more lable Zr (III) complex. Specifically, as discussed in Chapter 3, synthesis of the bis-azido complex **3.2** required high heating conditions and use of coordinating dioxane in order to exchange both chlorido ligands for two azido ligands. In contrast, an *in situ* reduction of **3.1** (Zr (IV)) to 5.2 (Zr(III)) with KC₈ concurrent with addition of NaN₃ resulted in lability of the Zr–Cl bond and methathesis to a $Zr-N_3$ at room temperature in Et₂O. This complex then underwent disproportionation to **3.2** (Scheme 5.2). Complex **3.2** was easily identified in the ³¹P NMR, although this did not provide a facile synthesis to **3.2** because there was significant contamination of **5.1**, likely from **3.1** disproportionating faster than the competing reaction with NaN₃. Excess NaN₃ did not change the outcome of the relative components of the reaction miture. The same methathesis/disproportionation pathway was also observed in in situ reductions of **3.1** with KC₈ in Et₂O, along with the addition of Na(OCP)(dioxane)_{2.5}, resulted in the formation of $(PN)_2Zr(OCP)_2$ (A8), again presumably after metathesis with 5.1 to (PN)₂Zr(OCP), followed by disproportionation of this species (Scheme 5.2). The relative ease of this reaction was confirmed by directly treating **3.1** with NaN₃. Even when heated to high temperatures (in excess of °C), no reaction was observed. As can 152

been seen in the solid state structure of **A8**, the cisoid orientation of the PN⁻ ligands again occurs in a six-coordinate environment. More information on the crystallographic details of $(PN)_2Zr(OCP)_2$ can be found in the Appendix of Molecules.¹⁹



Figure 5.3. Solid-state structures of complexes **5.2** (top) and **5.3** (bottom) displaying thermal ellipsoids at the 50% probability level. H-atoms have been omitted for clarity. Selected distances (Å) for **5.2**: Zr1–Cl1, 2.4294(7); Zr1–N1, 2.1705(2); Zr1–N2, 2.1906(2); Zr1–P1, 2.7666(5); Zr1–P2, 2.7509(5). For **5.3**: Hf1–Cl1, 2.3964(6); Hf1–N1, 2.164(2); Hf1–N2, 2.147(2); Hf1–P1, 2.7134(6); Hf1–P2, 2.7162(6).

X-band EPR Spectroscopic Studies.



Figure 5.4. CW X-band EPR spectra of **1.1** (left), **5.2** (middle), and **5.3** (right) at 96 or 8 K, recorded in ~1 mM frozen solution in respective solvent (black trace), and its simulation (red trace). The simulation was performed with effective *g*-values of: $g_1 = 1.97$, $g_2 = 1.97$, $g_3 = 1.87$ for **1.1**, $g_1 = 1.96$, $g_2 = 1.92$, $g_3 = 1.79$ for **5.2**, and $g_1 = 1.64$, $g_2 = 1.54$, $g_3 = 1.23$ for **5.3** and super-hyperfine coupling to two nitrogen nuclei (¹⁴N, *I* = 1, 99.6 %) of A₁ = A₂ = 2.10 mT (56.9 MHz), A₃ = 2.66 mT (71.9 MHz) for (PN)₂TiCl; A₁ = 1.33 mT (35.9 MHz), A₂ = 2.22 mT (59.9 MHz), A₃ = 3.10 mT (83.9 MHz) for **5.2** and A₁ = 19.4 mT (524 MHz), A₂ = 9.41 mT (255 MHz), A₃ = 16.1 mT (435 MHz) for **5.3**. Detailed experimental conditions and simulation parameters are given in the end of the chapter (Figures 5.5-5.7).

The following EPR spectroscopic data was collected by Matthias Miehlich in the lab of Prof. Karsten Meyer. Given the propensity of these species to decompose rapidly at elevated temperatures, especially in the case of complex **5.3**, sample

preparation has to be carried out under exceedingly careful conditions with precooled glassware and at temperatures below 173 K. Equally important, data acquisition had to be performed at low temperatures, but even with greatest care, minor decomposition could not be prevented, especially during sample preparations and measurements of compound **5.3**. Thus, the main focus of the spectra simulation was directed on reproducing the spectrum's main features, whereas slightly deviating intensities due to underlying signals of potential impurities were tolerated.

X-band EPR spectroscopic studies on 1.1 (Figure 5.4, left), 5.2 (Figure 5.4, middle), and 5.3 (Figure 5.4, right) were conducted in frozen toluene solutions at T <100 K. Both complexes 5.2 and 5.3 reveal EPR spectra with rhombic symmetry and ligand super-hyperfine coupling to two equivalent nitrogen atoms (^{14}N , I = 1, 99.6%) from the PN ligands. The EPR g values are significantly smaller than g_e (2.0023), especially for the very heavy Hf species, and thus consistent with a metal-centered d^1 species; despite the lack of any resolved hyperfine coupling to the metal ion $({}^{91}$ Zr, I =5/2, 11.2%; ¹⁷⁷Hf, I = 7/2, 18.6% and ¹⁷⁹Hf, I = 9/2, 13.6%). This is due to strong spinorbit coupling in heavy metal systems. In order to compare these spectra to a similar but more stable d^1 species, we collected X-band EPR spectra on the stable first-row (PN)₂TiCl, **1.1**.¹⁷ In contrast to **5.2** and **5.3**, the EPR spectrum of **1.1**, recorded in frozen toluene at 96 K, displays a spectrum with axial symmetry and EPR *g*-values closer to g = 2 but, similar to 5.2 and 5.3, super-hyperfine coupling to two equivalent nitrogens. Notably, like **5.2** and **5.3**, no hyperfine coupling to the low abundant ⁴⁷Ti and ⁴⁹Ti isotopes (I = 5/2 (7.4 %) and 7/2 (5.4 %), respectively) or the ³¹P atom (I =½, 100 %) of the PN ligand could be resolved. Noteworthy, in contrast to **5.2** and **5.3**, complex **1.1** shows no evidence for disproportionation – even when thermolyzed at 100 °C – and can also be further reduced to form the bridging end-on dinitrogen complex {(PN)₂Ti}₂(μ -N₂)} (**1.4**) described in chapter 1 vide supra.¹⁷

Conclusion.

In conclusion, the isolation of rare examples of trivalent and mononuclear nonmetallocene complexes of Zr and Hf has been achieved by rapid, low temperature work-up of the reaction mixture, immediately following one-electron reduction of the corresponding dichloride precursor. Complexes **5.2** and **5.3** are clearly kinetic products formed upon reduction, and, when re-dissolved in polar solvents, rapidly undergo disproportionation to yield **3.1** and **5.1**, respectively, along with another decomposition product we have thus far been unable to characterize. These more labile M(III) complexes present a unique way, albeit in poor yield, of transmetallating salts while circumventing direct metathesis from the comparatively rather inert M(IV) precursors. Ideally, we would like to find a way to stabilize these complexes for longer lifetimes. As EPR spectroscopic data confirms, the PN⁻ ligand platform is essentially innocent, rendering these mononuclear complexes *d*¹ metal-centered radicals.

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Experimental Details

General Procedures

Unless otherwise stated, all operations were performed in a M. Braun Lab Master double-dry box under an atmosphere of purified dinitrogen or using high vacuum standard Schlenk techniques under an argon or dinitrogen atmosphere. Hexanes toluene, and tetrahydrofuran (THF) were purchased from Fisher Scientific and Et₂O was purchased from Sigma Aldrich. Solvents were sparged with argon for 20 minutes and dried using a two-column solvent purification system where the column 156 designated for hexanes and toluene were packed with Q5 and alumina respectively, and the columns designated for Et_2O and THF were packed with alumina. Deuterated benzene was purchased from Cambridge Isotope Laboratories (CIL) and was sparged with nitrogen for 20 minutes, then was dried over a potassium mirror, vacuum transferred to a collection flask, and degassed by freeze-pump-thaw cycles. All solvents were transferred into a dry box and were stored over 4 Å sieves. All sieves were heated to 200 °C under vacuum overnight prior to use. Celite used for filtrations was also heated to 200 °C under vacuum overnight prior to use. ¹H NMR spectra were recorded on a Bruker AVIII 400 and AVII 500 MHz spectrometer, ¹³C NMR spectra were recorded on a Bruker AVIII 500 MHz spectrometer, and ³¹P{¹H} spectra were recorded on a Bruker AVIII 400 spectrometer. ¹H NMR spectra are reported with reference to residual proteo solvent resonances of C₆D₆ at 7.16 ppm. ³¹P{¹H} NMR spectra were referenced to external H₃PO₄ (0 ppm). LiPN was prepared according to published literature procedures.¹⁵ MCl₄(THF)₂ were prepared by addition of THF into MCl₄ and recrystallized. Elemental analyses were measured by Midwest Microlab.

Synthesis of (PN)₂ZrCl₂ (3.1)

To a colorless suspension of solution of ZrCl₄(THF)₂ (543.5 mg, 1.44 mmol, 1 equiv.) in 3 mL toluene in a 20 mL vial was added a yellow 10 mL toluene solution of LiPN (1.00 g, 2.88 mmol, 2 eq.) while stirring at room temperature. After stirring for 12 hours, the reaction mixture turned bright orange, and a noticeable precipitate had formed, LiCl. The reaction mixture was filtered over Celite for removal of alkaline side product, and all volatiles were taken to dryness. The resulting orange oil is treated with hexane dropwise, while swirling the vial. Large orange crystals began to precipitate after swirling the oil and hexane mixture for one minute. After these initial crystals formed, they seeded the oil to form a large crystalline mass within another minute or less. The crystals were then triturated with hexanes to ensure removal of all toluene. The reaction has been confirmed by ¹H and ³¹P NMR to proceed in quantitative yields. The isolated crystalline solid is pure and can be used without further need for recrystallization (1.21 g, 1.44 mmol, 100%). To obtain crystals

suitable for single crystal X-ray diffraction, 100 mg of the solid can be dissolved in a minimum of toluene (3 mL), layered with 5 mL of hexane, and stored at -35 °C overnight, resulting in the deposition of orange needles. ¹H NMR (400 MHz, 298 K, **benzene-d**₆): δ 7.14-6.99 (m, unable to resolve *J* coupling value, 2H, C-*H*, Ar), 6.70 (d, $J_{\text{H-H}}$ = 8.9 Hz, 2H, C-H, Ar), 6.57 (s, $\Delta v_{1/2}$ = 4.2 Hz, 4H, C-H, m-tolyl Ar), 5.56 (dd, $J_{\text{H-H}}$ = 5.1, $J_{P-H} = 8.5$ Hz, 2H C-H, m-tolyl Ar), 2.61 (sept, ${}^{3}J_{H-H} = 7.1$ Hz, 4H, P-CHMe₂), 2.36 (s, $\Delta v_{1/2} = 3.7$ Hz, 12H, CH₃, o-tolyl Ar), 2.16 (s, $\Delta v_{1/2} = 3.9$ Hz, 6H, CH₃, p-Ar), 2.11 (s, $\Delta v_{1/2}$ = 4.2 Hz, 6H, CH_{3} , p-Ar), 1.38-1.51 (dd, two overlapping doublet of doublets, for one: ${}^{3}I_{H-H} = 5.6 \text{ Hz}, {}^{3}I_{P-H} = 13.0 \text{ Hz}$, for second, ${}^{3}I_{H-H} = 7.7 \text{ Hz}, {}^{3}I_{P-H} = 14.5 \text{ Hz}, 24\text{H}, P-CHMe_{2}$). ³¹P{¹H} NMR (162 MHz, 298 K, benzene-d₆): δ 11.44 (2P, Zr-P). ¹³C{¹H} NMR (125.8 MHz, 298 K, benzene-d₆): 157.6 (d, J_{C-P} = 4.5 Hz, 2C, C-Ar), 157.4 (d, J_{C-P} = 4.4 Hz, 2C, C-Ar), 140.5 (4C, C-Ar), 136.8 (2C, C-Ar), 133.5 (d, J_{C-P} = 2.2 Hz, 2C, C-Ar), 132.9 (2C, C-Ar), 130.9 (4C, C-Ar), 122.2 (d, $J_{C-P} = 2.7$ Hz, 2C, C-Ar), 121.1 (d, $J_{C-P} = 2.5$ Hz, 2C, *C*-Ar), 115.1 (d, ${}^{2}I_{C-P}$ = 9.0 Hz, 2C, *C*-Ar), 25.2 (d, I_{C-P} = 8.2 Hz, 4C, P-*C*HMe2), 21.4 (2C, *C*H₃-Ar), 20.9 (d, ²*I*_{C-P} = 2.0 Hz, 4C, P-CH*Me2*), 20.7 (4C, *C*H₃-Ar), 20.6 (d, ²*I*_{C-P} = 2.4, 4C, P-CHMe2), 20.6 (2C, CH₃-Ar). Anal. Calcd for C₄₄H₆₂N₂P₂Cl₂Zr: C, 62.69; H, 7.41; N, 3.32. Found: C, 62.46; H, 7.32; N, 3.02.

Synthesis of (PN)₂HfCl₂ (5.1)

To a colorless suspension of solution of $HfCl_4(THF)_2$ (334.4 mg, 0.72 mmol, 1 equiv.) in 3 mL toluene in a 20 mL vial was added a yellow 10 mL toluene solution of LiPN (500 mg, 1.44 mmol, 2 eq.) while stirring at room temperature. After stirring for 12 hours, the reaction mixture turned darker yellow, and a noticeable precipitate had formed, LiCl. The reaction mixture was filtered over Celite for removal of alkaline side product, and all volatiles were taken to dryness. The resulting yellow oil is treated with hexane dropwise, while swirling the vial. Large yellow crystals began to precipitate after swirling the oil and hexane mixture for one minute. After these initial crystals formed, they seeded the oil to form a large crystalline mass within another minute or less. This solid is then dissolved in 1 mL of toluene and layered with 5 mL hexanes and stored at -35 °C overnight, resulting in the deposition of large yellow 158 crystalline plates suitable for single crystal X-ray diffraction (577.5 mg, 0.52 mmol, 72%). ¹H NMR (400 MHz, 298 K, benzene-d₆): δ 7.14-6.99 (m, unable to resolve *J* coupling value, 2H, C-*H*, Ar), 6.73 (d, *J*_{H-H} = 8.7 Hz, 2H, C-*H*, Ar), 6.59 (s, $\Delta v_{1/2}$ = 4.4 Hz, 4H, C-*H*, m-tolyl Ar), 5.63 (dd, *J*_{H-H} = 5.1, *J*_{P-H} = 8.4 Hz, 2H C-*H*, m-tolyl Ar), 2.66 (sept, ³*J*_{H-H} = 7.0 Hz, 4H, P-C*H*Me₂), 2.35 (s, $\Delta v_{1/2}$ = 3.8 Hz, 12H, C*H*₃, o-tolyl Ar), 2.16 (s, $\Delta v_{1/2}$ = 4.7 Hz, 6H, C*H*₃, p-Ar), 2.13 (s, $\Delta v_{1/2}$ = 4.6 Hz, 6H, C*H*₃, p-Ar), 1.32-1.53 (dd, two overlapping doublet of doublets, for one: ³*J*_{H-H} = 6.2 Hz, ³*J*_{P-H} = 13.2 Hz, for second, ³*J*_{H-H} = 3.3 Hz, ³*J*_{P-H} = 11.6 Hz, 24H, P-CH*Me*₂). ³¹P{¹H} NMR (162 MHz, 298 K, benzene-d₆): δ 8.76 (2P, Hf-*P*). ¹³C{¹H} NMR (125.8 MHz, 298 K, benzene-d₆): 157.6 (d, *J*_{C-P} = 25.1 Hz, 2C, *C*-Ar), 140.2 (4C, *C*-Ar), 136.2 (2C, *C*-Ar), 133.4 (2C, *C*-Ar), 133.0 (2C, *C*-Ar), 130.8 (4C, *C*-Ar), 119.9 (2C, *C*-Ar), 26.2 (d, two overlapping doublets, unable to resolve J coupling, 4C, P-CHMe2), 21.3 (*C*H₃-Ar), 20.7 (*C*H₃-Ar), 20.5 (*C*H₃-Ar), 20.9 (br, $\Delta v_{1/2}$ = 5.0 Hz 8C, P-*C*H*Me*2). Anal. Calcd for C₄₄H₆₂N₂P₂Cl₂Hf: C, 56.81; H, 6.72; N, 3.01. Found: C, 55.52; H, 6.69; N, 2.66.

Synthesis of (PN)₂ZrCl (5.2)

To an orange solution of **3.1** (100 mg, 0.12 mmol, 1 equiv.) in 2 mL THF in a 20 mL vial was added a 5 mL THF slurry of KC₈ (19.3 mg, 0.14 mmol, 1.2 eq.) while stirring. Both were chilled to -35 °C prior to addition. Immediately upon addition, a very distinct color change to red was observed. The mixture was then immediately filtered over Celite and taken to dryness. Due to the rapid disproportionation of **5.2** in polar solvents, the mixture must be kept cold (-196 °C in a coldwell is the preferred method) during this process. The residue was then dissolved in 5 mL hexanes and filtered once more to remove KCl. This solution was stored at -35 °C overnight, resulting in the deposition of a mixture of orange needles of **3.1** as well as large red crystalline plates. These crystals were suitable for single crystal X-ray diffraction, and were identified as **5.2** (25 mg, 0.03 mmol, 25.7%). Note that this yield is reported for the isolated crystals of **5.2**, which can be manually separated from **3.1**. Reported below are selected peaks from the paramagnetic ¹H NMR spectra attributable to complex **5.2**.

¹**H** NMR (400 MHz, 298 K, benzene-d₆): δ 12.28, 11.09, 3.73. Anal. Calcd for C₄₄H₆₂N₂P₂Cl₂Hf: C, 65.44; H, 7.44; N, 3.47. Found: C, 65.08; H, 7.73; N, 3.14.

Synthesis of (PN)₂HfCl (5.3)

To a yellow solution of **5.1** (135 mg, 0.12 mmol, 1 equiv.) in 5 mL ether in a 20 mL vial was added a 5 mL ethereal slurry of KC₈ (20 mg, 0.13 mmol, 1.2 eq.) while stirring. Both were chilled to -35 °C prior to addition. Immediately upon addition, a very distinct color change to dark red was observed. The mixture was then immediately filtered over Celite and taken to dryness. Due to the rapid disproportionation of **5.3** in polar solvents, the mixture must be kept cold (-196 °C in a coldwell is the preferred method) during this process. The residue was then dissolved in 5 mL hexanes and filtered once more to remove KCl. This solution was stored at -35 °C overnight, resulting in the deposition of a mixture of yellow needles of **5.3** as well as large red crystalline plates. These crystals were suitable for single crystal X-ray diffraction, and were identified as **5.3**. Unfortunately, due to the much more rapid disproportionation of **5.3** compared to **5.2**, only a few crystals of **5.3** survive for single crystal X-ray diffraction. We are also able to collect EPR data in toluene as a glass. Reported below are selected peaks from the paramagnetic ¹H NMR spectra attributable to complex **5.3**. ¹**H NMR (400 MHz, 298 K, benzene-d**₆): *δ* 13.65, 11.80, 4.34. Attempts to obtain satisfactorily combustion analysis failed due to the thermal sensitivity of the compound.

Crystallographic Experimental Details

Crystallographic data are summarized Table 5.1. Suitable crystals for X-ray analysis of **3.1** and **5.1-5.3** were placed on the end of a Cryoloop coated in NVH oil. Data for single crystal structure determination of **3.1** and **5.3** were taken on a Bruker ApexII with a CCD, while **5.1** and **5.2** were taken on a Bruker D8 with CMOS area detector employing graphite-monochromated Mo-K α radiation (λ =0.71073 Å) at a temperature of 100(1) K. Rotation frames were integrated using SAINT,²⁰ producing 160 a listing of non-averaged F^2 and $\sigma(F^2)$ values The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS.²¹ The initial structure of **3.1** was solved by direct methods – SIR2004.²² The initial structure of **5.1** was solved by direct methods – SHELXS.²³ The initial structures of **5.2** and **5.3** were solved by dual methods – SHELXT.²³ Refinement was by full-matrix least squares based on F² using SHELXL-2014.²⁴ All reflections were used during refinement. Nonhydrogen atoms were refined anisotropically and hydrogen atoms were refined with riding models. These results were checked using the IUCR's CheckCIF routine. The alerts in the output are related to the co-crystallized solvents.

For **3.1**, two sites occupied by hexane molecules were identified in the asymmetric unit. These sites were considerably disordered and were treated by SQUEEZE as a diffuse contribution.²⁵ In the resulting void space, a contribution of 881 e⁻ per unit cell was found and taken to represent two hexane molecules in the asymmetric unit.

Compound	$3.1 \cdot C_6 H_{14}$	5.1 · C ₇ H ₈	
Molecular formula	$C_{44}H_{62}Cl_2N_2P_2Zr$, C_6H_{14}	C ₄₄ H ₆₂ Cl ₂ N ₂ P ₂ Hf, C ₇ H ₈	
Formula weight	1015.35	1114.55	
Temperature (K)	100(1)	100(1)	
Crystal system	Orthorhombic	Orthorhombic	
Space group	$P 2_1 2_1 2_1$	$P 2_1 2_1 2_1$	
Cell constants:			
a (Å)	13.3448(6)	13.3358(6)	
b (Å)	25.7942(13)	25.5782(13)	

Table 5.1. Crystallographic Data of compounds **3.1**, and **5.1-5.3**.

Compound	5.2	5.3
Goodness-of-fit on <i>F2^c</i>	1.025	1.058
$wR_{2^{b}}$	0.0844	0.0617
R_1^{a}	0.0393	0.0248
Refinement method	Full-matrix least- squares on F ²	Full-matrix least squares on F ²
# Reflns collected	21835	24113
<i>h, k, l</i> ranges collected	$-17 \le h \le 17$ $-33 \le k \le 33$ $-41 \le l \le 41$	$-17 \le h \le 17$ $-33 \le k \le 33$ $-41 \le l \le 37$
θ range for data collection (°)	1.993 to 27.562	2.836 to 27.551
Wavelength	0.71073	0.71073
F(000)	4352	4608
Abs coeff (mm-1)	0.394	2.116
Density (calcd mg/m3)	1.233	1.363
Z	8	8
Volume (ų)	10940.5(9)	10861.5(9)
Gamma Angle	90	90
Alpha Agle Beta Angle	90 90	90 90
c (Å)	31.7835(15)	31.8420(14)

Molecular formula	$C_{44}H_{62}ClN_2P_2Zr$	$C_{44}H_{62}ClN_2P_2Hf$
Formula weight	807.56	894.83
Temperature (K)	100(1)	100(1)
Crystal system	Monoclinic	Monoclinic
Space group	P 1 2 ₁ /n 1	P 1 2 ₁ /n 1
Cell constants:		
a (Å)	17.7014(6)	17.7270(5)
b (Å)	13.7831(5)	13.7111(4)
c (Å) Alpha Agle Beta Angle Gamma Angle	17.8222(7) 90 99.9610(10) 90	17.8490(5) 90 99.7730(10) 90
Volume (ų)	4282.7(3)	4275.4(2)
Z	4	4
Density (calcd mg/m3)	1.252	1.390
Abs coeff (mm-1)	0.425	2.609
F(000)	1708	1836
Wavelength	0.71073	0.71073
θ range for data collection (°)	2.956 to 27.568	2.956 to 27.568
<i>h, k, l</i> ranges collected	$-23 \le h \le 23$ $-17 \le k \le 17$ $-22 \le l \le 23$	$-23 \le h \le 23$ $-17 \le k \le 17$ $-23 \le l \le 23$
# Reflns collected	9863	9830

Refinement method	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²
$R_1^{\rm a}$	0.0356	0.0232
$wR_{2^{b}}$	0.0978	0.0483
Goodness-of-fit on F2 ^c	1.099	1.051

a R1 = (|Fo| - |Fc|) / |Fo|. b wR2 = [[w(Fo2 - Fc2)2] / [w(Fo2)2]]1/2. c Goodness-of-fit = [[w(Fo2 - Fc2)2]/Nobservns Nparams)]1/2, all data.

Electron Paramagnetic Resonance (EPR) Experimental Details

EPR spectra were recorded on a JEOL continuous wave spectrometer JES-FA200 equipped with an X-band Gunn oscillator bridge, a cylindrical mode cavity, and a helium cryostat. The samples were freshly dissolved in the respective solvent in an air-tight quartz EPR tube under nitrogen atmosphere in the glovebox. The solutions in the tube were frozen in liquid nitrogen upon exiting the glovebox and kept frozen until measured. Analysis and simulation of the data was done using the software "eview" and "esim" written by E. Bill (mail: ebill@gwdg.de, MPI for Chemical Energy Conversion, Mülheim an der Ruhr).



Figure 5.5. CW X-band EPR spectra of **1.1** at 96 K, recorded in ~1 mM frozen solution in toluene (black trace), and its simulation (red trace). Experimental conditions:

microwave frequency v = 8.959 GHz, modulation width = 0.4 mT, microwave power = 1.0 mW, modulation frequency = 100 kHz, time constant = 0.1 s. Simulation parameters: effective spin S = 1/2, effective g-values $g_1 = 1.98$, $g_2 = 1.94$, $g_3 = 1.86$, line widths $W_1 = 1.5$ mT, $W_2 = 1.7$ mT, $W_3 = 1.8$ mT, and super hyperfine coupling to two nitrogen nuclei (¹⁴N, I = 1, 99.6 %) of $A_1 = 1.56$ mT (41.9 MHz), $A_2 = 2.33$ mT (62.9 MHz), $A_3 = 2.56$ mT (68.9 MHz).



Figure 5.6. CW X-band EPR spectra of **5.2** at 96 K, recorded in ~1 mM frozen solution in toluene (black trace), and its simulation (red trace). Experimental conditions: microwave frequency v = 8.956 GHz, modulation width = 0.4 mT, microwave power = 1.0 mW, modulation frequency = 100 kHz, time constant = 0.1 s. Simulation parameters: effective spin S = 1/2, effective *g*-values $g_1 = 1.96$, $g_2 = 1.92$, $g_3 = 1.78$, line widths $W_1 = 0.98$ mT, $W_2 = 1.6$ mT, $W_3 = 2.6$ mT, and super hyperfine coupling to two nitrogen nuclei (¹⁴N, I = 1, 99.6 %) of $A_1 = 1.19$ mT (31.5 MHz), $A_2 = 2.09$ mT (55.2 MHz), $A_3 = 3.18$ mT (83.9 MHz) as well as to one phosphorus nucleus (³¹P, I =0.5, 100 %) of $A_1 = 0.0$, $A_2 = 4.99$ mT (132 MHz), $A_3 = 0.0$.



Figure 5.7. CW X-band EPR spectra of **5.3** at 8 K, recorded in 1 mM frozen solution in THF (black trace), and its simulation (red trace). Experimental conditions: microwave frequency v = 8.961 GHz, modulation width = 0.4 mT, microwave power = 1.0 mW, modulation frequency = 100 kHz, time constant = 0.1 s. Simulation parameters: effective spin S = 1/2, effective *g*-values $g_1 = 1.64$, $g_2 = 1.56$, $g_3 = 1.23$, line widths of W₁ = 10.5 mT, W₂ = 4.2 mT, W₃ = 15.0 mT, and super hyperfine coupling to two nitrogen nuclei (¹⁴N, I = 1, 99.6 %) of $A_1 = 24.7$ mT (515 MHz), $A_2 = 23.6$ mT (491 MHz), $A_3 = 20.88$ mT (434 MHz).

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Chapter 6:

Phosphaethynolate Chemistry of Scandium to Stabilize Diisophosphaethynolate

Phosphaethynolate Chemistry, Background and Reactivity in Electropositive Metals.

Introduction. For generations, the ubiquitous cyanate ion, -OCN, has captivated the attention of the inorganic community. So thorough are these studies, the extensive reach of the literature in this field has documented the many binding modes of this ligand across transition metals.¹⁻⁴ Largely, *N*-binding predominates in mononuclear complexes,^{3,4} although in the case of dinuclear complexes a 1,3-binding fashion in which both N and O atoms coordination is often observed.² Even in the case of electropositive early transition metals, relatively few examples exist of O-bound cyanato ligands.¹ Cyanate, which is normally formed by the heated reaction of sodium carbonate and urea, would be more attractively and sustainably synthesized from dinitrogen. It has been well documented by Chirik and co-workers that hafnium complexes capable of activating dinitrogen can be further carbonylated to ultimately cleave the N₂ fragment to form *N*-bound cyanato ligands.⁴ There is also precedence for the microscopic reverse whereby the cyanate ligand reductively decarbonylates resulting in the synthesis of transition metal nitrides.^[3k] Given the diverse array of reports on cyanate binding modes and reactivity, interest in the reactivity of the respective heavier congeners, $\neg OCX (X = P, As)$ presented an opportunity to explore a much more polarizable and also vulnerable C–X bond involving the pnictogen atom.

Phosphaethynolate or -OCP, the phosphorous analogue of cyanate, was introduced to the inorganic community by Becker and co-workers in 1992 (Figure 6.1, compound **1**)^{5a-c} but given that this procedure was not facile, reproducible on larger scales, in addition to the thermal degradation of the original lithium salt, the reactivity of this reagent remained uncharted for nearly two decades. Since the recent advent of a simple, bulk procedure to synthesize the phosphaethynolate reagent, Na(OCP)(1,4-dioxane)_{2.5} (Figure 6.1, compound **2**),^{5d-h} there has been a drastic shift in the use of this reagent as a P-atom transfer source, as well as for the functionalization of other inorganic scaffolds including transition metals,^{6a-f} actinide,^{6g,h} lanthanide,⁶ⁱ and alkaline earth metals.^{6j} It should be noted that it is likely 169

that the 0.5 equivalents of (1,4-dioxane) are in the crystal lattice and not coordinated to the Na cation. The formation of new main group compounds⁷ and the development of organic syntheses⁸ has been a hallmark of phosphaethynolate chemistry as well. Perhaps one of the most unique features of this reagent is that it is ambidentate, binding either *via* the O or P atom depending on the oxidation state of the metal and supporting ligand scaffold. In contrast to the aforementioned isocyanate anion in which O (3.5) and N (3.0) do not have great disparities in electronegativity, moving down the group to P (2.2) results in the significant polarization of this reagent as well as the installation of a much "softer" binding site. Studies with more electropositive metals are still in their infancy, spanning merely a few examples in groups 3-6 as well as a small number of actinide and rare earth examples.^{6e,f,i,l,m}

The diverse reactivity of phosphaethynolate with a range of metals gives us a glimpse of how this reagent can be bound as well as transformed. In organic synthesis, new (phosphino)phosphaketene reagents have been developed which boast a broad array of reactivity including the development of new organic compounds following isocyanide activation (Figure 6.1, compound **4**). When looking at main group elements, novel germanium phosphacyclobutadiene complexes have been synthesized *via* phototriggered decarbonylation pathways (Figure 6.1, compound **5**).^{7a} With electron rich transition metals such as cobalt (I) supported by an electron donating PDI (PDI = pyridinediimine) ligand, the coordination mode has been shown to prefer binding *via* the phosphorous atom (Figure 6.1, compound **3**),^{6b} as well as for low valent mid transition metals such as the tungsten pentacarbonyl (W(CO)₅) (Figure 6.1, compound **6**).^{6c}



Figure 6.1. The phosphaethynolate reagent and diverse chemistry. 1: original reported reagent Li(OCP)(DME)₂ by Becker and coworkers.^{5a} 2: $[Na(OCP)(DME)_2]_2$.^{5d} 3: A cobalt PCO complex (P-bound).^{6b} 4: Phosphaethynolate can be used to synthesize (phosphino)phosphaketenes; shown here is the reaction product of the (phosphino)phosphaketene with adamantyl isocyanide.⁷ⁱ 5: A digermanium phosphacyclobutadiene product after decarbonylation of PCO.^{7a} 6: A P-bound low valent tungsten carbonyl complex with counter cation of K(2.2.2-Kryptofix).^{6c} In all complexes, Ar = 2,6-*i*Pr₂C₆H₃.

In addition to our contibutions to the rising field of phosphaethynolate chemistry, which will be the topic of the next three chapters, several other groups have demonstrated the use of this reagent with electropositive metal scaffolds. In rareearth scaffolds, reactivity with Na(OCP)(1,4-dioxane)_n resulted in salt metathesis,⁶ⁱ with the ⁻OCP group being bound *via* the *O*-atom as a pseudo halide. However, unlike for the case of Sc, these complexes have not been shown to undergo any further transformations on their respective metal centers. All complexes in these series were supported amidinato (DippForm)₂Y(OCP)(THF) by ligands and as (DippForm)₂Nd(OCP)(THF) (DippForm N,N'bis(2,6-diisopropylphenyl)-= formamidinate) (Scheme 6.1, top). If instead two equivalents of phosphaethynolate

used, along with 18-crown-6 (18-c-6), were [Na(18-c- $6)(THF)_2][(DippForm)_2Y(OCP)_2(THF)]$ and [Na(18-c-6)(THF)₂][(DippForm)₂Nd(OCP)₂(THF)] are formed, both still containing an Obound OCP (Scheme 6.1, center). In the case of Sm, compound [(DippForm)Sm(OCP)(18-crown-6)] was isolated via encapsulation of the Sm ion (Scheme 6.1, bottom). The reactivity of the -OCP ligand has only been probed with Nd and found to further react towards dimerization *via* bridging OCP ligands upon abstraction of THF (Scheme 6.1, top).⁶ⁱ As of yet, these examples of Nd and Sm are the only lanthanide elements shown to demonstrate the coordination of -OCP.



Scheme 6.1. Synthesis of (DippForm)₂Y(OCP)(THF) and (DippForm)₂Nd(OCP)(THF) from (DippForm)₂Ln(THF)(Cl) and Na(OCP). Dimerization is observed for the Nd analogue *via* addition of $B(C_6F_5)_3$ to form (DippForm)₂Nd(OCP)₂ (top). Synthesis of $[Na(18-c-6)(THF)_2][(DippForm)_2Y(OCP)_2(THF)]$ and $[Na(18-c-6)(THF)_2][(DippForm)_2Nd(OCP)_2(THF)]$ from salt metathesis using Na(OCP) (center). Synthesis of (DippForm)Sm(OCP)(18-c-6) from [(DippForm)Sm(THF)(18-c-6)][DippForm] and Na(OCP) (bottom). In all instances Ar = $2,6^{-i}Pr_2C_6H_3$. (1,4-dioxane)_{2.5} refers to all listed dioxanes.

Indeed, similar principles have been applied towards the development of this reagent with actinide complexes. In initial studies of the phosphaethynolate reagent with "harder" uranium and thorium (IV) complexes, Arnold and coworkers reported the *O*-bound complex M(OCP)(amid)₃ (M = U, Th, amid = N,N'-bis-(trimethylsilyl)benzamidinate) (Scheme 6.2).^{6g} As can be seen in Scheme 6.2, the binding mode is of the phosphaethynolato resonance is essentially linear (\angle M–O–C° = 170.9(3) M = U, 176.4(3) M = Th). This feature corroborates the observed binding in the aforementioned Sc complex were \angle M–O–C° = 170.89(17). In the U and Th complexes, the binding mode stands in contrast to the divergent reactivity observed for the same precursors MCl(amid)₃ with -OCN and -SCN, which bind *via* the *N*-atom in both instances (Scheme 6.2). This indeed shows that in the case of -OCP, the more dramatic shift in polarization drastically changes the coordination chemistry when compared to classical reactions with the ubiquitous cyanate. In the case of this harder M(IV) complex, the *O*-bound -OCP moiety was maintained at ambient conditions, free from decarbonylation or other rearrangement.



Scheme 6.2. Synthesis of $M(OCP)(amid)_3$ (top) (M = U, Th, amid = N,N'-bis-(trimethylsilyl)benzamidinate), from $M(amid)_3$. Cyanate and thiocyanate complex syntheses are also shown for comparison, $M(NCO)(amid)_3$ and $M(NCS)(amid)_3$ (middle and bottom). R = trimethylsilyl. (1,4-dioxane)_{2.5} refers to all listed dioxanes.

Further work from Meyer and co-workers has demonstrated that by softening the U center, the paradigm of this reactivity can deviate.^{6h} By instead selecting a uranium (III) precursor, ((^{Ad,Me}ArO)₃N)U^{III}(DME) ((^{Ad,Me}ArO)₃N³⁻ = trianion of tris(2-hydroxy-3-(1-adamantyl)-5-methylbenzyl)- amine), treatment with Na(OCP)(1,4-dioxane)_{2.5} resulted in the formation of the μ-0 complex, [Na(2.2.2crypt)][{(($^{Ad,Me}ArO$)_3N)U^{IV}(DME)}(μ -O){(($^{Ad,Me}ArO$)_3N)U^{IV}(CP)}] when also treated with 2.2.2-crypt (2.2.2-crypt = 2,2,2-Kryptofix)) as shown in Scheme 6.3. Most uniquely, the participation of electron rich U(III) nuclei in this reaction could promote the two-electron reduction of the -OCP moiety to cleave the C–O bond and form the cyaphido ligand, CP-, isoelectronic to the ubiquitous cyanido ligand. The only other

examples of metal cyaphido complexes are $(dppe)_2Ru(H)(CP)$ and $(dppe)_2Ru(CCR)(CP)$ (R = CO₂Me, C₆H₄OMe).⁹ It should also be noted that Meyer and coworkers also recently reported the synthesis of the arsenic analogue of this species, $[Na(2.2.2\text{-}crypt)][\{((^{Ad,Me}ArO)_3N)U^{IV}(THF)\}(\mu\text{-}O)\{((^{Ad,Me}ArO)_3N)U^{IV}(CAs)\}]$ prepared from $[Na(18\text{-}crown\text{-}6)][OCAs].^{10}$ Thus, this presents a unique entryway to unexplored heavy congeners to cyanide, and shows that reduced states of electropositive metal may open the doorway to new and unexpected reactivity of - OCP and the As congener.



Scheme 6.3. Synthesis of $[Na(2.2.2-crypt)][\{((^{Ad,Me}ArO)_3N)U^{IV}(DME)\}(\mu-O)\{((^{Ad,Me}ArO)_3N)-U^{IV}(CP)\}]$ from $[((^{Ad,Me}ArO)_3N)U^{III}(DME)]$ (above) and $[((^{Ad,Me}ArO)_3N)U^{IV}(DME)(OCP)]$ from $[((^{Ad,Me}ArO)_3N)U^{IV}(DME)(CI)]$ (below). (1,4-dioxane)_{2.5} refers to all listed dioxanes.

To further illustrate the importance of a U(III) reagent, the aforementioned study revealed that by use of a more thermodynamically U(IV) precursor, reductive cleavage of -OCP could not be achieved and instead, when ((^{Ad,Me}ArO)₃N)U^{IV}(DME)(Cl)

was treated with Na(OCP)(1,4-dioxane)_{2.5}, the result was only metathesis to form ((^{Ad,Me}ArO)₃N)U^{IV}(DME)(OCP) (Scheme 6.3), as akin to that observed for the tris(amidinato) U^{IV} and Th^{IV} precursors (*vide supra*). Similarly, no decarbonylation or C–O bond breaking was observed in the U(IV) complex.

As aforementioned, the $(CO)_5W(PCO)^-$ complex in which the metal was maintained at a reduced state^{6c} resulted in a *P*-bound ⁻OCP moiety. When instead a higher valent tungsten ion is employed, differing chemistry can be accomplished with -OCP, as well as -OCN and -OCAs. In these transformations, the powerful π -base complex W(OAr)₄ (Ar = $2,6^{-i}Pr_2C_6H_3$) reagent was a suitable platform, in terms of both electronic structure as well as its coordination geometry, to *reductively decarbonylate* the phosphaethynolato moiety, concurrent with a two-electron oxidation at the metal center to form the respective terminal pnictide complexes (Scheme 6.4).^{6d} This is a unique example of decarbonylation resulting in one phosphorous atom transfer per transition metal center compared to other systems that dimerize or couple upon extrusion of CO^{6b,e,7a-c,f} The ability to deliver one phosphorous atom provides a more selective installation of phosphorous when compared with the unpredictable stoichiometry from P₄ given its enthalpically uphill to fragment into P and P₃ or 4 P atoms.¹¹ Given the propensity of phosphorous to catenate, this example shows that this reagent can provide a more convenient and selective form for delivering a P-atom when compared to the more common P-atom transfer reagent P₄.



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Scheme 6.4. Synthesis of terminal tungsten pnictinido complexes supported by phenoxido ligands. Ar = $2,6^{-i}Pr_2C_6H_3$. TBA=tetrabutylammonium. (1,4-dioxane)_{2.5} refers to all listed dioxanes.

Exploring the Reactivity of Phosphaethynolate with Scandium.

Diisooxocyan, OCN–NCO, is a highly unstable species that can be generated *via* oxidation of ubiquitous [NCO]⁻.¹² We inquired if the analogous OCP–PCO, diisophosphaethynolate, could be stabilized with early transition metals, especially under reducing conditions, given the more likely ability of phosphorous to catenate. Since the recent report of the facile synthesis of the phosphaethynolate ion, Na(OCP)(dioxane)_{2.5},⁵ we sought to determine if the ⁻OCP reagent could reductively couple instead of decarbonylate using a redox-inactive and oxophilic ion such as Sc³⁺.

Results and Discussion



Reactivity of Scandium Complexes with Phosphaethynolate.

Scheme 6.5. Synthesis of complexes **6.2-6.4**, starting from (nacnac)ScCl₂(THF) (**6.1**) where Ar represents 2,6-*i*Pr₂C₆H₃. (1,4-dioxane)_{2.5} refers to all listed dioxanes.

In order to test this hypothesis, we synthesized (nacnac)ScCl(OAr)(THF), **6.2**, in 27% isolated yield (Scheme 6.5) from the reported precursor (nacnac)ScCl₂(THF) and NaOAr.¹³ The identity of this white powder was confirmed by ¹H NMR spectroscopy with a concentrated sample in C₆D₆, featuring resonances assignable for both nacnac and aryloxide ligands, as well as for a single Sc-bound THF ligand. ¹H NMR spectroscopic resonances attributable to the backbone methyls of the nacnac ligand, as well that of isopropyl methyl and methine groups of the nacnac ligand, suggests that there is symmetry across the ligand due to fluxional behavior in solution. Despite not being able to obtain single crystals of **6.2** for a single crystal X-ray diffraction study, this complex should possess a five-coordinate Sc³⁺ complex having pseudo-*C_s* symmetry in solution at room temperature based on the NMR spectroscopic data. The THF ligand in complex **6.2** is also labile, since dilute benzene solutions significantly change the color from translucent to teal presumably by forming (nacnac)ScCl(OAr), whereas addition of THF reverses the process.



Figure 6.2. Molecular structure of complexes **6.3** (left) and **6.4** (right) showing thermal ellipsoids at the 50% probability level. The ^{*i*}Pr groups on the nacnac aryls and aryloxides have been omitted for clarity.

Treatment of **6.2** with Na(OCP)(dioxane)_{2.5} (sample of Na(OCP)(dioxane)_{2.5} was provided by Riccardo Suter in the Grützmacher group) in THF and stirring the reaction overnight at room temperature led to color change from nearly colorless to pale yellow, with concurrent formation of a white precipitate. Workup of the reaction mixture and subsequent crystallization at -35 °C in a THF/hexanes mixture produced pale yellow crystals of (nacnac)Sc(OAr)(OCP)(THF) (6.3) (Scheme 6.5) in 43% yield. It should be noted that formation of **6.2** and **6.3** are nearly quantitative, with isolated yields being lower than quantitative due to their enhanced solubility. Akin to 6.2, the ¹H NMR spectrum of complex **6.3** implies pseudo- C_s symmetry in solution at room temperature, with one coordinated THF molecule. In the ³¹P NMR spectrum, the P resonance attributable to the -OCP moiety was located at -343.5 ppm at only a slightly lower frequency from that of salt reagent Na(OCP)(dioxane)_{2.5} and reported O-bound actinide complexes.^{6g,h} A solid-state structure confirms the O-binding mode of the -OCP ligand in addition to the system being monomeric (Figure 6.2, left). The molecular structure of **6.3** also reveals the metrical parameters of the -OCP ligand to be similar to Na(OCP)(dioxane)_{2.5},⁵ given the metrics C42–O2 (1.235(3) Å) and C–P (1.558(2) Å) as well as the linear angle of P1–C42–O2 of 179.9(3)^o and a Sc1–O2–C42 angle of 170.89(2)°. The XRD of 6.3, along with its similar ¹H NMR spectral data to 6.2 corroborate our hypothesis about 6.2 being a 5-coordinate monomer (vide supra). IR spectroscopy of 6.3 strong v(O-C-P) at 1702.8 cm⁻¹ that is likely attributable to the ⁻ $O-C \equiv P$ ion due to its similarity to that of free $-OCP.^{5}$

When a recrystallized sample of **6.3** was dissolved in Et₂O to give a pale-yellow solution and treated with a stoichiometric amount of KC₈ at -35 °C suspended in Et₂O, a rapid color change to dark orange was observed, with no noticeable effervescence. Workup of the reaction mixture and subsequent crystallization of the material from Et₂O at -35 °C resulted in the deposition of dark orange crystalline blocks of a new material in 22% isolated yield. Unfortunately, this new complex is quite thermally unstable and poorly soluble in arenes. Despite this challenge, ¹H NMR spectral data of a dilute solution reveals this species to possess overall similar symmetry in solution to precursors **6.2** and **6.3**. A ³¹P NMR spectrum of this new complex indicated that 179

reduction of **6.3** had indeed altered the electronics of the -OCP moiety since a rather downfield signal at 69.7 ppm was observed. In addition, an IR spectrum of isolated crystals do not show any signatures for the OCP anion, but instead only features are observed in the fingerprint region of 1500-400 cm⁻¹. XRD studies identified this species to be the dinuclear-ate complex [K(OEt₂)]₂[(nacnac)Sc(OAr)]₂(OCPPCO) (6.4) (Figure 6.2, right, Scheme 6.5) where each CO unit of the OCPPCO ligand binds in an η^2 fashion to the metal center, and where the former O–C–P group is significantly bent. Notably, complex 6.4 contains two OCP scaffolds unified by P-P single bond (2.227(3) Å). Unlike [(nacnac)Ti(OAr)]₂(μ_2 : η^2 , η^2 -P₂), which forms from reductive decarbonylation of the -OCP ion and P–P coupling,⁵ the phosphaethynolate motifs in compound **6.4** reductively couples without extrusion of CO to form a diisophosphaethynolate ligand, [OCPPCO]⁴⁻. In the OCPPCO unit, the angles about this ligand are quite distorted (O2–C42–P1, 125.4(3)°) when compared to the linear mode observed in 6.3. Additionally, metrical parameters imply that while the C42-O2 distance remains more in accord with a single bond given a slight elongation to 1.359(5) Å, the C42–P1 distance has been lengthened considerably, arguably, to yield a double bond (1.705(4) Å). Two K⁺ ions complete the coordination sphere, being P and O chelated by the OCPPCO ligand, but also having a coordinated Et₂O and K⁺...arene interactions with a proximal Ar group from the nacnac ligand. In the solid state, it should also be noted that there is an inversion center relating each $[K(OEt_2)][(nacnac)Sc(OAr)](\eta^2-OCP)$ unit, with overall C_i symmetry. To the best of our knowledge, the connectivity of 6.4 reveals the first example of an [OCPPCO] unit, which is metal stabilized to formally yield a diisophosphaethynolate [OCPPC0]⁴⁻ ligand.

Computational Studies Scrutinizing the Orbitals Involved in 6.3 and 6.4.



Figure 6.3. Computed equilibrium geometry of **6.3**. Structural metrics in Å and degree computed and (measured) are: d(Sc-O1)=2.023 (2.032) , d(O1-C1)=1.254 (1.235), d(C1-P1)=1.593 (1.558), d(Sc-O2)=1.911 (1.898), d(Sc-O3)=2.236 (2.190), d(Sc-N1)=2.187 (2.166), d(Sc-N2)=2.220 (2.177) and <(Sc-O1-C1) = 168.5 (170.9).



Figure 6.4. Computed equilibrium geometry of **6.4**. Structural metrics in Å and degree computed and (measured) are: d(Sc-O1)= 2.045 (2.009), d(Sc'-O1')= 2.043 (2.009), d(Sc-C1)= 2.155 (2.144), d(Sc'-C1')= 2.154 (2.144), d(C1-O1)= 1.347 (1.358), d(C1'-O1')= 1.347 (1.358), d(C1-P1)= 1.723 (1.705), d(C1'-P1')= 1.719 (1.705), d(P1-P1')= 2.257 (2.227), d(O1-K)= 2.602 (2.531), d(O1'-K')= 2.564 (2.531), d(P1-K')= 3.108 (3.168) and d(P1'-K)= 3.149 (3.168).

Given the possible canonical forms in [OCPPCO]^{4–} we decided to investigate the electronic structure of **6.4** using computational methods in order to elucidate the bonding for this so far unprecedented ligand. Dr. Balazs Pinter conducted the following calculations, using the ⁻OCP anion in **6.3** for comparison. Figures 6.3 and

6.4 depict the equilibrium structures computed for the full model of **6.3** and for a slightly truncated version of **6.4**, respectively, which are quite similar to their molecular structures established by XRD studies. Most importantly, the simulated equilibrium structures exhibit the aforementioned η^1 Sc–OCP binding with a linear OCP in **6.3**, while the η^2 Sc–OCP interactions are significantly bent (126.5 °) in the OCPPCO fragment in **6.4**, indicating that our computer models capture the most characteristic features of these two species.



Figure 6.5. Most relevant orbital interactions clarifying the different Sc–OCP binding modes in **6.3** and **6.4**. For **6.4**, only one [Sc(OCP)] unit is shown for clarity with the equivalent side being joined *via* a P–P bond. Note that the notation of orbitals is kept consistent to that of **6.3**, so readers can intuitively follow their transformations upon reduction-dimerization and subsequent structural change. ^Land ^{II} indicates if the orbital is perpendicular or parallel, respectively, to the Sc–OAr axis.

The preferred binding mode of the -OCP ligand to Sc³⁺ in complex 6.3 and $[OCPPCO]^{4-}$ in **6.4** can be best understood from the contributions of π -type ligand orbitals to the metal-ligand interactions. Figure 6.5 depicts the most important MO's for the linear Sc-OCP scaffold in 6.3 and correlate these orbitals to the side-on OCP motif in 6.4, with the P-P interaction in 6.4 having been excluded for clarity. In addition, and for comparison purposes, labels are retained for these orbitals when examining complex 6.4, but taking into account the fact that in-phase and out-ofphase combinations (denoted with \pm) are present for the combination of two For complex **6.3**, the near linear OCP $[(nacnac)Sc(OAr)(OCP)]^{-}$ fragments. arrangement is the result of the OCP σ components with little, if any, Sc–OCP π -type interactions. As a result, the eight π electrons of the -OCP ligand in 6.3 remain distributed in quasi-degenerate π_1 and π_2 sets of orbitals, being mostly localized in C-O and C-P π -bonds, respectively (Figure 6.5, left). One-electron reduction and subsequent dimerization of **6.3** to **6.4** results in an extra *pair* of π electrons about each 'OCP' unit; one electron deriving from KC₈, whereas the other extra π electron is promoted from the σ -subspace upon P–P bond formation. As a result, there is a population of the high-energy ${}^{L}\pi_{3}$ orbital (antibonding along O–C and C–P) when shifting from $[OCP]^-$ to $[OCPPCO]^{4-}$. This leads to an ideal situation for η^2 -binding, allowing each OCP fragment to develop two σ -type metal-ligand dative interactions through the efficient overlap of OCP's ${}^{L}\pi_{1}$ and ${}^{L}\pi_{3}$ with the Sc d orbitals, as portrayed by Figure 6.5, right. The potassium ions also play an important role in **6.4** by electrostatically stabilizing the lone pair at each phosphorous and oxygen atom (π_2 and σ_1 orbitals, respectively, in Figure 6.5, right), especially given the "overcharged" nature of the [OCPPCO]⁴⁻ ligand.

As noted before, the right component of Figure 6.5 portrays the MOs that conceptually describe the Sc–OCP binding at each metal site in **6.4**, such fragment MOs of the two sites form bonding (+) and antibonding (–) combinations given the inversion center relating the two fragments. Amongst these molecular orbitals, Figure

6.6 depicts the combinations of ${}^{L}\pi_{3}$ (${}^{L}\pi_{3} + {}^{L}\pi_{3}$ and ${}^{L}\pi_{3} - {}^{L}\pi_{3}$) and ${}^{II}\pi_{2}$ (${}^{II}\pi_{2} + {}^{II}\pi^{2}$ and ${}^{II}\pi_{2}$) fragment orbitals leading to the rare Sc–OC η^{2} -binding and localized π interactions along the C=P–P=C motif, respectively. In the case both ${}^{II}\pi_{2}$, both the bonding and the antibonding combinations of this interaction are filled, hence resulting in no net contribution to the P=P π -bond, therefore rendering this a single bond.



Figure 6.6. Bonding and antibonding combinations of ${}^{L}\pi_{3}$ and ${}^{II}\pi_{2}$ fragment MOs in **6.4**.

To further understand the most likely canonical forms of the OCP and OCPPCO ligands in both 6.3 and 6.4, Dr. Pinter computed Mayer bond orders. Accordingly, the Sc-O bond order is calculated to be 0.44 for the η^1 Sc-OCP binding in **6.3** whereas it stays similar at 0.50 in 6.4, augmented with an Sc-C interaction of bond order of 0.70. Also, in agreement with the electronic structural change in 6.4 implied by the scrutinized MOs, the C-O bond weakens slightly (bond order drops from 1.1 in 6.3 to 0.9 in 6.4) whereas the C-P interaction weakens significantly (bond order drops from 2.7 to 1.6) upon going from 6.3 to 6.4. The single bond character of P-P is well supported by the Mayer bond order of 1.0 in 6.4 and in accord with the filled π_2 combinations illustrated in Figure 6.6. These findings imply that the binding modes and net electronic structural changes upon reduction and dimerization of 6.3 can also be relatively well described with a localized Lewis structure shown in Scheme 6.6, where the diisophosphaethynolate ligand can be best represented as [O-C=P-P=C-O]⁴⁻ with formal charges on both the oxygen and carbon atoms. The charge at carbon changes significantly, from -0.02 e (QTAIM) in free OCP⁻ to -0.5 e in **6.4**. Concomitant to the σ -to- π electron promotion and C=P bond formation, the P atoms become characteristically more positive in 6.4 to free -OCP (by about 0.2/0.5 e according to QTAIM/NBO methods). It is likely that the oxophilicity of Sc prevents decarbonylation as in the case of titanium.



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Scheme 6.6. Binding modes and underlying electronic structures of Lewis structures in **6.3** and **6.4**.

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Conclusion.

Through experimental and computational data, we have shown how two Sc³⁺ ions have supported the unprecedented formation of the diisophosphaethynolate ion, [OCPPCO]⁴⁻. The OCP⁻ ion in the Sc–OCP precursor, **6.3**, remains electronically and spectroscopically quite similar to Na(OCP)(dioxane)_{2.5}.⁵ However, upon one electron reduction there is P–P radical coupling to form a bent [OCPPCO]⁴⁻ ligand, sandwiched between two scandium centers. The significantly different spectroscopic signatures of [OCPPCO]⁴⁻ ligand to ⁻OCP is related to the substantially altered Sc–OCP binding mode and ⁻OCP bond characteristics as scrutinized by single crystal X-ray diffraction data as well as computational methods.



Figure 6.7. Molecular structure of complexes **A12** showing thermal ellipsoids at the 50% probability level. Disorder of the As atom and one isopropyl group have been removed for clarity.

More recently, we have had interest in extending the reactivity of the phosphaethynolate reagent to the arsenic analogue, Na(OCAs)(dioxane)_{2.5}.¹⁴ Although this reagent is much more reactive and unstable than Na(OCP)(dioxane)_{2.5}, we were able to isolate the arsenic analogue of **6.3**, (nacnac)Sc(OAr)(OCAs) (A12) (Figure 6.7, Scheme 6.7). The preparation of this complex follows the same procedure outlined below for 6.3. Crystallographic details for this complex can be found in the Appendix of Molecules.¹⁵ Although the products of reduction have yet to be isolated, that due time will be able isolate we expect in we to [K(OEt₂)]₂[(nacnac)Sc(OAr)]₂(OCAsAsCO) (**6.5**) (Scheme 6.7).



Scheme 6.7. Synthesis of complex **A12**, starting from (nacnac)ScCl₂(THF) (6.1) where Ar represents 2,6-^{*i*}Pr₂C₆H₃. Proposed synthesis of **6.5** from **A12**.

Experimental Details

General Procedures

Unless otherwise stated, all operations were performed in a M. Braun Lab Master double-dry box under an atmosphere of purified dinitrogen or using high vacuum standard Schlenk techniques under an argon or dinitrogen atmosphere. Hexanes, tetrahydrofuran (THF) and toluene were purchased from Fisher Scientific and Et₂O was purchased from Sigma Aldrich. Solvents were sparged with argon for 20 minutes and dried using a two-column solvent purification system where columns designated for hexanes and toluene were packed with Q5 and alumina respectively, and columns designated for Et₂O and THF were packed with alumina. Deuterated benzene was purchased from Cambridge Isotope Laboratories (CIL) and was sparged with nitrogen for 20 minutes, then was dried over a potassium mirror, vacuum transferred to a collection flask, and degassed by freeze-pump-thaw cycles. All solvents were transferred into a dry box and were stored over 4 Å sieves. All sieves were heated to 200 °C under vacuum overnight prior to use. Celite used for filtrations was heated to 200 °C under vacuum overnight prior to use. ¹H NMR spectra were recorded on a Bruker AVIII 400 and AVII 500 MHz spectrometer, ¹³C NMR spectra were recorded on a Bruker AVIII 500 MHz spectrometer, and ³¹P{¹H} spectra were recorded on a Bruker AVIII 500 MHz spectrometer, and ³¹P{¹H} spectra were recorded on a Bruker AVIII 400 spectrometer. A high resolution 500 MHz cryoprobe was also used for collection of data for complex **6.4**. ¹H NMR spectra are reported with reference to residual proteo solvent resonances of C₆D₆ at 7.16 ppm. ³¹P{¹H} NMR spectra were referenced to external H₃PO₄ (0 ppm). IR spectra were recorded on a JASCO FT/IR-4600LE Spectrometer using clear disks and mini KBr plates. NaOAr was synthesized from HOAr and NaN(SiMe₃)₂ in toluene followed by filtration of the pale solid, and washed with copious amounts of toluene, and then dried under reduced pressure. Na(OCP)(dioxane)_{2.5}^{5d} and (nacnac)ScCl₂(THF)¹³ were prepared according to published literature procedures. Elemental analyses were measured by Midwest Microlab.

Synthesis of (nacnac)ScCl(OAr)(THF) (6.2)

To a light yellow solution of (nacnac)ScCl₂(THF) (**6.1**) (2.13 g, 3.52 mmol, 1 equiv.) in 10 mL THF in a 20 mL vial chilled to -35 °C for 15 minutes was added a 5 mL THF solution of NaOAr (703.4 mg, 3.52 mmol, 1 eq.), also chilled to -35 °C for 15 minutes prior to addition. NaOAr was added dropwise while stirring, and warmed to room temperature. After stirring for 16 hours, the reaction mixture turned colorless, and a noticeable precipitate had formed, NaCl. All volatiles were taken to dryness, and the residue was extracted in 15 mL of toluene, and filtered over Celite for removal of alkaline side product. Upon removing the volatiles in arene solvent, a very notable color change to a bright green occurs concomitant with loss of THF. This is reversed back to a colorless solution by dissolving the residue in THF after taking all toluene to dryness. This colorless THF solution is then layered with 10 mL of hexanes and stored at -35 °C overnight, resulting in the deposition of large amounts of a white microcrystalline powder. The isolated powder is also very pure, but as confirmed by 191 an aliquot of the crude reaction mixture, this material is very pure and can be used for in situ experiments without further purification. (680 mg, 0.92 mmol, 26.2%). ¹H **NMR (500 MHz, 298 K, benzene-d₆):** δ 7.24-7.06 (overlapping m, 8H, unable to measure / values as peaks overlap with benzene, but these are identifiable in the HSQC as the C- H_{Ar} resonances) 6.99 (dd, ${}^{3}J_{H-H}$ = 7.3, 7.0 Hz, 1H, para-CHAr_{OAr}), 5.24 (s, $\Delta v_{1/2} = 7.4$ Hz, 1H, HC(C(Me)NAr)2), 3.65 (m, 4H, CH₂(2,5)_{bound-THF}), 3.49 (br, $\Delta v_{1/2} =$ 31.2 Hz, 2H, CHMe_{20Ar}), 3.42 (sept, 2H, ${}^{3}J_{H-H}$ = 6.1 Hz, CHMe_{2NacNac}), 3.24 (sept, ${}^{3}J_{H-H}$ = 6.3 Hz, 2H, CHMe_{2NacNac}), 1.66 (s, $\Delta v_{1/2}$ = 8.0 Hz, 6H, HC(C(Me)NAr)2), 1.51 (d, ³/_{H-H} = 3.1 Hz, 6H, CHMe_{2NacNac}), 1.38 (m, 4H, CH₂(3,4)_{bound-THF}), 1.19 (d, ${}^{3}J_{H-H}$ = 3.1 Hz, 6H, CH*Me*_{2NacNac}), 1.25 (d, ³*J*_{H-H} = 3.0 Hz, 12H, CH*Me*_{2OAr}). ¹³C{¹H} NMR (125.8 MHz, 298 K, benzene-d₆): 168.9 (2C, CH(C(Me)NAr)2), 157.8 (Ar, ipso), 143.3 (2C, ortho-C_{NacNac}), 142.9 (2C, ortho-C_{NacNac}), 142.5 (Ar, ipso), 137.2 (2C, ortho-C_{OAr}), 127.2 (Ar, C-H), 124.6 (Ar, C-H), 123.2 120.4 (1C, para-C_{0Ar}), 98.4 (1C, CH(C(Me)NAr)2), 69.1 (2C, CH₂(2,5)_{bound-THF}), 29.1 (2C, CHMe2_{NacNac}), 28.4 (2C, CHMe2_{NacNac}), 27.0 (2C, CHMe2_{0Ar}), 25.3 (2C, CH₂(3,4)_{bound-THF}), 25.1 (2C, CHMe2_{NacNac}), 25.0 (2C, CHMe2_{NacNac}), 24.7 (4C, CHMe2_{NacNac} (2 overlapping signals, 2C each)), 24.6 (4C, CHMe2_{OAr}), 24.5 (2C, CH(C(*Me*)NAr)2), Anal. Calcd for C₄₅H₆₆N₂O₂ClSc: C, 72.31; H, 8.90; N, 3.75. Found: C, 71.99; H, 8.78; N, 3.86.

¹H NMR for base free complex: (400 MHz, 298 K, benzene-d₆): δ 7.14-7.00 (m, 8H, C-*H*_{Ar}), 6.91 (dd, ³*J*_{H-H} = 7.7, 7.4 Hz, 1H, *para*-CHAr_{OAr}), 5.16 (s, $\Delta v_{1/2}$ = 2.3 Hz, 1H, *H*C(C(Me)NAr)2), 3.58 (m, 4H, C*H*₂(2,5)_{free}-THF), 3.41 (sept, ³*J*_{H-H} = 6.5 Hz, 2H, CHMe_{2NacNac}), 3.27 (br, $\Delta v_{1/2}$ = 46.7 Hz, 2H, CHMe_{2OAr}), 3.15 (sept, ³*J*_{H-H} = 6.7 Hz, 2H, CHMe_{2NacNac}), 1.58 (s, $\Delta v_{1/2}$ = 2.7 Hz, 6H, HC(C(*Me*)NAr)2), 1.46 (d, ³*J*_{H-H} = 3.7 Hz, 6H, CH*Me*_{2NacNac}), 1.40 (m, 4H, C*H*₂(3,4)_{free}-THF), 1.19-1.10 (two overlapping d, ³*J*_{H-H} unable to resolve due to overlapping peaks, 18H, (6H for CH*Me*_{2NacNac}, 12 for CH*Me*_{2OAr})), 1.07 (d, ³*J*_{H-H} = 3.3 Hz, 6H, CH*Me*_{2NacNac}), 1.04 (d, ³*J*_{H-H} = 3.3 Hz, 6H, CH*Me*_{2NacNac}).

Synthesis of (nacnac)Sc(OAr)(OCP)(THF) (6.3)

To a colorless solution of **6.1** (505 g, 0.68 mmol, 1 equiv.) in 5 mL THF in a 20 mL vial was added a 5 mL THF solution of Na(OCP)(dioxane)_{2.5} (216.5 mg, 0.68 mmol, 1 eq.) 192

dropwise at room temperature while stirring. After stirring for 16 hours, the reaction mixture turned a light yellow color, and a noticeable precipitate had formed, NaCl. All volatiles were taken to dryness, and the residue was extracted in 10 mL of toluene, and filtered over Celite for removal of alkaline side product. The toluene is then taken to dryness, followed by dissolution in 3 mL THF, which is then layered with 15 mL of hexanes and stored at -35 °C overnight, resulting in the deposition of large light yellow crystals. These crystals are suitable for single X-ray diffraction. The isolated crystals are very pure, but as confirmed by an aliquot of the crude reaction mixture, this material is also very pure and can be used for in situ experiments. (225 mg, 0.29 mmol, 42.9%). ¹H NMR (500 MHz, 298 K, benzene-d₆): δ 7.24-7.12 (overlapping m, 8H, unable to measure J values as peaks overlap with benzene, but these are identifiable in the HSQC as the C-H aryl resonances), 7.02 (dd, ${}^{3}J_{H-H}$ = 7.6, 7.4 Hz, 1H, para-CHAr_{0Ar}), 5.21 (s, Δν_{1/2} = 6.3 Hz, 1H, HC(C(Me)NAr)2), 3.64 (m, 4H, CH₂(2,5)_{bound}-THF), 3.64 (overlapping sept with THF, ${}^{3}J_{H-H}$ unable to resolve due to overlapping peaks, 2H, CHMe_{20Ar}), 3.26 (sept, ³/_{H-H} = 6.8 Hz, 2H, CHMe_{2NacNac}), 3.10 (sept, ³/_{H-H} = 6.7 Hz, 2H, CHMe_{2NacNac}), 1.66 (s, $\Delta v_{1/2}$ = 6.6 Hz, 6H, HC(C(Me)NAr)2), 1.42 (d, ³J_{H-H} = 6.9 Hz, 6H, CHMe_{2NacNac}), 1.37 (d, ³/_{H-H} = 3.8 Hz, 12H, CHMe_{2OAr}), 1.31 (m, 4H, CH₂(3,4)_{bound}-THF), 1.22-1.04 (three overlapping d, ${}^{3}J_{H-H}$ unable to resolve due to overlapping peaks, 18H, (6H per CH*Me*_{2NacNac}). ³¹P{¹H} NMR (162 MHz, 298 K, benzene-d₆): δ-343.5 (s, $\Delta v_{1/2}$ = 13.0 Hz, 1 P, OCP). ¹³C{¹H} NMR (125.8 MHz, C₆D₆, 298 K): δ 168.3 (2C, CH(*C*(Me)NAr)2), 157.4 (Ar, ipso), 154.2 (d, ¹*J*_{C-P} = 10.0 Hz, 1C, 0*C*P), 146.0 (Ar, ipso), 143.4 (2C, ortho-C_{NacNac}), 141.1 (2C, ortho-C_{NacNac}), 137.2 (2C, ortho-C_{OAr}), 126.6 (Ar, C-H), 125.1 (Ar, C-H), 123.8 (Ar, C-H), 123.3 (Ar, C-H), 120.5 (1C, para-C_{OAr}), 99.04 (1C, CH(C(Me)NAr)2), 71.6 (2C, CH₂(2,5)_{bound-THF}), 29.7 (2C, CHMe2_{NacNac}), 28.0 (2C, CHMe2_{NacNac}), 26.7 (2C, CHMe2_{OAr}), 25.3 (4C, CHMe2_{OAr}), 25.1 (2C, CHMe2_{NacNac}), 25.1 (2C, CHMe2_{NacNac}), 25.0 (2C, CH(C(Me)NAr)2), 24.9 (2C, CHMe2_{NacNac}), 24.7 (2C, $CH_2(3,4)_{bound-THF}$, 24.1 (2C, CH*Me2*_{NacNac}). IR (KBr, cm⁻¹): v (C–0):1259.3,(C-P): 1702.8. Anal. Calcd for C₄₆H₆₆N₂O₃PSc: C, 71.66; H, 8.63; N, 3.63. Found: C, 71.99; H, 8.69; N, 3.63.

Synthesis of [K(OEt₂)]₂[(nacnac)Sc(OAr)]₂(OCPPCO) (6.4)

To a light yellow solution of **6.3** (100 mg, 0.13 mmol, 1 equiv.) in 5 mL Et_2O in a 20 mL vial was added a 5 mL ethereal slurry of KC₈ (17.5 mg, 0.13 mmol, 1 eq.) while stirring. Both were chilled to -35 °C prior to addition. Immediately upon addition, a very distinct color change to dark orange was observed. After warming to room temperature for five minutes with no further color change, the solution was filtered over Celite for removal of carbon. All volatiles were taken to dryness, and the residue was dissolved in a mixture of 5 mL Et₂O. This is stored at -35 °C overnight, resulting in the deposition of large orange crystals. These crystals were suitable for single crystal X-ray diffraction (25 mg, 0.01 mmol, 21.7%). Note that this yield is reported for the isolated crystals of **6.4**. A small amount of these isolated crystals, (<4%), shows an initial impurity in the ¹H NMR spectrum taken in C₆D₆. Although this is likely due to the incredibly unstable nature of this complex in solution, it cannot be ruled out that a small impurity cocrystallizes. Due to the instability of this complex, this reaction was carried out many times on small scales as the yield is higher than when done on large scales. Note that isolated crystals are rather insoluble in most solvents (<10 mg will dissolve for an NMR sample in \sim 1 mL C₆D₆) and are unstable in solution. ¹H NMR is reported for one [(nacnac)Sc(OAr)] unit in the symmetric structure.

¹H NMR is reported for monomer unit. ¹H NMR (500 MHz, 298 K, benzene-d₆): δ 7.26 (m, 2H, Ar), 7.07-6.80 (overlapping m, 7 H, Ar), 5.06 (s, $\Delta v_{1/2} = 3.7$ Hz, 1H, HC(C(Me)NAr)2), 3.88 (sept, ${}^{3}J_{\text{H-H}} = 6.7$ Hz, 1H, $CHMe_2$), 3.71 (sept, ${}^{3}J_{\text{H-H}} = 6.5$ Hz, 1H, $CHMe_2$), 3.43 (sept, ${}^{3}J_{\text{H-H}} = 6.7$ Hz, 1H, $CHMe_2$), 3.26 (q, 8 H, $CH_{2\text{Ether}}$, both Et₂O molecules have dissociated in solution, as well as trace Et₂O from isolation), 1.60 (s, $\Delta v_{1/2} = 4.3$ Hz, 6H, HC(C(Me)NAr)2), 1.46 (d, ${}^{3}J_{\text{H-H}} = 6.9$ Hz, 6H, $CHMe_2$), 1.35 (d, ${}^{3}J_{\text{H-H}} =$ 6.0 Hz, 6H, $CHMe_2$), 1.31 (d, ${}^{3}J_{\text{H-H}} = 6.5$ Hz, 6H, $CHMe_2$), 1.19-1.14 (two overlapping d, ${}^{3}J_{\text{H-H}}$ unable to resolve due to overlapping peaks, 12H, (6H per $CHMe_2$), 1.11 (t, 12H, $CH_{3\text{Ether}}$, both Et₂O molecules have dissociated in solution, as well as trace Et₂O from isolation), 0.96 (d, ${}^{3}J_{\text{H-H}} = 5.4$ Hz, 6H, $CHMe_2$). ${}^{31}P{}^{1}H{}$ NMR (162 MHz, 298 K, benzene-d₆): δ 69.74 (br, $\Delta v_{1/2} = 63.9$ Hz, 1P per OCP). Instability and poor solubility of **3** prevent us from acquiring ¹³C NMR spectra. The thermal instability of **6.4** prevents us from acquiring the elemental analysis and discernable ¹³C NMR data.

Crystallographic Experimental Details

Crystallographic data are summarized Table 6.1. Suitable crystals for X-ray analysis of **6.3** and **6.4** were placed on the end of a Cryoloop coated in NVH oil. Data for single crystal structure determination of **6.3** was taken on an Bruker ApexII with a CCD, while **6.4** was taken on a Bruker D8 with CMOS area detector employing graphitemonochromated Mo-K α radiation (λ =0.71073 Å) at a temperature of 100(1) K. Rotation frames were integrated using SAINT,¹⁶ producing a listing of non-averaged F^2 and $\sigma(F^2)$ values. The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS.¹⁷ The initial structures were solved by direct methods – SIR2004.¹⁸ The structures were solved by direct methods – SHELXT.¹⁹ Refinement was by full-matrix least squares based on F² using SHELXL-2014.²⁰ All reflections were used during refinement.

Compound	6.3	6.4 · 2(C ₄ H ₁₀ O)
Molecular formula	$C_{46}H_{66}N_2O_3PSc$	$\begin{array}{c} C_{92}H_{136}K_2 \ N_4O_6P_2Sc_2,\\ 2(C_4H_{10}O) \end{array}$
Formula weight	770.93	1772.34
Temperature (K)	100(2)	100(1)
Crystal system	Monoclinic	Monoclinic
Space group	C 1 2/c 1	P 1 2 ₁ /c 1
Cell constants:		

Table 6.1. Crystallographic Data of compounds **6.2** and **6.3**.

a (Å)	37.9436(8)	12.8401(9)
b (Å)	11.2259(2)	12.9211(9)
c (Å) Alpha Agle Beta Angle Gamma Angle	20.8309(4) 90 92.4060(1) 90	31.537(2) 90 99.940(2) 90
Volume (Å ³)	8865.1(3)	5153.6(6)
Z	8	2
Density (calcd mg/m3)	1.155	1.142
Abs coeff (mm-1)	0.242	0.296
F(000)	3328	1916
Wavelength	0.71073	0.71073
θ range for data collection (°)	1.957 to 27.554	3.079 to 27.519
<i>h, k, l</i> ranges collected	$-49 \le h \le 49$ $-14 \le k \le 14$ $-27 \le l \le 27$	$-16 \le h \le 16$ $-16 \le k \le 16$ $-41 \le l \le 41$
# Reflns collected	10222	11861
Refinement method	Full-matrix least- squares on F2	Full-matrix least- squares on F2
$R_1^{\rm a}$	0.0525	0.0870
$wR_{2^{b}}$	0.1143	0.1877
Goodness-of-fit on F2 ^c	1.012	1.068

*a R*1 = (|Fo| - |Fc|) / |Fo|. *b wR*2 = [[*w*(Fo2 - Fc2)2] / [*w*(Fo2)2]]1/2. *c* Goodness-of-fit = [[*w*(Fo2 -Fc2)2]/Nobservns Nparams)]1/2, all data.

Computational Details

All calculations were carried out using DFT as implemented in the ORCA program package.²¹ Geometry optimizations were performed with BLYP²² functional and the all-electron def2-SV(P)-ZORA²³ basis set in combination with the auxiliarv basis set def2-SVP/J.²⁴ To accelerate geometry optimizations we used the resolution of the identity, RI, approximation.²⁵ Already for optimizations a tight convergence of the wave function was demanded on grid quality of Grid4. Our experience with the optimizations of the investigated extended molecules (e.g. truncated 6.4 consists of 208 atoms) is that the convergence to the equilibrium structure is much faster when optimizing in Cartesian coordinates (COPT). Subsequent single point calculations for refined energies have been carried out using the hybrid B3LYP functional in combination with def2-TZVP(-f) basis set (with RI and COSX, on Grid4 and Grid4x). The scalar relativistic zero'th order regular approximation (ZORA)²⁶ was employed to take account relativistic effects whereas dispersion was considered using Grimme's D3 method²⁷ in all these calculations. While **6.3** has been modeled without any modification to the respective experimental structure, 6.4 was slightly truncated in order to be able to facilitate the above-described calculations. This truncation only included the replacement of the isopropyl groups of the OAr ligands to methyl groups.

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Chapter 7:

Phosphaethynolate Chemistry of Titanium to Form a Ti₂P₂ Complex

Introduction. Incorporating P-atoms onto transition metal complexes is typically delivered *via* reactive molecules such as white P₄. Depending on the congested nature and redox state of the metal ion in question, P₄ can deliver one or multiple P-atoms (Figure 7.1).¹⁻³ Only in exceptional cases, where the metal ion is sterically protected and in low-valent oxidation states, can one or two P-atoms be delivered from white P₄.¹ Given our interest in preparing highly reactive metal-ligand multiple bonds with 3d transition metals we inquired whether other P-based reagents could cleanly deliver a phosphorus atom to a transition metal center. We therefore again turned our attention to the heavier congener of the ubiquitous isocyanate ligand, the phosphaethynolate ion -OCP,⁴ as an alternate P-atom transfer reagent, akin to N₃⁻ or -OCN ligands that are known to deliver N-atoms by extruding N₂ and CO under reducing conditions, respectively.^{5,6} In this chapter, we show that Na(OCP) can react cleanly with the Ti(III) precursor (nacnac)TiCl(OAr) (nacnac⁻ = $[ArNC(CH_3)]_2CH$; Ar = $2,6^{-i}Pr_2C_6H_3$) to yield an almost planar Ti₂P₂ butterfly-like core where the P₂ unit binds in a $\mu_2:\eta^2,\eta^2$ fashion by forming complex [(nacnac)Ti(OAr)]₂($\mu_2:\eta^2,\eta^2-P_2$) (7.3). We propose complex 7.3 to occur *via* a phosphide radical or phosphidyl species, which then P–P couples to ultimately furnish the bridging Ti₂P₂ core. Complex **7.3** has been fully characterized spectroscopically as well as by a solid-state structure. The bonding and unique electronic structure of the planar Ti₂P₂ core hase also been interrogated using theoretical methods.



Figure 7.1. Diverse reactivity of P₄ to form *cyclo*-P₃,^{11b} *cyclo*-P₄,^{11c,d} and transient P₂ complexes.^{11d} In all instances Ar = 2,6-^{*i*}Pr₂C₆H₃.

Results and Discussion
Synthesis of a P₂ Complex of Titanium.

Given that there is some precedence for early-transition metal isocyanate complexes to undergo reductive decarbonylation to furnish nitride salts,⁶ we questioned whether the same strategy could be applied to low-valent titanium reagents using Na(OCP). Accordingly, treatment of (nacnac)TiCl(OAr), (7.2) a complex that can be NaOAr. readilv prepared from (nacnac)TiCl₂(THF)⁷ (7.1) with with $Na(OCP)(dioxane)_{2.5}$ (sample of $Na(OCP)(dioxane)_{2.5}$ was provided by Riccardo Suter in the Grützmacher group) in THF resulted in an immediate color change from dark magenta to dark red-brown with noticeable effervescence. Removal of the precipitate, presumed to be NaCl, and workup of the reaction mixture allowed for isolation of a red-brown crystalline material, $[(nacnac)Ti(OAr)]_2(\mu_2:\eta^2,\eta^2-P_2)$ (7.3) in \sim 48% yield, based on a combination of multinuclear NMR spectroscopic experiments and a solid state X-ray structure (XRD, Scheme 7.1). We propose that this reaction progresses *via* a mononuclear *P*-bound OCP species [(nacnac)Ti(OAr)(PCO)] (7A) (Scheme 7.1), which we determined to be more stable by about 7 kcal mol⁻¹ than its isomeric O-bound [(nacnac)Ti(OAr)(OCP)] using DFT as calculated by Prof. Balazs Pinter. Intermediate 7A most likely dimerizes in a 1,3-bridging fashion to produce 7B given its ambidentate nature.⁸ We propose such bridging of the OCP moiety to occur, akin to what is observed in the close analogue having 1,3-bridging isocyanate or azide ligands, namely the structurally characterized species [(nacnac)Ti(OAr)(μ_2 -1,3-NCO]₂, **7.4** (Figure 7.2) and [(nacnac)Ti(OAr)(μ_2 -1,3-N₃)]₂,⁹ respectively. From **7A** or reductive decarbonylation ensues to form a phosphide 7B, radical [(nacnac)Ti(OAr)(P)] (7C) (Scheme 7.1) or dimer. We cannot refute however the possibility of a phosphidyl species such as $[(nacnac)Ti(OAr)(P)](\mu-1,3-PCO)$ being formed enroute to 7.3. As opposed to titanium nitridyls, which readily abstract Hatoms to form parent imides,¹⁰⁻¹² the presumed phosphide radical **7C** (or dimer) catenates instead to form 7.3.



Figure 7.2. Molecular structure of **7.4**, showing thermal ellipsoids at 50% probability level. The *i*Pr methyls on nacnac aryls and aryloxides have been omitted for clarity. Crystals suitable for single crystal X-ray diffraction were grown from a concentrated solution (25 mg in 3 mL diethyl ether) after storage at -35 °C for one week. The ethereal solution was dark green, and crystals obtained were dark emerald plates.



Scheme 7.1. Synthesis of complex **7.3**, including proposed intermediates. The formation of a PCO dimer *en route* to **7.3** is also a plausible pathway.



Figure 7.3. Molecular structure of complex **7.3** showing thermal ellipsoids at the 50% probability level. The ^{*i*}Pr methyls on the nacnac aryls and aryloxides have been omitted for clarity.

Complex **7.3** displays diagnostic NMR spectral features consistent with a C_2 symmetric system. The ¹H NMR spectrum shows the presence of four ^{*i*}Pr aryl environments in a 2:1 ratio, with two sharp methine resonances deriving from the OAr ligands and two very broadened methine resonances from the nacnac ligands, whereas only one β -methyl group in the N_aC_bC_gHC_bN_a frame of the nacnac ligand is observed. The most salient spectroscopic signature of **7.3** is the observation of a highly downfield ³¹P NMR signal at 907 ppm that is extremely broad ($\Delta v_{1/2} \sim 4034$ Hz at 298 K) and that corresponds to the bound P₂ fragment. The only documented cases of structurally characterized high valent P₂ systems were reported by Figueroa and Cummins, and Wolczanski and co-workers, namely [(Ar[Np]N)₃Nb]₂(μ_2 : η^2 , η^2 -P₂) (**7.5**) (Ar = 3,5-Me₂C₆H₃, Np = CH₂^tBu) and [(silox)₃M]₂(μ_2 : η^1 , η^1 -P₂) (M = Nb, Ta; silox⁻ = OSi^tBu₃), respectively.^{2a,2j} Although these systems differed primarily in the bonding mode of the P₂ ligand (bent butterfly versus zig-zag) the ³¹P NMR spectrum revealed 207

a broad resonance at 399 ppm for **7.5** whereas theoretical methods predicted a shift of ~400 ppm for $[(silox)_3Nb]_2(\mu_2:\eta^1,\eta^1-P_2)$. Work by Stephan and coworkers also proposed the formation of a P₂ complex of zirconium supported by cyclopentadienyl ligands, $[Cp^*_2Zr]_2(\mu_2:\eta^2,\eta^2-P_2)$, in which the reported ³¹P NMR chemical shift was significantly deshielded at 959.5 ppm.¹³ However, this complex was not structurally characterized, making our Ti₂P₂ complex, to the best of our knowledge, the only structurally characterized P₂ complex of a group 4 transition metal. Intrigued by the highly downfield ³¹P NMR signal of **7.3**, along with its broadened nature, low temperature NMR spectroscopic experiments were performed to determine whether or not fluxionality in solution had an effect on the shape of this resonance. Upon cooling a solution of **7.3** in C₇D₈ to 214 K, no major changes in the line shape or chemical shift of the resonance were observed in the ³¹P NMR spectrum (Figures 7.7-7.14).

To establish the exact bonding mode of the Ti_2P_2 scaffold in 7.3, a solid state structure analysis of a single crystal was undertaken. As the X-ray structure reveals in Figure 7.3, the P–P bond distance of 2.1119(2) Å is confined between that of a single and double bond.^{3d} Also quite notable is the significantly long Ti–P distances, about 2.42 and 2.60 Å, when compared with the few reported terminally bound titanium phosphinidene complexes with characteristic Ti–P distances of ca. 2.15 Å.¹⁴ The observed Ti-P distances composing the Ti₂P₂ core are irregular with the shorter values being smaller than those of reported in titanium terminal phosphide complexes (Ti-PR₂, 2.6-2.7 Å).¹⁵ Unlike other known systems with a bridging P_2 moiety that are described as a bent "butterfly" motif,¹⁶ the structure of complex 7.3 has instead a rather topologically planar Ti-P₂-Ti geometry (dihedral angles Ti1-P1-P2-Ti2, 164.42(6)° and Ti1-P2-Ti2-P1, 17.43(6)°). For direct comparison, the aforementioned P₂ complex 7.5 reported by Cummins and coworkers exhibits a Nb-P–P–Nb dihedral angle of 135.61(5)^{o.2a} This prompted us to question the character of the P_2 ligand, that is, whether it has a formal -2 charge instead of the expected -4observed in the few examples of bridging P₂ complexes with group V metals. Given the sharp resonance in the ¹H NMR spectrum of **7.3**, one would anticipate a closed 208

shell singlet ground state, which intuitively would imply two d⁰, i.e. Ti(IV) centers. However, the broadened ³¹P NMR spectrum, coupled with the nearly planar geometry of the Ti₂P₂ core, short P–P distance and longer Ti–P distances (Figure 7.4), led us to question if two Ti(3+) ions could be coupling antiferromagnetically in **7.3** to exhibit an overall open shell singlet state. Alternatively, a fluxional behavior involving the Ti₂P₂ core rearranging could account for such broadening. As a note, related planar P₂ cores were certainly reported by Driess and Zhao using Ge.¹⁷ With regard to reactivity of **7.3**, largely we unfortunately observed no reaction or decomposition in all instances. While CV data would suggest that this complex could potentially be reduced to a phosphide anion (Figure 7.15), attempts at reduction with KC₈, in addition to other attempts at reduction various concentrations of Na/Hg amalgam resulted in no reaction. Given all these interesting spectral features in addition to the unusual bonding mode of the P₂ we turned to computational methods to help understand why this molecule adopts this unusual structure.

Theoretical Analysis of the Ti₂P₂ Core.

Because of their divergent bonding modes of a near planar Ti_2P_2 core in **7.3** *versus* a bent Nb₂P₂ butterfly core in **7.5** we scrutinized each motif using theoretical methods based on DFT. These calculations were conducted by Prof. Balazs Pinter. Figure 7.4 depicts the equilibrium structures computed for the full models of **7.3** and **7.5**, which are quite similar to their respective molecular geometries established by XRD studies. The computed ³¹P NMR chemical shifts of 822 and 438 ppm for **7.3** and **7.5**,^{2a} respectively, agree reasonably well with the values experimentally observed (Figure 7.3), indicating that our computer models capture the most salient features of these complexes. Most importantly, beyond planarity, Figure 7.4 also emphasizes the asymmetric binding of the P₂ unit to each Ti1 and Ti2. The Ti1–P1 and Ti2–P2 (2.40 Å) bonds are characteristically shorter than Ti1–P2 and Ti2–P1 (2.62 Å) assigning a zig-zag character to the Ti₂P₂ core in **7.3**. Bond order values (Figure 7.4) also clearly support this asymmetric zig-zag binding mode in the Ti₂P₂ core (rhombic like core).





 π^*

 $\mathsf{d}_{\mathsf{x}\mathsf{z}}$

bent butterfly : 7.5

Figure 7.4. Top, equilibrium structures computed for **7.3** and **7.5** together with the theoretical and experimental ³¹P NMR chemical shifts, average Mulliken charges, q(Ti), q(Nb) and q(P), and Mayer bond order (BO) indices. Computed structural metrics for **7.3** (in Å): Ti1–P1, 2.409; Ti1–P2, 2.620; P1–P2, 2.163; Ti1–Ti2, 4.496. For **7.5**: Nb1–P1, 2.526 (2.505(2))^{2a}; P1-P2, 2.206 Å (2.160(2))^{2a}; Nb1-Nb2, 4.149 (4.205(1)).^{2a} Experimental data have been obtained from Ref. 2a. Bottom, plausible interactions of π -type metal d-orbitals with the out-of-plane π^* orbital of P₂ in bent-

butterfly and zig-zag arrangements and orbital argument for the lack of interaction in a planar-butterfly core.

To help understand the characteristic bent-butterfly structure in **7.5** and the near planar zig-zag structure in **7.3**, we examined the planar-butterfly arrangement (Figure 7.4, bottom) invoking the out-of-plane π^* orbital of P₂ with respect to the two π -type metal d orbitals, d_{xz} and d_{xy}. This arrangement clearly results in a lack of overlap with either the in-plane (d_{xy}) or out-of-plane (d_{xz}) π -symmetry metal d orbitals. Hence, for the out-of-plane $\pi^*(P_2)$ orbital to engage in an inphase combination with these d orbitals either in a zig-zig (for d_{xz}) or a bent-butterfly (for d_{xy}) rearrangement all M–P interactions have the right symmetry and be in-phase. The bottom of Figure 7.4 depicts how a near planar zig-zag or a bent-butterfly structure would allow for an effective interaction of $\pi^*(P_2)$ with the titanium dorbitals. Examination of the HOMO of **7.3** and **7.5** (Figure 7.5, top) reveals strikingly distinct orbitals involving these M₂P₂ cores. Whereas the HOMO in **7.5** shows an inphase d- π interaction of two in-phase d_{xy} orbitals with the π^* of P₂, complex **7.3** possesses instead a HOMO according to a zig-zag orientation involving two in-phase d_{xz}- π interactions in a contiguous fashion but still invoking the π^* of P₂.



Figure 7.5. Top: Most important molecular orbitals representing the main differences in the bonding of **7.3** (left) and **7.5** (right), given with their corresponding schematic view, energy and composition. Bottom: Some of the most reasonable resonance structures for **7.3** and showing **7.5** for comparison.

The bottom of Figure 7.5 illustrates the most likely canonical forms for **7.3**, namely **7.3a**, **7.3b** and **7.3c**, as well as the only dominant resonance for **7.5**. The relative weights of the former Lewis structure extremes are also given in Figure 7.5 as determined by a "local" Natural Resonance Theory analysis (NRT) subjected to the Ti_2P_2 core of the molecule (Figure 7.16). The Lewis obtained for **7.5** that characterizes the bent-butterfly Nb₂P₂ core in **7.5** can be alternatively construed as the fusion of two-three-membered NbP₂ rings with identical Nb–P single bonds as well as a P–P single bond (P–P distance is 2.160(2) Å.^{2a} Therefore, the core structure in **7.5** implies the formation of a P₂^{4–} ligand sandwiched by two Nb(V) centers.

Although resonance structures **7.3a**, **7.3b** and **7.3c** capture the most salient features observed in the geometry, computed bond orders, and HOMO of **7.3**, these Lewis structures do not account for the slightly higher bond order of 0.93 involving the P–P unit (compared to 0.87 b.o. observed in **7.5**), which suggests a minor degree of P=P bond character and that the P₂ unit is less reduced in **7.3** than in **7.5**. This is further corroborated by the lower Ti1–P2 bond orders of 0.78 when compared to **7.5** (Figure 7.4) and by the computed charges of phosphorous atoms shown at the top of Figure 7.4 (*vide infra*).

To test the nature of the Ti=P double bonds we analyzed the covalency and metal character in the metal-ligand π -bonding. This analysis, particularly the HOMO of **7.3** suggests some Ti(III) character evolving from the covalent nature of the Ti–P π -interaction represented in Figure 7.5 (top) to be comprised of 50% involvement from the two metal centers. This feature, i.e. a minor contribution from the Ti(III)–P₂^{2–}– Ti(III) configuration, is further supported by a Natural Bond Orbital analysis showing valence non-Lewis type density on both Ti centers of 0.32*e*. Finally, different electronic structure analyses univocally reveal a non-negligible Ti•••Ti interaction implied for example by a Mayer bond order of 0.45, Wiberg bond index of 0.26 and Natural Binding Index of 0.53. These descriptors clearly imply some degree of communication of the titanium centers through the P₂ fragment, as the planar arrangement and large interatomic Ti–Ti distance does not allow the formation of a direct Ti–Ti bond. The molecular orbital that most plausibly represents this interaction is shown in Figure 7.17.

It is also worth mentioning the strikingly different ³¹P NMR chemical shifts observed, 904 ppm vs. 399 ppm, and computed, 822 ppm vs. 438 ppm, for **7.3** and **7.5**, respectively. We recently demonstrated for *cyclo*-P₃ complexes of vanadium(V) that it is the paramagnetic shielding contribution that has such prominent effect on the chemical shift of heavy nuclei.^{3a} Paramagnetic shielding evolves from the electron density fluctuations generated by the external magnetic field; within the wavefunction theory it is seen as the mixing of the ground state wavefunction and low-lying excited state wavefunctions in a magnetic field. The latter process can be 213 approximated, to a reasonable degree, within the framework of MO theory by the mixing of high-lying occupied and low-lying unoccupied orbitals. Accordingly, the characteristic features of frontier orbitals and their energy gaps, e.g. HOMO and LUMO and $\Delta E_{HOMO-LUMO}$, can be used to help rationalizing the chemical shifts of heavy nuclei. In the case of **7.3** and **7.5**, our investigation on the contributions of various orbitals to the shielding reveals that mixing of HOMO orbitals (Figure 7.5) into low-lying virtual orbitals results in qualitatively differing density flows within the M₂P₂ core of **7.3** and **7.5**, which ultimately produce different paramagnetic shielding contributions and, accordingly, distinct ³¹P NMR spectroscopic shifts for these species. Accordingly, the different metal-P₂ interaction modes, which is in large extent reflected by their different HOMO's, are directly manifested in the observed distinct ³¹P NMR shifts (904 ppm vs. 399 ppm).

Conclusion.



Scheme 7.2. Synthesis of complex **A14** from (^{*t*Bu}nacnac)TiCl(Ntolyl₂). Reduction of **A14** results in reductive cleavage of the nacnac ligand and formation of imido complex **A15**.

In conclusion, we have reported the first example of a structurally characterized P_2 complex of a group 4 transition metal, using the phosphaethynolate, \neg OCP, as a source of a P-atom. Unlike the butterfly structure observed in a Nb₂^(V,V) system, our system possesses a unique nearly planar Ti₂P₂ core where each metal ion interacts *via* a zig-zag like bridge. The Ti–P–P angles in this zig-zag rearrangement are acute enough to allow for the metals to communicate in a $\mu_2:\eta^2,\eta^2-P_2$ fashion. Presumably

due to sterics as well as the stabilization of high-valent states, this type of interaction is discouraged in the Ta_2P_2 system reported by Wolczanski, where the P_2^{4-} binds in an μ_2 :n¹,n¹ fashion. As an alternative to the dimerization observed in the formation of this complex, we instead turned to the tert-butyl substituted nacnac ligand and synthesized the complex (*t*^{Bu}nacnac)TiCl(Ntolyl₂).¹² Treating this complex with Na(OCP) in toluene, there was a sluggish metathesis reaction (as monitored by the disappearance in the paramagnetic ¹H NMR spectrum of (tBu nacnac)TiCl(Ntolyl₂) and the appearance of new paramagnetic resonances. A study by single crystal X-ray diffraction determined the connectivity of this complex to be an O-bound (t^{Bu}nacnac)Ti(OCP)(Ntolyl₂) (A14) (Figure 7.6, Scheme 7.2). Note that there was only 75% of this as a component of this complex in the solid state structure, and that the remaining 25% could be resolved as a chloride component attributable to the starting material. Interestingly, in this complex, the -OCP is not bound linearly with the metal center, which is atypical for O-bound OCP complexes, with a Ti1-O1-C50 angle of $142.4(4)^{\circ}$ although linearity is still retained within the ligand (O1-C50-P1 = 179.6(3)°). Unfortunately, upon reduction of this complex, reductive cleavage of the nacnac ligand occurs to form the monaazadiene (MAD) (MAD = $ArN=C^{t}Bu-CH=C^{t}Bu$) ligand, and a titanium aryl imido ligand, (*t*^{Bu}MAD)Ti(NAr)(Ntolyl₂) with loss of the phosphaethynolato ligand, which has been observed in other nacnac systems (A15) (Scheme 7.2).^{18,19} Although this system has not provided results as hoped for, it has demonstrated that in a Ti(III) system supported by a nacnac ligand, we can isolate an *O*-bound OCP complex, furthering our understanding of this reagent with early transition metal complexes. Crystallographic tables for these molecules can be found in the Appendix of Molecules.²⁰



Figure 7.6. Molecular structure of complex **A14** showing thermal ellipsoids at the 50% probability level. The chloride disorder with the OCP ligand has been omitted for clarity.

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Experimental Details

General Procedures

Unless otherwise stated, all operations were performed in a M. Braun Lab Master double-dry box under an atmosphere of purified dinitrogen or using high vacuum standard Schlenk techniques under an argon or dinitrogen atmosphere. Hexanes, tetrahydrofuran (THF), and toluene were purchased from Fisher Scientific. Solvents were sparged with argon for 20 minutes and dried using a two-column solvent purification system where columns designated for hexanes and toluene were packed with Q5 and alumina respectively. Deuterated benzene was purchased from Cambridge Isotope Laboratories (CIL) and was sparged with argon for 20 minutes, then was dried over 4 °A sieves, and degassed by freeze-pump-thaw cycles. All solvents were transferred into a dry box and were stored over 4 Å sieves. All sieves were heated to 200 °C under vacuum overnight prior to use. Celite used for filtrations was also heated to 200 °C under vacuum overnight prior to use. NMR spectra were recorded on a Bruker UNI 400 MHz spectrometer for ¹H and ³¹P{¹H} spectra. ¹H NMR spectral data are reported with reference to residual proteo solvent resonances of benzene-d6 at 7.16 ppm. ${}^{31}P{}^{1}H$ NMR spectra were referenced to external H₃PO₄ (0 ppm). Electrochemical data was measured on a BAS Inc. E2 Epsilon autolab potentiostat/galvonostat instrument. NaOAr was synthesized from HOAr and NaN(SiMe₃)₂ in toluene followed by filtration of the pale solid, and washed with copious amounts of toluene, and then dried under reduced pressure. $(nacnac)TiCl_2(THF)^7$ and $Na(OCP)(dioxane)_{2.5}^{4d}$ were prepared according to published literature procedures. (nacnac)Ti(OAr)Cl was prepared by addition of 1 eqiuvalent of NaOAr in a THF solution to a THF solution of (nacnac)TiCl₂(THF) at room temperature. The reaction mixture immediately turns from the deep red-green color of $(nacnac)TiCl_2(THF)$ to a dark magenta and is used for in situ experiments with stoichiometric quantities of Na(OCP)(dioxane)_{2.5}. Elemental analysis was measured by Desert Analytics (ALS Global).

Synthesis of [(nacnac)Ti(OAr)]₂(μ_2 : η^2 , η^2 -P₂) (7.3)

To a deep magenta solution of (nacnac)Ti(OAr)Cl (**7.2**) (160 mg, 0.24 mmol, 1 equiv.) in 5 mL THF in a 20 mL vial was added a 3 mL yellow solution of Na(OCP)(dioxane)_{2.5}, dropwise at room temperature while stirring. An immediate color change to a deep red-brown color was observed, as well as a noticeable effervescence. The solution was stirred for another ten minutes at room temperature; no further color change was observed. All volatiles were taken to dryness, and the dark residue was triturated with 5 mL of hexanes. The product is then extracted into 10 mL toluene, and filtered over celite for removal of alkaline side product. The solution was then extracted with 7 mL toluene and stored at -35 °C overnight, resulting in the deposition of dark redbrown crystals on the walls of the vial (115 mg, 48.3%). Crystals suitable for X-ray 217

diffraction were grown from a concentrated toluene solution (20 g in 3 mL) with several drops of hexane added followed by storage at -35 °C for a week. ¹H NMR (400 **MHz, 298 K, benzene-d**₆): δ 7.27 (d, ³J_{H-H} = 3.9 Hz, 2H, *para-CHAr*_{ODipp}), 7.12 (d, ³J_{H-H} = 3.8 Hz, 4H, *para*-CHAr_{nacnac}), 6.98 (d, br, Δν_{1/2} = 45.1 Hz 8H, *meta*-CHAr_{nacnac}), 4.86 (s, $\Delta v_{1/2}$ = 4.4 Hz, 2H, *H*C(C(Me)NAr)2), 3.77 (sept, ³J_{H-H} = 6.5 Hz, 2H, CHMe_{20DIPP}), 3.48 (sept, 3 J_{H-H} = 4.0 Hz, 2H, CHMe_{20DIPP}),3.35 (br, $\Delta v_{1/2}$ = 81.8 Hz, 4H, 2.97, CHMe_{2nacnac}), 2.71 (br, $\Delta v_{1/2}$ = 80.2 Hz, 4H, 2.97, CHMe_{2nacnac}, 1.21-1.48 (2 sets of broadened overlapping doublets 48H, $\Delta v_{1/2}$ = 65.8 Hz, CH*Me*_{2nacnac}), 1.55 (d, ³J_{H-H} = 7.0 Hz, 12H, $CHMe_{20DIPP}$), no backbone CH_3 resonances were detected due to overlapping resonances in the aliphatic region. ³¹P{¹H} NMR (162 MHz, 298 K, benzene-d₆): δ 907.1 (br, Δν_{1/2} = 4033.7 Hz, 2P, P₂). ¹³C{¹H} NMR (125.8 MHz, 298 K, benzene-d₆): δ 163.6 (*C*H(C(Me)NAr)2), 152.9 (Ar), 141.6 (Ar), 140.9 (Ar), 140.1 (Ar), 137.7 (Ar), 129.3 (Ar), 126.2 (Ar), 125.7 (Ar), 124.8 (Ar), 123.7 (Ar), 123.3 (Ar), 122.6 (Ar), 103.4 (CH(C(Me)NAr)2), 28.9 (CHMe2), 27.7 (CHMe2), 26.7 (CHMe2), 25.7 (CHMe2), 25.3 (CH(C(*Me*)NAr)2). Anal. Calcd for C₈₆H₁₂₅N₄O₂P₂Ti₂: C, 73.54; H, 8.97; N, 3.99. Found: C, 71.34; H, 8.16; N, 3.79. We attribute the slightly low carbon identification to incomplete combustion.

³¹P{¹H} NMR Low Temperature Experiments with 7.3



Figure 7.7. ³¹P{¹H} NMR Spectrum of **7.3** in C₇D₈, 162 MHz, 290 K



Figure 7.8. ³¹P{¹H} NMR Spectrum of **7.3** in C₇D₈, 162 MHz, 280 K



Figure 7.9. ${}^{31}P{}^{1}H$ NMR Spectrum of 7.3 in C₇D₈, 162 MHz, 270 K



Figure 7.10. $^{31}P\{^{1}H\}$ NMR Spectrum of 7.3 in C7D8, 162 MHz, 260 K



Figure 7.11. ${}^{31}P{}^{1}H$ NMR Spectrum of 7.3 in C₇D₈, 162 MHz, 250 K



Figure 7.12. ³¹P{¹H} NMR Spectrum of **7.3** in C₇D₈, 162 MHz, 240 K



Figure 7.13. ³¹P{¹H} NMR Spectrum of 7.3 in C₇D₈, 162 MHz, 230 K



Figure 7.14. ${}^{31}P{}^{1}H$ NMR Spectrum of 7.3 in C₇D₈, 162 MHz, 219 K

Electrochemical Data

Electrochemical procedure: Cyclic voltammetry data was collected in a solution of 100 mM dried [TBA][PF6] (*n*-tetrabutylammonium hexafluorophosphate) in anhydrous THF. Data was collected with an E2 Epsilon (BAS) autolab potentiostat/galvanostat instrument using BAS software. Data collection was conducted under a N2 atmosphere in the glovebox at 25 °C.



Figure 7.15. CV data of complex **7.3 (**1.5 mM), (cathodic scan) in THF with $[N^nBu_4][PF_6]$ as the electrolyte (100 mM). This sample was referenced to a standard of FeCp₂^{0/+}. The scan rate was 250 mV/s.

Crystallographic Experimental Details

Crystallographic data are summarized Table 7.1. Suitable crystals for X-ray analysis of **7.3** and **7.4** were placed on the end of a Cryoloop coated in NVH oil. Data for single crystal structure determination of **7.3** and **7.4** were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-K α radiation (λ =0.71073 Å) at a temperature of 100(1)K. Rotation frames were integrated using SAINT,²¹ producing

a listing of non-averaged F^2 and $\sigma(F^2)$ values. The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS.²² The structure of **7.3** was solved by direct methods – SHELXS.²³ The structure of **7.4** was solved by dual methods – SHELXT.²⁴ There was a region of disordered solvent in **7.3** for which a reliable disorder model could not be devised; the X-ray data were corrected for the presence of disordered solvent using SQUEEZE.²⁵ Refinement was by full-matrix least squares based on F² using SHELXL-2014.²⁶ All reflections were used during refinement.

Compound	7.3	2(7.4) · 2(C ₄ H ₁₀ O)
Molecular formula	$C_{82}H_{116}N_4O_4P_2Ti_2$	2(C ₈₄ H ₁₁₆ N ₆ O ₄ Ti ₂), 2(C ₄ H ₁₀ O)
Formula weight	1419.67	2887.48
Temperature (K)	100(2)	100(1)
Crystal system	Monoclinic	Triclinic
Space group	P 1 2 ₁ 1	P -1
Cell constants:		
a (Å)	14.2792(3)	12.8386(6)
b (Å)	24.5954(6)	25.2183(14)
c (Å) Alpha Agle Beta Angle Gamma Angle	24.2905(6) 90 105.8080(10) 90	26.7673(14) 84.058(3) 86.759(3) 81.169(3)
Volume (Å ³)	8208.2(3)	8510.4(8)
Z	4	2

Density (calcd mg/m3)	1.149	1.127
Abs coeff (mm-1)	0.281	0.239
F(000)	3072	3120
Wavelength	0.71073	0.71073
θ range for data collection (°)	2.44 to 27.44	2.36 to 27.34
<i>h, k, l</i> ranges collected	$-18 \le h \le 18$ $-31 \le k \le 31$ $-31 \le l \le 31$	$-16 \le h \le 14$ $-32 \le k \le 32$ $-34 \le l \le 34$
# Reflns collected	37586	38294
Refinement method	Full-matrix least- squares on F2	Full-matrix least- squares on F2
R_{1}^{a}	0.0601	0.0845
$wR_{2^{b}}$	0.1254	0.1910
Goodness-of-fit on F2 ^c	0.975	1.030

^{*a*} *R*1 = (|Fo| - |Fc|) / |Fo|. ^{*b*} *wR*2 = [[*w*(Fo2 - Fc2)2] / [*w*(Fo2)2]]1/2. ^{*c*} Goodness-of-fit = [[*w*(Fo2 -Fc2)2]/Nobservns Nparams)]1/2, all data.

Note: Two molecules of **7.4** crystallize in the unit cell, with one molecule of Et_2O per dinuclear complex.

Computational Details

All calculations were carried out using DFT as implemented in the ORCA program package.²⁷ Both **7.3**, $[(nacnac)Ti(OAr)]_2(\mu_2:\eta^2,\eta^2-P_2)$, $(nacnac^- = [ArN(CH_3)C]_2CH$; Ar = 2,6-ⁱPr₂C₆H₃), and **7.5**, $(Ar[Np]N)_3Nb(\mu_2:\eta^2,\eta^2-P_2)Nb(N[Np]Ar)_3$, $(Ar = 3,5-Me_2C_6H_3$, Np = CH₂^tBu), have been modeled without any modification or truncation to the respective experimental structure. Final geometry optimizations were performed 225

using the BLYP^{28,29} functional and the all-electron def2-TZVP(-f)-ZORA³⁰ basis set in combination with the auxiliary basis set def2-TZV/J²⁹ and using grid quality Grid4. To accelerate geometry optimizations we used the resolution of the identity, RI,³² approximation. The scalar relativistic zero'th order regular approximation (ZORA)³³ was employed to take into account relativistic effects whereas to dispersion was considered using Grimme's D3 method in all ORCA calculations. Our experience with the optimizations of the investigated extended molecules (both **7.3** and **7.5** consists of 208 atoms) is that the convergence to the equilibrium structure is much faster when optimizing in Cartesian coordinates (COPT). Finally, the above-described final geometry optimizations were started from pre-optimized structures obtained *via* a lower level of theory (BLYP/def2-SV(P), def2-SVP/J, ZORA, RI, d3, LooseSCF, Grid3), which were initiated using the X-ray structures as guiding geometries.

We used the NMR module of ADF2013³⁴ code to compute ³¹P NMR chemical shifts on the equilibrium structures obtained *via* the protocol described above. The functional employed consisted of the local density approximation of Vosko, Wilk, and Nusair (LDA VWN)³⁵ augmented with the nonlocal gradient correction for exchange interactions from Perdew and Wang (PW91x).³⁶ The full electron basis set TZVP was utilized in these calculations and scalar relativistic effects were taken into account using the Pauli formalism. The computed isotropic shielding values of complexes were referenced to that of phosphoric acid modeled in the same way.

The Natural Resonance Theory analysis was carried out using the GenNBO6 module of the NBO6 software package using wavefunction at the BLYP/cc-pVDZ level of theory obtained from Gaussian09. To be able to carry out this NRT analysis we used a smaller model of complex **7.3** (with geometry fixed to the equilibrium geometry of the full complex), shown in Figure 7.16, as well as, we used the "local"NRT option of NBO6 for the four-atom Ti_2P_2 core of the latter model structure.



Figure 7.16. Molecular structure of the model that was used to carry out the "local" NRT analysis of the central Ti_2P_2 core.



Figure 7.17. Molecular orbital (HOMO-17, -5.959 eV, 10% $Ti_2 / 60\% P_2$) that most plausibly represent the Ti...Ti interaction through the P₂ fragment resulting in a non-negligible bond index between the titanium centers.

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Chapter 8:

Phosphaethynolato Chemistry of Vanadium: Challenging the Binding Mode of -OCP in Early Transition Metals

Introduction. The last two chapters have thoroughly detailed the first document reactivity of the phosphaethynolate reagent¹ with early transition metal complexes. As explained in the introduction of Chapter 6 and as demonstrated with the scandium complexes of Chapter 7, in "harder" and electropositive metal ions, O-bound coordination of -OCP is expected to be dominant^{2,3h-k} (Figure 6.1), whereas with highly electron-rich W(0) and low-valent Ge, coordination is via the P-atom (Figure 6.1).^{3a-f} Based on Hard/Soft Acid Base (HSAB) theory we inquired if the uncommon phosphaketenyl binding mode³¹ (*P*-bound) to an early-transition metal ion could be accessed. Although one could anticipate that making the metal electron-rich should promote P-binding to the now softer metal site, reductive decarbonylation often prevents identification of such putative species (Scheme 6.4).^{3g} In this chapter, we show how a vanadium(III) precursor can allow for isolation and fully characterize a high-spin P-bound vanadium(III)-PCO complex that is resistant to decarbonylation. In addition to structural characterization and DFT analysis in collaboration with Prof. Balazs Pinter, we report high-frequency and -field EPR (HFEPR) spectral data and solid-state magnetization data in accord with such species being a high-spin d² complex (*S* = 1 ground state). The latter data was collected in collaboration with Prof. Josh Telser and Dr. Jurek Krzystek.

Results and Discussion

Synthesis of a P-Bound Phosphaethynolate Complex of Vanadium.

Following the procedure used for the previously reported Ti and Sc complexes, $(nacnac)VCl(OAr)^4$ (8.2) $(nacnac^- = [ArNC(CH_3)]_2CH$; $Ar = 2,6-^iPr_2C_6H_3$) (synthesized from $(nacnac)VCl_2$ (8.1) was treated with 1 equiv. of Na(OCP)(1,4-dioxane)_{2.5}^{1a} as a slurry in toluene at room temperature, and the mixture was allowed to stir for 12 h (Scheme 8.1). Examination of the crude reaction mixture revealed formation of a new species displaying broadened resonances in the ¹H NMR spectrum in the 0.5 to 9 ppm

range, whereas the paramagnetic resonances attributable to the starting material **8.2** were no longer present. Although Na(OCP)(1,4-dioxane)_{2.5} is not soluble in toluene, it is critical that coordinating solvents such as THF be avoided in the protocol since their use results in rapid decomposition of the product. To characterize the identity of the green material formed in this reaction, a concentrated toluene solution stored for 16 hours at –35 °C afforded green crystals of (nacnac)V(OAr)(PCO) (**8.3**) (Scheme 8.1) in 89% yield for which V–P, as opposed to V–O connectivity was unambiguously confirmed by single crystal X-ray diffraction (XRD) studies (Figure 8.1).



Scheme 8.1. Synthesis of complex **8.2** from **8.1**. Treatment of 8.2 with Na(OCP)(dioxane)_{2.5} resulted in the formation of **8.3**. Reduction of **8.3** with KC₈ formed dicarbonyl anionic V(I) complex **8.4**. Although the fate of the phosphorous atom is not known in the reduction step, we propose it is being lost as P₄. For all instances, Ar represents 2,6-*i*Pr₂C₆H₃.

In addition to XRD confirming the atypical binding mode of OCP- to an earlytransition metal center, the coordination geometry of the phosphaethynolato ligand reveals an unusual angle due to significant pyramidalization at the phosphorus atom. In contrast to (nacnac)Sc(OAr)(OCP)(THF), where much like the Na(OCP)(1,4dioxane)_{2.5} precursor the OCP- ion binds through the O-atom in a near-linear fashion with the metal center (\angle Sc-O-C of 170.89(2)°) with no other exceptional metrical features, the binding mode of OCP⁻ in **8.3** is essentially perpendicular to the V–P vector, with a \angle V–P–C of 85.93(5)°. This resembles the binding mode of OCP⁻ with late transition metals such as Re (92.6)° and Au (86.2)°.^{3a-c}



Figure 8.1 Molecular structure of complex **8.3**, nacnac and aryloxide 'Pr groups and all hydrogen atoms omitted for clarity (left); expansion of the PCO⁻ ligand coordinated to the [(nacnac)V(OAr)]⁺ scaffold showing only the first coordination sphere of the latter (right). All thermal ellipsoids are shown at the 50% probability level. All bond lengths shown are measured in angstroms (Å) and all angles shown are measured in degrees (°).

However, linearity within the OCP⁻ moiety is still maintained in **8.3** with a P1–C42– O2 angle of 176.31(1)°. A strong v(C–O) of 1876 cm⁻¹ was seen in the IR spectrum (Figure 8.2), which is similar to the other few known P-bound OCP⁻ moieties involving late transition metals (Co: 1851 cm⁻¹, Re: 1885 cm⁻¹).^{3a,b} Notably, the long V–P bond distance of 2.4502(4) Å significantly diverges from other P-bound examples of OCP⁻ to 3d metals such as Co–P: 2.263(1) Å and Cu–P: 2.2244(5) Å.^{3b} It is also significantly longer than known vanadium phosphinidene complexes (V–P: 2.14-2.19 Å).⁵⁻⁷ Perhaps the most notable metrical parameter in the solid-state structure of **2** is the P–C bond length of 1.6360(18) Å, which falls more in the range of a single or double bond, but is clearly longer than that of the precursor $[Na(OCP)(dme)_2]_2$, 1.575(3) Å and 1.589(3) Å.^{1a} The C–O bond length of 1.174(2) Å is commonly observed for systems possessing a double and triple bond and is slightly shorter than the aforementioned precursor, 1.203(4) Å and 1.213(3) Å.^{1a}



Figure 8.2. IR Spectrum of **8.3**. The ν (C–O) of 1876 cm⁻¹ has been annotated with a red dot. This spectrum was recorded on a JASCO FT/IR-4600LE Spectrometer using clear disks and mini KBr plates. The calculated ν (C–O) is 2000 cm⁻¹.



Scheme 8.2. Synthesis of complex **8.3** from **8.2** (which is prepared from $[(nacnac)VCl_2]$ by reaction with NaOAr).⁴ For all instances, Ar represents 2,6-*i*Pr₂C₆H₃. Three possible canonical forms for **8.3** are represented, of which **8.3c** is unfavored based on bond distances.

In accordance with these observations, Scheme 8.2 presents the canonical structures that should be considered. As shown in Scheme 8.2, structures **8.3a** and **8.3b**, are each quite reasonable based on the P–C and C–O distances and will be discussed further in light of computational studies. The metallophosphaketene resonance **8.3c** is the least likely, on basis of metrical parameters, chiefly the V–P distance, observed in the solid-state structure. Further characterization of **8.3** by an Evans NMR spectroscopic method confirmed the *S* = 1 nature of **8.3** in toluene solution at room temperature, i.e., a high-spin d² complex with a μ_{eff} = 2.47 μ_B (expected value for an *S* = 1 complex is 2.83 μ_B). With this unique complex in hand, we wondered if, similar to known isocyanate and other OCP complexes,⁸ if we could reductively decarbonylate the PCO moiety from this rather stable complex. Treatment of complex **8.3** at –35°C in Et₂O with a slurry of KC₈ (slight excess), resulted in an immediate effervescence was observed, along with a stark color change from 236

green to dark brown (Scheme 8.1). Workup of the reaction mixture and crystallization from an Et_2O /toluene mixture resulted in the deposition of only a few dark brown crystals on the walls of the vial, determined to be paramagenetic by NMR measurement. A single crystal X-ray diffraction experiment revealed this connectivity of this molecule as an anionic dinuclear masked V(I) dicarbonyl complex, 8.4 [[K][(nacnac)V(OAr)(CO)₂]]₂ (Figure 8.3). Note that it was also possible to isolate a few crystals [[Na(dioxane)][(nacnac)V(OAr)(CO)₂]]₂ (A16) when 8.3 was instead treated with a slight excess of Na/Hg amalgam. While these transformations present a puzzle for us still without knowledge of the identity of the phosphorous containing byproduct and no hints by ³¹P NMR spectroscopy (including no signal attributable to our reported *cyclo*-P₃ complex),⁹ we propose the following. Given that there are two carbonyl ligands per vanadium center, we propose that, in accord with the observed effervescence, there is likely the loss of one equivalent of CO, and the other two equivalents of CO forming the dinucear-ate complex, 8.4, as a max of 1/6 of the reaction mixture since this transformation requires 3 equiv. of OCP- per vanadium center. While unfortunately no reliable yield could be obtained for this complex, the isolation of only a few crystals in the reaction mixture provides some support for this complex being only a small component of the product distribution.



Figure 8.3. Molecular structure of complex **8.4**, nacnac and aryloxide ^{*i*}Pr groups and all hydrogen atoms as well as one molecules of toluene in the asymmetric unit have been omitted for clarity. All thermal ellipsoids are shown at the 50% probability level.

As can been in the solid state structure of 8.4, there is an interaction of the potassium cations with the arene ring of the aryloxide ligands, which are significantly bent to account for this interaction (V1-O1-Caryloxide: 131.7(2)°, relative to 153.87(9)° for 8.3). Surprisingly on the reduced vanadium center, the C-O bond distances of 1.190(3) and 1.185(4) Å imply that there is in fact very little change in electronic character from free CO 1.16 Å. Given the highly reduced nature of the metal center, it might have been expected to observe an elongation in the C-O bond, implying backbonding and a higher oxidation state character at the metal center. However, since this is not observed, the hypothesis is that in fact this metal center behaves more like V(I). While IR spectroscopy on this sample was performed, unfortunately no distinct stretches for the carbonyl ligands were observed. Attempts to decarbonylate using photolysis to form a terminal phosphide were attempts with a Xenon lamp. However, photolysis of **8.3** in C₆D₆ in a J-Young NMR tube resulted in the formation of a brown paramagnetic solution which, based on what was observed upon reduction, is likely a neutral V(II) dicarbonyl complex (nacnac)V(OAr)(CO)₂. Since this four coordinate precursor 8.3 did not deliver the desired result of a vanadium phosphide, we postulated that perhaps in a four-coordinate environment, which is not ideal for metal ligand multiple bonding, and which the knowledge of the MO diagram of our 5-coordinate PN⁻ complexes that is ideal for this overlap, *vide supra*, it seemed a logical choice to use a inner-sphere oxidant to both oxidize the metal center to V(IV) and force the system into a five-coordinate geometry. Additionally, by starting with a V(IV) system, the desired phosphide anion would be V(V). When starting with 8.3, we would have expected a V(IV) anion unless the photolytic decarbonylation had worked to give the neutral V(V). V(V) in this system would be preferred so we could obtain information on where in the ³¹P NMR spectrum the phophide moiety appears. Treating 8.3 with ferrocenium triflate, we were 238

disappointed to access (nacnac)V(OAr)(OTF) (A17). A crystallographic table for this molecule can be found in the Appendix of Molecules.¹⁰ However, questions as to why this occurred were later resolved by the recent report that demonstrated that electrochemical oxidation of phosphaethynolate results in the deposition of phosphorous containing deposits.¹¹ This also explained that during our reaction, a dark insoluble material formed on the walls of the vial.

Magnetic and HFEPR Studies of the V-PCO Complex.

The solid-state magnetic behavior of **8.3** was also probed using DC susceptibility. These measurements were performed by Ekaterina Lapsheva of the Schelter group and the data was analyzed by Josh Telser. As shown in Figure 8.4, **8.3** clearly has an *S* = 1 ground state with a sharp decrease in χT below ~20 K due to the effect of zerofield splitting (zfs). The phenomenon of zfs is key to the desired behavior of d-block single ion magnets, which property is not the goal here. However the zfs itself, chiefly the magnitude and sign of the axial zfs parameter, *D*, provides valuable information on electronic structure, such as the nature of the frontier MOs and the accessibility of electronic excited states.¹² It was not possible *via* fitting to distinguish between a positive and a negative value for *D*, which is a common phenomenon.¹²⁻¹⁵ As a result, the possibility of rhombic zfs (*E* parameter) was not explored. Our fit suggested a magnitude of *D* on the order of 4 cm⁻¹, exhibiting temperature independent paramagnetism (TIP), which is qualitatively the consequence of the contribution of thermally populated spin triplet excited states not accounted for by the simple *S* = 1 spin Hamiltonian (sH) employed.^{13,14}


Figure 8.4. Plot of experimental molar χT values for **8.3** (black triangles; two datasets are included: one as up triangles and one as down triangles). Fit lines using both positive (green line) and negative (red line) *f* values are shown with the fit parameters for each given on the plot.

To further address the electronic structure of complex **8.3**, HFEPR spectra were recorded on a ground polycrystalline sample, analogous to that used for the DC susceptibility measurements. These experiments were conducted by Josh Telser and Jurek Krzystek. The spectra produced by **8.3** could be recognized as originating from a triplet (S = 1) state with moderate zfs. The number and intensities of turning points could indeed be readily simulated. An HFEPR spectrum at a relatively low frequency (113 GHz, Figure 8.5) provided the best representation of a triplet powder pattern,¹⁶ but the frequency was too low to unambiguously determine the absolute sign of D.¹⁶ For this reason, a spectrum at higher frequency (257 GHz, Figure 8.6) was needed. The relative amplitudes of the experimental turning points belonging to the

transitions originating from the $|S, M_S\rangle = |1, 0\rangle$ spin sublevel are higher than those originating from one of the $|1, \pm 1\rangle$ sublevels, which clearly shows the positive sign of D. To determine the full set of S = 1 sH parameters, particularly the g values and rhombic parameter E, a complete field-frequency dependence of the HFEPR transitions was recorded.¹⁷ Such a dependence is shown in Figure 8.7, from which the sH parameters can be extracted with high precision and accuracy as: D = +2.60(1) cm⁻¹, |E| = 0.346(5) cm⁻¹, $g_x = 1.962(5)$, $g_y = 1.938(5)$, $g_z = 1.953(5)$.



Figure 8.5. An HFEPR spectrum of **8.3** at 10 K and 113 GHz. The black trace is experiment in which the V(IV) impurity signal at g = 1.98 was left out; the colored traces are simulations using following spin Hamiltonian (sH) parameters: S = 1, |D| = 2.62 cm⁻¹, |E| = 0.36 cm⁻¹, $g_x = 1.96$, $g_y = 1.94$, $g_z = 1.95$. Blue trace: negative *D*; red trace: positive *D*. These parameters represent the best fit at this particular frequency and thus differ slightly from Figure 8.6, which result from consensus fits of spectra recorded at multiple frequencies (see Figure 8.7).

The sH parameters obtained for **8.3** can be placed into the context of those for related species inasmuch as possible. We have previously employed HFEPR to extract the zfs of a V(III) complex related to 8.3, $[(nacnac)V(N_3)(Ntolyl_2)]$ (tolyl = 4-MeC₆H₄) (8.5), which gave D = -1.65 cm⁻¹, |E| = 0.20 cm^{-1.18} This previously studied complex shares the nacnac ligand with **8.3** and is likewise four-coordinate. That the *D* values for two such [(nacnac)V^{III}(X)(Y)] complexes (X = -OAr, Y = -PCO in **8.3**; X = N₃⁻, Y = -NR₂ in **8.5**) are of opposite sign indicates the difficulty in generalizing the correlation between zfs and coordination sphere of a metal ion. An ideally tetrahedral d² complex should exhibit no zfs, and homoleptic four-coordinate V(III) complexes such as $[V(Ar^{nCl})_4]^-$ ($Ar^{nCl} = C_6Cl_5$, 2,4,6-trichlorophenyl, or 2,6-dichlorophenyl) indeed exhibit smaller magnitude zfs ($0.45 \le |D| \le 0.59$ cm⁻¹) than that observed here for such heteroleptic complexes,¹⁹ which is expected based on ligand-field theory for pseudotetrahedral d^2 complexes. Clearly, a greater database on zfs in four-coordinate V(III) complexes is needed to further evaluate the magnitude and absolute sign of the zfs in **8.3**. Moreover, the unusual PCO⁻ coordination means that **8.3** may even be distinct amongst mononuclear [(nacnac)V^{III}(X)(Y)] complexes.



Figure 8.6. An HFEPR spectrum of **8.3** recorded at 10 K and 257 GHz (black trace). A V^{IV} impurity signal at g = 1.98 (~9.3 T) has been removed. Colored traces are

simulations using sH parameters: S = 1, |D| = 2.62 cm⁻¹, |E| = 0.36 cm⁻¹, $g_x = 1.96$, $g_y = 1.94$, $g_z = 1.95$. The particular turning points are labelled by canonical direction (*x*, *y*, *z*) of the magnetic field with respect to the **D** tensor and have subscripts 1 for those that belong to the transition originating from the $|S, M_S\rangle = |1, 0\rangle$ spin sublevel while those with subscripts 2 originate from one of the $|1, \pm 1\rangle$ sublevels.



Figure 8.7. A 2D field vs. frequency (energy) plot of HFEPR spectral turning points in **8.3**. Squares are experimental data; curves were simulated using sH parameters as in the text. Red curves: turning points with magnetic field parallel to the *x*-axis of the zfs tensor; blue curves: $B_0 \parallel y$; black curves: $B_0 \parallel z$. The two vertical dashed lines indicate the frequencies at which the spectra shown in Figures 8.5 and 8.6, respectively, were recorded.

Computational Studies of the Vanadium Phosphaethynolato Moeity.

To elucidate the electronic structure of **8.3** in detail and reveal the most likely canonical resonance of the OCP⁻ ligand in **8.3**, we turned to DFT (B3LYP/def2-TZVP(f)). These calculations, conducted by Prof. Balazs Pinter, were performed on nontruncated models revealed an equilibrium structure for **8.3** with metrics in good agreement with the X-ray structural parameters. For example, the quasiperpendicular \angle V–P–C angle (85.0°) and distances V–P (2.46 Å), P–C (1.66 Å) and C– O (1.17 Å) are well reproduced by these DFT calculations, substantiating the method of calculation. To characterize the bending and bonding of the V–PCO motif in **8.3** we used quasi-restricted orbitals (QROs). QROs offer a reliable and intuitive description of the unrestricted wavefunctions (with different α and β orbital subsets) through a conceptual picture resembling that of the restricted open-shell solution. The two singly occupied QRO's of **8.3**, d_{z2} and d_{x2-y2}, (Figures 8.8 and 8.9) unmistakably reveal metal-centered unpaired electrons without notable delocalization to any of the ligands, i.e., a d² V(III) center, conforming to a spin density of 1.96 calculated for the vanadium of **8.3** using the Löwdin method, and consistent with the HFEPR results. Close inspection of the orbital entitled $\pi_{PCO}+d_{xz}$ in Figure 8.8 unveils the vanadium– PCO σ bond, which is the main V–PCO interaction, as originating from the overlap of one of the π orbitals of the OCP⁻ fragment and a σ -type vanadium d orbital, d_{xz}, in the quasi-tetrahedral arrangement of **8.3**.



Figure 8.8. Relevant QROs of triplet **8.3**. The upper two QROs represent the V-centered unpaired electrons, while HOMO-4 depicts the V–P σ interaction. Isodensity values are +/-0.04.

The spatial characteristics of this PCO π -bond account for most of the striking structural features observed, such as the elongated P–C and significantly shortened C–O distances in the OCP⁻ ligand. These spatial features indicate that this π_{PCO} orbital has bonding character along P–C and antibonding character along C–O, which, under normal circumstances like in the free ligand, lead to a short P–C and a long C–O bond (i.e. to P=C–O⁻ formally). In **8.3** however, electron donation takes place from this π_{PCO} orbital to the vanadium, witnessed by the $\pi_{PCO}+d_{xz}$ molecular orbital in Figure 8.8, from which partial depopulation of π_{PCO} results in diminished attraction and diminished repulsion along the P–C and C–O axes. The latter effects lead to the weakening of the P–C and strengthening of the C–O bonds relative to that of free OCP-

, consistent with the structural features in **8.3**. Also, due to the polarization of this PCO π -bond towards the phosphorous atom, the \angle V–P–C deviates from angles typical of side-on or κ^2 coordination and towards a perpendicular κ^1 -type binding at P. As a result, this MO analysis implies that the formal electronic structure of OCP- changes from P=C–O- (in free ligand) to -P=C=O upon binding to V(III) and, concomitantly, that the Lewis structure of **8.3** is dominated by resonance **8.3a** (Scheme 8.2). The OCP- structural motif is further supported by the Mayer bond indices of 1.75 and 2.06 calculated for P=C and C=O, respectively, in **8.3**.



Figure 8.9. Singly occupied and high lying doubly occupied QROs of **8.3**.

Exploring Chemistry of the Arsenic Analogue, OCAs-



Figure 8.10. Molecular structure of complex **A18** (left), nacnac and aryloxide ^{*i*}Pr groups and all hydrogen atoms as well as one molecule of ether and disorder of the As atoms have been omitted for clarity. All thermal ellipsoids are shown at the 50% probability level. *Cyclo*-As₃ core expansions from two different viewpoints (right).

Extending this reactivity to the arsenic analogue of phosphaethynolate Na(OCAs)(dioxane)_{2.5} (arsaethynolate),²⁰ we wanted to see if we access similar scaffolds using the same precursors. However, as aforementioned in Chapter 6, this reagent is much more reactive, and a more potent reductant than phosphaethynolate. The first attempt at treating **8.2** with Na(OCAs)(dioxane)_{2.5} resulted in the formation of a green paramagnetic material. It was confirmed by a single crystal X-ray diffraction study that we had obtained a dinuclear complex bridged by a *cyclo*-As₃ moiety (**A18**) (Figure 8.10, Scheme 8.3). As can be observed in the solid-state structure (Figure 8.10, left), the cycl0-As₃ moiety is constrained to 60° angles, where As1-As2-As3 = 59.90(7)°, As2-As3-As1 = 61.00(7)° and As2-As1-As3 = 59.10(7)°. Bond distances within the bridging unit include As1-As2 = 2.410(2) Å, As2-As3 = 2.365(3) Å and As1-As3 = 2.384(2) Å. Comparing this to our previously discussed Ti₂P₂ complex, it can be seen that there is elongation of ~0.3 Å, which is logical given

the larger atomic radius of As. Finally, if we only look at the V₂As₂ portion of this core (Figure 8.10, right) which is comprised of V1As1As3V2 (ignoring the top As₂ of the *cyclo*-As₃), dihedral angles of V1–As1–As3–V2 = 144.01(6)° and V1–As1–V2–As3 = 34.14(6)°, it can be seen that this portion is bent further out of planarity than the Ti₂P₂ complex (*vide supra*).



Scheme 8.3. Synthesis of complex **A18** from **8.2**. For all instances, Ar represents 2,6- ${}^{i}Pr_{2}C_{6}H_{3}$. Note that due to contamination in our sample of OCAs(dioxane)_{2.5}, which contains NaOMe and HO^tBu, the aryloxido ligands are substituted in the final product. To account for this, we also include in this reaction balance the loss of NaOAr and HOAr.

This result was indeed quite exciting until moments later the realization set in that the aryloxide ligands were no longer bound to the metal center. In fact, these had puzzlingly been replaced by a methoxide ligand on one of the vanadium centers, and on the other a *tert*-butoxide ligand. "How?" was the first question when there should have been no contamination with these reagents in reactivity. However, after reaching out to our suppliers of this reagent, the Grützmacher group, we were informed that there could possibly be contamination of this reagent in synthesis if not purified properly by the student who conducted the synthesis as the material is made by the following reaction²⁰:

AsH₃ + 3 NaO^tBu + O=C(OMe)₂
$$\rightarrow$$
 Na(OCAs) + 2 NaOMe + 3 ^tBuOH

Therefore, it was clarified that because the contaminated sample we received (this material is difficult to separate and purify from other byproducts), we might expect

to have ligand exchange for the less bulky alkoxides as observed in product A18. After receiving a new batch of OCAs⁻, the project commenced. However, frustratingly, this time, as opposed to clean *cyclo*-As₃ product, we obtained again a green paramagnetic solution, but with different resonances in the ¹H NMR spectrum. Isolation of this material and a X-ray diffraction analysis showed that we had made a carbonyl anion complex, [[Na(Et₂O)][(nacnac)V(OAr)(CO)₂]]₂ (A19) (Figure 8.11), directly reducing to this species analogous to that which was obtained by reducing 8.3 (only this time with a coordinating molecule of ether as opposed to dioxane in A16). This demonstrates that indeed the arsenic analog of this reagent is a much more powerful reductant. From this same reaction mixture, a crystal of a decomposition product, likely from disproportionation, is $[Na(Et_2O)_2][V(OAr)_4]$ (A20) (Figure 8.11). Crystallographic tables for **A18-A20** can be found in the Appendix of Molecules.¹⁰ As an additional point, it should be annotated that all these complexes are almost exactly the same bright green color, and all paramagnetic as well. Unfortunately, these reactions area not clean, but it is with hope that modification of the system or reaction conditions will allow for the formation of clean products.



Figure 8.11. Molecular structure of complex **A19** (left), and **A20** (right) nacnac and aryloxide ^{*i*}Pr groups and all hydrogen atoms as well as one molecules of ether have been omitted for clarity. All thermal ellipsoids are shown at the 50% probability level.

Conclusion.

In summary, this chapter has discussed the first example of the OCP- reagent binding to a highly electropositive 3d early transition metal, vanadium(III), *via* the Patom, and the unexpected \angle V–P–C of 85.93(5).^o Our perception is that the HSAB concept's "soft-soft" argument, which can be translated into the MO framework as the electron-rich V(III) having a better orbital energy match with phosphorous orbitals than with oxygen orbitals, explains the site-selective P-binding of OCP- to vanadium(III). On the other hand, the almost perpendicular binding and elongated/shortened P–C/C–O bonds of OCP- can be best rationalized, as detailed above, through the characteristics of the π_{PCO} orbital that forms the σ interaction with the vanadium center (Figure 8.8). Further, we have demonstrated that under reducing conditions these complexes decarbonylate to dicarbonyl anion V(I) complexes with an unknown phosphorous containing byproduct. Finally, the reactivity of OCAs- from the same vanadium precursor was demonstrated to produce a myriad of products, mostly indicating contamination of the arsenic containing precursor, as well as its ability to act as a potent reductant.

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Experimental Details

General Procedures

Unless otherwise stated, all operations were performed in a M. Braun Lab Master double-dry box under an atmosphere of purified dinitrogen or using high vacuum standard Schlenk techniques under an argon or dinitrogen atmosphere. Hexanes, tetrahydrofuran (THF) and toluene were purchased from Fisher Scientific and Et₂O was purchased from Sigma Aldrich. Solvents were sparged with argon for 20 minutes and dried using a two-column solvent purification system where columns designated 251 for hexanes and toluene were packed with Q5 and alumina respectively, and columns designated for Et₂O and THF were packed with alumina. Deuterated benzene was purchased from Cambridge Isotope Laboratories (CIL) and was sparged with nitrogen for 20 minutes, then was dried over a potassium mirror, vacuum transferred to a collection flask, and degassed by freeze–pump–thaw cycles. All solvents were transferred into a dry box and were stored over 4 Å sieves. All sieves were heated to 200 °C under vacuum overnight prior to use. Celite used for filtrations was heated to 200 °C under vacuum overnight prior to use. IR spectra were recorded on a JASCO FT/IR-4600LE Spectrometer using clear disks and mini KBr plates. Elemental analyses were measured by Midwest Microlab. NaOAr was synthesized from HOAr $(Ar = 2,6-iPr_2C_6H_3)$ and NaN(SiMe₃)₂ in toluene followed by filtration of the pale solid, and washed with copious amounts of toluene, and then dried under reduced pressure. [(nacnac)VCl₂]²¹ (nacnac⁻ = [ArNC(CH₃)]₂CH; Ar = 2,6-*i*Pr₂C₆H₃), [(nacnac)VCl(OAr)]⁴ and [Na(OCP)(dioxane)_{2.5}]^{1a} were prepared according to published literature procedures.

Synthesis of [(nacnac)V(OAr)(PCO)] (8.3)

To a dark green solution of [(nacnac)VCl(OAr)] (329.1 mg, 0.48 mmol, 1 equiv.) in 10 mL toluene in a 20 mL vial was added a 5 mL toluene slurry of [Na(OCP)(dioxane)_{2.5}] (154.8 mg, 0.48 mmol, 1 equiv.). After stirring for 16 hours, the reaction mixture turned a lighter green color, and a noticeable precipitate had formed, NaCl. The solution was filtered over Celite for removal of alkaline side product. All volatiles were removed in vacuo, and the green residue was dissolved in a minimum (5 mL) of toluene, and was stored at -35 °C overnight, resulting in the deposition of large green crystals suitable for single crystal X-ray diffraction. These were decanted and dried over vacuum and isolated good yield. Yield: (303 mg, 0.43 mmol, 89%). Anal. Calcd. for C₄₂H₅₈N₂O₂PV: C, 71.57; H, 8.29; N, 3.97. Found: C, 69.99; H, 8.23; N, 3.76.

Crystallographic Experimental Details

Crystallographic data are summarized Table 8.1. Suitable crystals for X-ray analysis of **8.3-8.4** was placed on the end of a Cryoloop coated in NVH oil. Data for single crystal structure determination of **8-3-8.4** were taken on a Bruker D8 with CMOS area detector employing graphite-monochromated Mo-Kα radiation (λ =0.71073 Å) at a temperature of 100(1) K. Rotation frames were integrated using SAINT,²² producing a listing of non-averaged F^2 and $\sigma(F^2)$ values. The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS.²³ The initial structure of **8.3** was solved by dual methods – SHELXT.²⁴ Refinement was by fullmatrix least squares based on F² using SHELXL.²⁵ All reflections were used during refinement.

Compound	8.3	8.4 · 2(C ₇ H ₈)
Molecular formula	$C_{42}H_{58}N_2O_2PV$	C ₄₃ H ₅₈ KN ₂ O ₃ V, 2(C ₇ H ₈)
Formula weight	704.81	925.22
Temperature (K)	100(1)	100
Crystal system	Monoclinic	Triclinic
Space group	P 1 2 ₁ /n 1	P -1
Cell constants:		
a (Å)	11.7814(6)	13.1318(11)
b (Å)	21.2101(10)	14.5225(13)
c (Å)	17.8807(8)	15.6427(14)
Alpha Agle	90	73.252(3)
Beta Angle	109.211(2)	65.990(2)
Gamma Angle	90	72.227(2)

Table 8.1. Crystallographic Data of compounds 8.3 and 8.4.

Volume (Å ³)	4219.3(4)	2548.5(4)
Z	4	2
Density (calcd mg/m3)	1.110	1.206
Abs coeff (mm-1)	0.307	0.321
F(000)	1512	992
Wavelength	0.71073	0.71073
θ range for data collection (°)	2.956 to 27.568	2.97 to 27.47
h, k, l ranges collected	$-15 \le h \le 15$ $-23 \le k \le 27$ $-23 \le l \le 23$	$-15 \le h \le 17$ $-18 \le k \le 17$ $0 \le l \le 20$
# Reflns collected	9712	11746
Refinement method	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²
$R_{I^{a}}$	0.0358	0.0675
$wR_{2^{b}}$	0.0883	0.1156
Goodness-of-fit on F2 ^c	1.025	1.100

a R1 = (|Fo| - |Fc|) / |Fo|. b wR2 = [[w(Fo2 - Fc2)2] / [w(Fo2)2]]1/2. c Goodness-of-fit = [[w(Fo2 - Fc2)2]/Nobservns Nparams)]1/2, all data.

SQUID Magnetometry Experimental Details

Magnetic susceptibility data for **8.3** was collected on a Quantum Design Magnetic Property Measurement System (MPMS-7). Temperature-dependent data were collected under applied 1 T DC fields from 2 to 300 K. Corrections for the intrinsic diamagnetism of **8.3** was made using Pascal's constants.²⁶ Samples of microcrystalline **8.3** (10 – 20 mg) in the glove box were loaded into plastic drinking straws that had been evacuated overnight, and had been previously sealed at one end (~9.5 cm from the top) with heated forceps. Quartz wool (<10 mg, dried at 250 °C) was used to cap the sample, followed by sealing of the other end of the straw. The sample and quartz wool masses were weighed to the nearest 0.1 mg, and the value used was the average of four mass measurements. The data were fitted by use of the locally written program DSUSFITP,²⁷ which employs the Hamiltonian in eq. 1 assuming an isolated ground spin state and collinear **D** (axial component D, rhombic component E) and **g** matrixes, along with a temperature independent paramagnetism (TIP) term (not shown in eq. (1)) to account for contributions from excited spin states. True powder averages in three dimensions are calculated. A least-squares minimization using experimental data optimizes the spin Hamiltonian parameters. For simplicity, fits with only an isotropic g were employed, and the effect of E was not explored since rhombicity is best obtained from HFEPR spectroscopy (see main text). Error associated with these parameters was estimated using the standard deviations of several fits with very similar goodness-of-fit values.

$$H = \beta_{e} B \cdot g \cdot \hat{S} + D \left[\hat{S}_{z}^{2} - S \left(S + 1 \right) / 3 \right] + E \left(\hat{S}_{x}^{2} - \hat{S}_{y}^{2} \right)$$
(1)

HFEPR Experimental Details

HFEPR spectra were recorded using a spectrometer that has been described previously,²⁸ with a difference of using a Virginia Diodes (Charlottesville, VA) source operating at 13 ± 1 GHz, amplified and multiplied by a cascade of frequency multipliers. Multifrequency HFEPR data were fitted using the spin Hamiltonian in eq. (1), as used with the magnetic susceptibility data.

Computational Details

All calculations were carried out using DFT as implemented in the ORCA (version 4.0.1.2) program package.²⁹ Geometry optimizations were performed with B3LYP functional³⁰ and the all-electron def2-SV(P)³¹ basis set in combination with the auxiliary basis set def2-SV(P)/J.³² To accelerate geometry optimizations we used the resolution of the identity approximation for Coulomb and chain of spheres approximation for exchange interactions (RIJCOSX).³³ Already for optimizations a tight convergence of the wavefunction was demanded on grid quality of Grid4 and GridX4. Grimme's D3 method³⁴ was employed to take dispersion effects into account in all these calculations. We also carried out harmonic vibrational frequency calculations at the same level of theory that was for used for optimizations (B3LYP/def2-SV(P)) in order to confirm that the obtained structures indeed correspond to local minima of the potential energy surface.

Subsequent single point calculations for refined energies have been carried out using the B3LYP functional in combination with def2-TZVP basis set (without RI, on Grid5 and Grid5x). The electronic structure of **8.3** has been scrutinized, including QRO's, at the latter level of theory.

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Chapter 9:

A Cobalt Azido Complex in a *Cis*-Divacent Octahedral Geometry

Introduction. Late 3d transition metal imido complexes have received significant attention recently given their role in group transfer catalysis, particularly their ability to conduct amination and aziridination reactions. These species are sufficiently reactive to perform nitrene insertion reactions to even the less reactive "non-functionalized" hydrocarbon C–H bonds.^{1–14} As a result, there is great interest in harnessing these reactive groups for the purpose of hydrocarbon conversion.



Figure 9.1. d-Orbital splitting diagram for complex (pyrr2py)Fe=NAd and a hypothetical complex (pyrr₂py)Co=NR in a *cis*-divacant octahedral geometry.

Our group recently reported the synthesis of a low-spin (S = 0) Fe(IV) imido complex, supported by a bulky, dianionic bis(pyrrolyl)pyridine pincer ligand $[pvrr_2pv^{2-} = 3,5 \ ^tBu_2bis(pvrrolyl)pvridine]$, namely $(pvrr_2pv)Fe=NAd$ (Ad = 1adamantyl).^{15,16} The meridional nature of this pincer ligand coupled with the strong σ -donating pyrrole groups constrains the geometry of the metal ion to an unusual *cis*-divacant octahedron when a fourth ligand occupies the coordination sphere. The ability of this ligand scaffold to support highvalent Fe(IV) imidos, which showed remarkable inertness toward C–H bonds and olefins, led us to pursue a more electron rich Co(IV) system. Shifting to Co, one would expect this species to contain an unpaired electron in an M=N π^* (dyz) orbital (Figure 9.1), thus rendering this ligand "iminyl"-like. As demonstrated by Holland, Betley, and co-workers,^{5,7} the presence of an unpaired electron in their Fe=NR motif (imidyl group) offers diverse reactivity toward C-H bonds. Warren and co-workers have also observed C-H amination in even more electron rich transition metal nitrenes supported by nacnac ligands.¹⁰ As a result, we sought to extend the use of the pincer ligand pyrr₂py for the synthesis of an electron rich cobalt imido species having imidyl character (Figure 9.1) and even attempt the isolation of a low-spin Co(V) imido system $[(pyrr_2py)Co=NR]^+$ that would be isoelectronic to our previously reported (pyrr₂py)Fe=NAd. A limited number of Co imido complexes have been reported or proposed, and the majority of such species consist of low-spin Co(III) centers that are relatively stable.¹⁷⁻²² A few exceptions to this trend include work by Theopold and Betley, in which Co(III) imido complexes access high-spin states under certain conditions (imidyl character), therefore resulting in insertion into a peripheral C– H bond of the supporting ligand.^{7,11} More recently, Deng and co-workers reported the first examples of Co(IV) and even Co(V) bis-imido (IMes)Co(NDipp)₂ (IMes = 1,3-bis(1',3',5'complexes, trimethylphenyl)imidazol-2-ylidene, dvtms = divinyltetramethyldisiloxane).¹³ When heated, their Co(IV) species was found to engage in intramolecular C-H amination of the supporting NHC ligand.¹³ We report here the synthesis of new Co complexes supported by the bis(pyrrolyl)pyridine pincer ligand pyrr₂py. Attempts to prepare a Co-imido species from an organic azide reduction resulted instead in isolation of a 261

rare example of an "arrested" N_2 group on the organic azide, which is bound to Co(II) through the γ -nitrogen atom. Under photolytic conditions, the azide group does extrude N_2 to generate a transient Co–imido that immediately inserts into a C–H bond of the ligand. Complete characterization, including electrochemical studies of the Co(II) precursors as well as the product resulting from nitrene insertion into a C–H bond of a *tert*-butyl group on the pincer ligand, is presented and discussed.

Results and Discussion

1. K[N{SiMe₃}₂] (2 equiv.) ^tBu ^tBu ^tBu tBu CoCl Co[N(SiMe₃)₂]₂(THF) Et₂O - 2 HN{SiMe₃}₂ ŃН ΗŃ PyPyrr₂H₂ HN{SiMe₃}₂ ^tB′u ^tBu ^tΒ΄υ ^tBu 2 KCI OEt₂ 9.1-0Et₂

Synthesis and Reactivity of a Cobalt Azido Complex.

Scheme 9.1. Synthesis of complex 9.1-OEt₂ by two independent routes.

To access a Co(II) precursor, a slurry of CoCl₂ in THF was treated with $[K_2(pyrr_2py)]$,¹⁵ which was generated *in situ* by treatment of a THF solution of pyrr₂pyH₂ with K[N(SiMe₃)₂] that had been stirred for 2 h prior to metalation. Initial experiments were performed by Dr. Maria Carroll. Upon addition of the ligand salt to the CoCl₂ slurry, a gradual color change from blue to brown green was observed, and after 20 h, removal of THF under reduced pressure resulted in a dark solid. After the solid was extracted into pentane and filtered and the filtrate dried, dark purple crystals of complex (pyrr₂py)Co(OEt₂) (**9.1**)-OEt₂ could be obtained in 39% yield by extracting the solid with Et₂O, filtering, and then cooling the filtrate to -35 °C overnight (Scheme 9.1). Alternatively, slow addition of H₂pyrr₂py to a diethyl ether solution of Co(N{SiMe₃}₂)₂²³ resulted in the formation of **9.1**-OEt₂ but with an improved yield of 82% after recrystallization from diethyl ether (Scheme 9.1). The ¹H

NMR spectrum of **9.1** in C₆D₆ features seven paramagnetically shifted resonances ranging from 135 to –23 ppm. The number of NMR spectroscopic signals is consistent with a C_s symmetric system akin to that observed for the analogue (pyrr₂py)Fe(OEt₂).¹⁶ A room-temperature magnetic susceptibility measurement in C₆D₆ reveals a μ_{eff} of 4.3 μ_{B} , consistent with a high-spin Co(II) (S = 3/2) complex.

Single crystals of X-ray quality were grown by cooling a concentrated diethyl ether solution of **9.1**-OEt₂ to -35 °C over the course of 2 days. Complex **9.1**-OEt₂ crystallizes in orthorhombic space group *Pbcm*, which is analogous to that of the Fe complex, $(pyrr_2py)Fe(OEt_2)$.¹⁶ Not surprisingly, the unit cell is also nearly identical to that of (pyrr₂py)Fe(OEt₂). In the solid state structure shown in Figure 9.2, the Co(II) center is four-coordinate with a meridionally bound pyrr₂py ligand. A diethyl ether molecule is bound in a *cis* position, therefore rendering the geometry at Co more in accord with a *cis*-divacant octahedron ($\tau_4 = 0.77$). This geometry is strikingly similar to that observed for the analogous Fe complex [($pyrr_2py$)Fe(OEt₂)] ($\tau_4 = 0.80$), in addition to similar metrical parameters for the bound Et_2O ligand: Fe- O_{Et2O} , 2.1103(19) Å; $Co-O_{Et20}$, 2.027(3) Å. To illustrate the similarity in their molecular geometry (based on bonds and angles), an overlay of the two structures is presented in Figure 9.3, where **9.1**-OEt₂ is colored blue in this figure and the Fe analogue is colored red in this figure. The only notable differences that cause these two geometries not to be 100% superimposable are the differing orientations of Et groups in the bound Et₂O. As a note, the overall geometry of **9.1**-OEt₂ is slightly distorted from a perfect *cis*-divacant octahedron, because the Co center is 0.55 Å deviated along the plane defined by the three pyrr₂py nitrogen atoms.





Figure 9.2. Molecular structures (top) of complexes **9.1**-OEt2 (left) and **9.2**·toluene (right) displaying thermal ellipsoids at the 50% probability level and the unit cell (bottom) of complex **9.2**·toluene showing the stacking of toluene between two molecules of **9.2** (oriented along the *a* axis). Note that the ellipsoid of the Co atom in **9.2**·toluene is elongated due to disorder above and below the mirror plane of the crystallographic mirror on which the atom is centered.

To understand the redox properties of **9.1**-OEt₂, we examined electrochemical data of this complex using the [NⁿBu₄][PF₆] electrolyte in 1,2-difluorobenzene. As shown in Figure 9.4, the CV data shows an irreversible cathodic wave at a very negative potential of approximately -2.70 V. Scanning anodically, however, one can easily observe two reversible one-electron waves at 0.38 and 0.10 V (vs the FeCp₂^{0/+} redox couple at 0.0 V and used as an internal standard). We observed that there are two reversible waves in the CV of equal intensity in the absence of FeCp₂, but upon addition of FeCp₂, the intensity of the wave at 0.10 V significantly increases because of the overlap of this wave with ferrocene. Despite being formally Co(II), complex **9.1**-OEt₂ should be readily oxidized by one and two electrons based on the two anodic waves shown in Figure 9.4. Unfortunately, chemical oxidations of **9.1**-OEt₂ by one-electron oxidants have so far been unfruitful, resulting in decomposition.



Figure 9.3. Overlay of **9.1**-OEt₂ (blue) and (pyrr₂py)Fe(OEt₂) (red) for qualitative comparison of their geometries.



Figure 9.4. CV data of complex **9.1** (anodic scan from -0.4 V) in 1,2-difluorobenzene with $[N^nBu4][PF_6]$ as the electrolyte (100 mM). This sample was run in the absence of FeCp₂^{0/+} to feature both the reversible feature at 0.38 V and a second reversible wave at 0.10 V. The concentration of complex **9.1**-OEt₂ was 1.5 mM, and the scan rate was 250 mV/s.

Attempts to remove the Et₂O ligand in **9.1**-OEt₂ were unsuccessful even when a solution was heated in toluene or other solvents at 80 °C for hours. However, the diethyl ether ligand in **9.1**-OEt₂ can be gradually removed with AlMe₃. (monitored by ¹H NMR spectroscopy) in toluene to form a new complex that we infer to be the toluene species, (pyrr₂py)Co·toluene, **9.2**·toluene, based on ¹H NMR spectroscopy. Formation of an arene complex, **9.2**·toluene, is evident from the presence of a singlet at 2.77 ppm integrating for three H atoms or nuclei, in the expected region for the toluene CH₃ group, as well as the presence of multiplets integrating for five hydrogens in the aromatic region. Interestingly, the arene in **9.2**·toluene is stable to exchange with benzene when the complex is dissolved in C₆D₆ at room temperature. This was confirmed by an independent synthesis of the benzene complex, (pyrr₂py)Co·benzene, which had a ¹H NMR spectrum markedly different from that of **9.2**·toluene in C_6D_6 . Complex **9.2**·toluene can be obtained in higher yield via treatment of $Co(N{SiMe_3}_2)_2$ with pyrr₂pyH₂ in the absence of donor solvents. Accordingly, treatment of $Co(N{SiMe_3}_2)_2$ with H_2pyrr_2py in toluene afforded 9.1-toluene in 67% yield (Scheme 9.2). Akin to that of the diethyl ether adduct, 9.1-OEt₂, the room-temperature magnetic susceptibility measurement of **9.2**·toluene in C_6D_6 reveals a μ eff of 4.6 μ_B , consistent with a high-spin Co(II) (S = 3/2) complex.

Complex **9.2**-toluene crystallizes in a different orthorhombic space group, *Cmcm*, where both the toluene and Co atoms are disordered (Figure 8.2). Surprisingly, the relatively long Co–C_{toluene} distances [3.453(5)–4.539(3) Å] indicate minimal interaction between the metal center and toluene molecule, hence suggesting this interaction is governed more by packing forces than by orbital interactions.^{17,25–31} In fact, the packing diagram shows the toluene to be intercalated in a π -like fashion between two [(pyrr₂py)Co] scaffolds (unit cell shown at the bottom of Figure 9.2. The methyl group of the intercalated toluene fits well into the space between the two ^tBu groups of the pyrrolyl moiety of the ligand. Because of the symmetry of the pyrrolyl ligand, the toluene methyl interacts equally with both pockets created by the ^tBu groups, resulting in disorder of the toluene molecule. Given this unique stacking 267

interaction, we tantalizingly refer to complex **9.2**·toluene as a three-coordinate Co(II) complex³²⁻³⁵ where the metal ion is T-shaped (N2–Co–N2', 165.59°; N1–Co–N2, 80.80°).



Scheme 9.2. Synthesis of **9.2**·toluene and formation of azide adduct **9.3** from **9.1**-OEt₂.

We next examined the reactivity of **9.1**-OEt2 with 1-adamantylazide, N₃Ad. Treatment of a toluene solution of 9.1-OEt₂ with 1 equiv. of N₃Ad at room temperature did not produce a significant color change, and no effervescence was observed. The solution remained dark green, and after the mixture had been stirred for 20 h and worked up, a new material could be crystallized from pentane in 67% yield. We proposed this species to be the azide adduct (pyrr₂py)Co(N₃Ad) (9.3) (Scheme 9.2). While the room-temperature solution magnetic study by the method of Evans reveals 1-N₃Ad to possess a μ_{eff} of 4.7 μ_B , in accord with this species being a high-spin Co(II) (S = 3/2) complex, the ¹H NMR spectrum of this new complex exhibits eight new paramagnetically shifted resonances (δ -24 to 125). To determine the degree of reduction of the azide moiety as well as its binding mode, X-ray diffraction single quality crystals were grown from a concentrated pentane solution at -35 °C, and a solid state structural diagram is shown in Figure 9.5. The molecular structure reveals a four-coordinate cobalt complex consisting of a meridionally coordinated pyrr₂py ligand and an N₃Ad ligand bound only through the γ -N atom. Akin to the Et₂O ligand in **9.1**-OEt₂, the azide is coordinated orthogonal to the plane defined by (pyrr₂py)Co, hence rendering this species a distorted *cis*-divacant octahedron (τ_4 =

0.70). Judging from the Co-N_{azide} [2.179(8) Å] and N-N [1.266(9) and 1.135(9) Å] distances of the azide, there is a minimal degree of reduction of the azide consistent with this species being a Co(II) complex having a dative N₃Ad group. Additional characterization of this complex by infrared spectroscopy reveals a strong azide stretch at 2736 cm⁻¹ (Figure 9.6), slightly reduced when compared to the free N₃Ad stretch at 2851 cm⁻¹. Although transition metal azide adducts are often invoked in the mechanism of formation of imido complexes, such adducts have been isolated and characterized.³⁶⁻⁴⁷ Even less common are examples of an azide ligand bound through the γ -N atom, which have been computed or speculated only en route to the nitrene group in transition metals.^{41,43–46,48} Hence, examples of an azide adduct bound through the γ -N atom are quite rare and restricted to precious metals such Ir, Ag, Pd, and Au.^{36,43–45} Nitrene formation from organic azides has been proposed to occur via a [2+2] retrocycloaddition, [2+3] retrocycloadditions, or by a metal nitrene capture.^{38-42,47} Unlike the (pyrr₂py)Fe(OEt₂) species, which readily undergoes a twoelectron oxidation with N₃Ad to form a stable imido complex (pyrr₂py)Fe=NAd,¹⁶ complex 9.3 is remarkably stable as a solid or in solution. To the best of our knowledge, examples of 3d metals showing this type of azide coordination are unknown.



Figure 9.5. Molecular structure of azide adduct **9.3** (left) and nitrene insertion product **9.4** (right) displaying thermal ellipsoids at the 50% probability level.

Over the course of a week, however, C₆D₆ solutions of **9.3** gradually convert to a darker green color, from which a new, less symmetric product retaining both the pincer ligand and the adamantyl group, (pyrrpypyrrNHAd)Co (**9.4**), was formed based on the ¹H NMR spectrum (Scheme 9.3). However, one can expedite the conversion of **9.3** to **9.4** within 1 h in aromatic solvents using irradiation with a 300 V Xe light source. Thermolytic control experiments conducted independently in the

absence of light demonstrated that this transformation is indeed photochemically promoted. When **9.3** is being irradiated, complex **9.4** could be isolated from the mixture in 83% yield by recrystallization from pentane at -35 °C. The solution state IR spectrum of **9.4** exhibits a diagnostic stretch at 2089 cm⁻¹ consistent with the presence of an N–H group. To conclusively establish the exact site of nitrene insertion or ligand activation, X-ray quality single crystals of **9.4** were grown from a concentrated solution of **9.4** in pentane at -35 °C.



Scheme 9.3. Synthesis of complex 9.4 *via* photolysis of 9.3 in benzene.

The molecular structure of **9.4** consists of a four-coordinate Co(II) center bound to the pincer ligand with a pendant secondary amine, in which the NAd group inserted into a C–H bond of a ^tBu group of the pyrr₂py ligand. The geometry of **9.4** is best described as a highly distorted square-planar complex, largely altered from the other complexes in this family that all favored *cis* divacent octahedral geometries (N1–Co1–N4, 90.62°; N1–Co1–N3, 158.4°; N3–Co1–N4, 108.18°; $\tau_4 = 0.37$). Also of intrigue is the significant decrease in the magnetic moment of **9.4** ($\mu_{eff} = 3.9 \mu_B$) relative to that of the *cis*-divacent structures (vide supra; $\mu_{eff} = 4.3$ or 4.7 μ_B), suggesting that the extent of spin–orbit coupling is likely affected by molecular geometry. Complex **9.4** is likely produced by N₂ loss that forms a nitrene species (pyrr₂py)Co=NAd (**9A**), which would then abstract a hydrogen atom from the proximal *tert*-butyl group and, then through radical recombination, forms a new C–N bond. It is also quite possible that upon H atom abstraction, the radical recombination results in the formation of a Co–C bond, akin to the transient imide system reported 271 by Theopold, $Tp^{t-Bu,Me}CoNSiMe_3$ ($Tp^- = [HB(C_3N_2H_3)]^-$, and a well defined imide reported by Betley (^{Ar}L)Co(NMes- d_{11}) ($^{Ar}LH = mesityl-1,9-(2,4,6-$ triphenylphenyl)dipyrromethene). 11a,12 Both of these imides ultimately form Co–C bonds from the ligand scaffold. However, and in our case, one would expect Co(IV) to readily undergo reductive elimination resulting in C–N bond formation, which is what is observed in the case of complex **9.4**.

Conclusion.

Above, the synthesis of several new Co(II) synthons using a pincer-like ligand that enforces a meridional configuration has been presented. Most importantly a rare example of a cobalt azide adduct in which the γ -N binds to the metal center was discussed, which provides a nice comparative example of a late transition metal azido ligand compared to my early transition metal studies. This type of bonding mode has been proposed as an intermediate en route to imido complexes. Furthermore, the binding mode of the organic azide through the γ -N is a motif rarely observed in the literature and often reported as a transient intermediate with an arrested N₂ or even as a transition state.⁴⁸ The *cis*-divacant octahedral geometry observed in species such as 9.1-OEt₂ and 9.3 is due to the meridional constraint imposed by the pincerlike pyrr₂py ligand. This electron rich scaffold allows for the observation of two anodic oxidation waves (in the case of **9.1**-OEt₂) and allows for a photochemical conversion to a transient Co(IV) nitrene (from 9.3) that ultimately inserts into an intramolecular ^tBu C–H bond. This is quite intriguiging when compared with previously discussed titanium azido complex **1.2** vide supra, which was photochemically demonstrated to produce nitridyl radicals. As opposed to C-H insertion, we saw that instead these early transition metal radicals either participated in H-atom abstraction or oxidation of the phosphorous arm of the PN ligand vide supra. Given that these two azido complexes are completely different in nature with one being Ti(III) and the other Co (II), in addition to the azido ligand binding through different nitrogen atoms to these respective precursors, we should indeed expect to observe very different results. All 272

that said, comparing these azido ligands across first row transition metals has been an integral part of my dissertation work at Penn and a subject of my continued interest.

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Experimental Details

General Procedures

Unless otherwise stated, all operations were performed in an M. Braun Lab Master double drybox under an atmosphere of purified dinitrogen or using high-vacuum standard Schlenk techniques under an argon atmosphere. Benzene, diethyl ether (Et2O), pentane, tetrahydrofuran (THF), and toluene were purchased from Fisher Scientific, with the exception of Et20, which was purchased from Sigma-Aldrich. Solvents were sparged with argon for 20 min and dried using a two-column solvent purification system in which columns designated for benzene, pentane, and toluene were packed with Q5 and alumina and columns designated for Et20 were packed with alumina. Deuterated benzene was purchased from Cambridge Isotope Laboratories (CIL), sparged with argon for 20 min, and dried using a two-column solvent purification system packed with Q5. All solvents were transferred into a drybox and stored over 4 Å sieves. All sieves were heated to 200 °C under vacuum overnight prior to use. Celite for filtrations was also heated to 200 °C under vacuum overnight prior to use. $Co[N(SiMe_3)_2]_2$ and H_2pyrr_2py were prepared following the reported literature procedures.^{15,23} All other chemicals were purchased from Strem Chemicals, Aldrich, or Alfa Aesar. ¹H NMR spectra were recorded on Bruker 500 or 400 MHz NMR spectrometers.²⁴

Synthesis of (pyrr₂py)Co(OEt₂) 9.1-OEt₂ via salt metathesis (Method A)

To a 20 mL scintillation vial containing a 3 mL yellow THF solution of H_2pyrr_2py (500 mg, 1.15 mmol) was added dropwise a 3 mL THF solution of K[N{SiMe_3}_2] (460 mg, 2.30 mmol). After being stirred for 2 hours at room temperature, the solution was added dropwise to a blue slurry of CoCl₂ (149 mg, 1.15 mmol) in 5 mL of THF, causing the color to change to dark brown green. The solution was stirred for 20 hours, then THF was removed in vacuo. The resulting brown solid was extracted into pentane and filtered through a pad of Celite. The filtrate was concentrated to dryness, and the resulting purple-brown residue was extracted into 60 mL of diethyl ether and was stirred for 12 hours at room temperature. Red-purple needles formed upon cooling the solution to -35 °C overnight. Yield: 39% (250 mg, 0.45 mmol).

Synthesis of (pyrr2py)Co(OEt₂) 9.1-Et₂O via Protonolysis (method B).²³

To a 20 mL scintillation vial containing a 10 mL green diethyl ether solution of $Co(N{SiMe_3}_2)_2(THF)$ (521 mg, 1.15 mmol) cooled to -35 °C was added a 5 mL diethyl ether solution of H2pyrr2py (500 mg, 1.15 mmol). No notable color change occurred upon addition of the ligand. The solution was warmed to room temperature and then allowed to stir for 18 h. Volatiles were removed in vacuo. The resulting brown solid was extracted into pentane and filtered through a pad of Celite. The filtrate was concentrated to dryness, and the resulting purple-brown residue was extracted into 60 mL of diethyl ether. Cooling the solution to -35 °C overnight resulted in the formation of red-purple needles: yield 82% (530 mg, 0.94 mmol).

¹**H NMR (400 MHz, 298 K, benzene-d₆):** δ 135.3 (s, 2H, Pyrr-*H*), 82.2 (s, 1H, Py-*H_{meta}*), 55.0 (s, 4H, O(C*H*₂CH₃)₂), 15.5 (s, 18H, PyPyrr₂-*t*Bu), -0.67 (s, 6H, O(CH₂C*H*₃)₂), -9.39 (s, 18H, PyPyrr₂-*t*Bu), -23.3 (s, 1H, s, Py-*H_{para}*); μ_{eff} = 4.3 μ_{B} (298 K, benzene-d₆, Evans' method). Multiple attempts to conduct satisfactorily elemental analysis failed.

Synthesis of (pyrr2py)Co·Toluene (9.2·toluene)

To a 20 mL scintillation vial containing a 5 mL green toluene solution of $Co(N{SiMe_3}_2)_2$ (260 mg, 0.686 mmol), which was cooled to -35 °C, was added a 3 mL 274

toluene solution of H_2pyrr_2py (300 mg, 0.692 mmol). The solution was warmed to room temperature, turning a deep red color, and was stirred for 16 h. The volatiles were removed in vacuo. The product was recrystallized from a 7 mL toluene solution at -35 °C overnight: yield 67% (270 mg, 0.463 mmol). Single dark red crystals of 1·toluene were grown by cooling a concentrated pentane solution to -35 °C.

¹**H NMR (400 MHz, 298 K, benzene-d₆):** δ 202.7 (s, 2H, Pyrr-*H*), 89.9 (s, 1H, Py-*H_{meta}*), 35.5 (s, 18H, PyPyrr₂-*t*Bu), 6.78–6.37 (m, 5H, Tol-Ar-*H*), 2.77 (s, 3H, Tol-C*H*₃), 0.74 (brs, 18H, PyPyrr₂-*t*Bu), –51.1 (s, 1H, s, Py-*H_{para}*); μ_{eff} = 4.6 μ_{B} (298 K, benzene-d₆, Evans' method). Anal. Calc'd. for **9.2**·toluene, CoN₃C₃₆H₄₉: C, 74.2; H, 8.48; N, 7.21. Found: C, 71.52; H, 7.99; N, 7.13.

Synthesis of (pyrr₂py)Co(N₃Ad) (9.3)

To a 20 mL scintillation vial containing a 15 mL green toluene solution of $Co(PyPyrr_2)(OEt_2)$ (500 mg, 0.885 mmol) was added a 5 mL toluene solution of 1-azido-adamantane, N₃Ad (157 mg, 0.885 mmol). No notable color change occurred upon addition, and the solution was stirred for 20 h. Toluene was removed in vacuo, leaving a green powder. The product, **9.3**, was recrystallized from a 12 mL pentane solution overnight at –35 °C: yield 67% (400 mg, 0.599 mmol). Single crystals suitable for X-ray diffraction were grown from a concentrated pentane solution at –35 °C.

¹**H NMR (400 MHz, 298 K, benzene-d₆):** δ 134.8 (s, 2H, Pyrr-*H*), 82.2 (s, 2H, Py-*H_{meta}*), 16.7 (s, 18H, PyPyrr₂-*t*Bu), -0.97 (s, 3H, NCHC*H*₂), -2.05 (s, 6H, NCHC*H*₂), -6.72 (s, 18H, PyPyrr₂-*t*Bu), -10.9 (s, 6H, NCHCH₂CHC*H*₂), -24.2 (s, 1H, s, Py-*H_{para}*); μ_{eff} = 4.7 μ_B (298 K, benzene-d₆, Evans' method); IR (toluene) ν_{N3} = 2117, 2090 cm⁻¹. Anal. Calc'd. for **9.3**, CoN₆C₃₉H₅₆: C, 70.14; H, 8.45; N, 12.58. Found: C, 69.40; H, 8.05; N, 11.06.

Photolysis of 9.3 To Form N Insertion Product (pyrrpypyrrNHAd)Co (9.4).

In a J-young NMR tube, a 2 mL C_6D_6 solution of **9.3** (50 mg, 0.075 mmol) was photolyzed with a 300 V xenon lamp for 1 h. The conversion was monitored by 1H NMR spectroscopy in a J-young tube. The J-young tube was brought into a glovebox, 275
where the contents were transferred to a 20 mL scintillation vial and concentrated to dryness under vacuum. The resulting green residue was extracted into 3 mL of pentane and cooled to -35 °C. Green microcrystalline material formed after 2 days at -35 °C: yield 83% (40 mg, 0.0625 mmol). Single crystals suitable for X-ray diffraction were grown from a concentrated pentane solution at -35 °C. ¹H NMR (400 MHz, 298 K, benzene-d₆): δ 128.5 (s, 1H, Pyrr-*H*), 94.3,

90.8, 88.9 (s, 1H ea, Pyrr-*H*, Py-*H_{meta}*), 50.5, 50.4 (s, 6H ea, Ad-*H*), 21.8 (s, 9H, PyPyrr₂-^{*t*}Bu), 5.7 (s, 9H, PyPyrr₂-^{*t*}Bu), -16.3 (s, 6H, PyPyrr₂-C(C*H*₃)₂), -19.8 (s, 3H, Ad-*H*), -21.2 (s, 9H, PyPyrr₂-^{*t*}Bu), -26.6 (s, 2H, PyPyrr₂-CC*H*₂), -44.5 (s, 1H, Py-*H_{meta}*), -92.85 (s, 1H, N*H*); μ_{eff} = 3.9 μ_{B} (298 K, benzene-d₆, Evans' method); IR (toluene) 2089 cm⁻¹. Anal. Calc'd. for CoN₄C₃₉H₅₆: C, 73.21; H, 8.82; N, 8.76. Multiple attempts to obtain satisfactorily elemental analysis failed given the thermal instability of **9.4**.



Figure 9.6. IR spectrum of **9.3**, in toluene. A red dot annotates the observed azide stretch at 2736 cm⁻¹.

Crystallographic Experimental Details

Crystallographic data are summarized Tables 9.1-9.2. Suitable crystals for X-ray analysis of **9.1-9.4** was placed on the end of a Cryoloop coated in NVH oil. Data for single crystal structure determination of **9.1-9.4** were taken on a Bruker ApexII with a CCD, employing graphite-monochromated Mo-Kα radiation (λ =0.71073 Å) at a temperature of 100(1) K. Rotation frames were integrated using SAINT,⁴⁹ producing a listing of non-averaged *F*² and σ (*F*²) values The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS.⁵⁰ The initial structures of **9.1-9.4** were solved by direct methods – SHELXS.⁵¹ Refinement was by full-matrix least squares based on F² using SHELXL-2014.⁵² All reflections were used during refinement. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined with riding models. These results were checked using the IUCR's CheckCIF routine. The alerts in the output are related to the co-crystallized solvents.

Compound	9.1-0Et ₂	9.2 · (C ₇ H ₈)
Molecular formula	$C_{33}H_{51}N_{3}OCo$	$C_{36}H_{49}N_{3}Co$
Formula weight	564.70	582.71
Temperature (K)	100(1)	100
Crystal system	Orthorhombic	Orthorhombic
Space group	Pbcm	Cmcm
Cell constants:		
a (Å)	7.0160(2)	6.8999(4)
b (Å)	18.7659(6)	18.8622(9)

Table 9.1. Crystallographic Data of compounds **9.1**-OEt₂ and **9.2** · toluene.

c (Å)	23.7144(7)	23.8702(11)
Alpha Agle	90	90
Beta Angle	90	90
Gamma Angle	90	90
Volume (Å ³)	3122.27(16)	3106.6(3)
Z	4	4
Density (calcd mg/m3)	1.201	1.246
Abs coeff (mm-1)	0.578	0.581
F(000)	1220	1252
Wavelength	0.71073	0.71073
$\boldsymbol{\theta}$ range for data collection (°)	1.72 to 27.54	1.71 to 27.50
h, k, l ranges collected	$-9 \le h \le 9$	$-8 \le h \le 8$
	$-24 \le k \le 24$	$-24 \leq k \leq 24$
	$-30 \le l \le 30$	$-30 \le l \le 30$
# Reflns collected	3679	1972
Refinement method	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²
R_{I}^{a}	0.0588	0.0569
$wR_{2^{b}}$	0.1539	0.1120
Goodness-of-fit on <i>F2</i> ^c	1.100	1.220

Table 9.2. Crystallographic Data of compounds 9.3 and 9.4.

Compound	9.3	9.4

Molecular formula	$C_{39}H_{56}N_6Co$	$C_{39}H_{56}N_4Co$
Formula weight	667.83	639.81
Temperature (K)	100(1)	100(1)
Crystal system	Monoclinic	Triclinic
Space group	P 2 ₁ /c	P -1
Cell constants:		
a (Å)	13.4981(4)	9.3711(5)
b (Å)	27.7120(7)	12.0040(6)
c (Å) Alpha Agle Beta Angle Gamma Angle	9.8034(3) 90 96.281(2) 90	15.5840(8) 95.925(3) 93.552(3) 99.093(3)
Volume (ų)	3645.04(18)	1716.30(15)
Z	4	2
Density (calcd mg/m3)	1.217	1.238
Abs coeff (mm-1)	0.506	0.533
F(000)	1436	690
Wavelength	0.71073	0.71073
heta range for data collection (°)	1.69 to 27.55	1.73 to 27.54
<i>h, k, l</i> ranges collected	$-17 \le h \le 17$ $-36 \le k \le 36$ $-11 \le l \le 11$	$-12 \le h \le 12$ $-15 \le k \le 15$ $-20 \le l \le 20$
# Reflns collected	8017	7791

Refinement method	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²
$R_1^{\rm a}$	0.0726	0.0434
$wR_{2^{b}}$	0.1422	0.1169
Goodness-of-fit on F2 ^c	0.999	1.101

a R1 = (|Fo| - |Fc|) / |Fo|. b wR2 = [[w(Fo2 - Fc2)2] / [w(Fo2)2]]1/2. c Goodness-of-fit = [[w(Fo2 - Fc2)2]/Nobservns Nparams)]1/2, all data.

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Appendix of Molecules



Figure A.1. Molecular structure of complex **A.1** showing thermal ellipsoids at the 50% probability level. All H-atoms have been omitted for clarity.



Figure A.2. Molecular structure of complex **A.2** showing thermal ellipsoids at the 50% probability level. All H-atoms and disorder of one isopropyl group have been

omitted for clarity. Note that a structure of **A.3** has not been included since this is the same complex, with one molecule of ether in the unit cell.



Figure A.3. Molecular structure of complex **A.4** showing thermal ellipsoids at the 50% probability level. All H-atoms and one molecule of toluene have been omitted for clarity.

Table A.1. Crystallographic Data of compounds **A.1-A.2**.

Compound	A.1	A.2
Molecular formula	$C_{66}H_{106}BKN_3O_{10}PTi$	$C_{44}H_{62}N_8P_2Hf$
Formula weight	1261.29	943.44
Temperature (K)	100(2)	100(1)
Crystal system	Monoclinic	Triclinic
Space group	P 1 2 ₁ /c	P -1
Cell constants:		
a (Å)	13.1383(13)	12.2655(5)

b (Å)	23.882(2)	13.5633(5)
c (Å)	22.580(2)	14.9733(6)
Alpha Agle	90	84.6980(10)
Beta Angle	100.020(5)	69.7100(10)
Gamma Angle	90	78.0800(10)
Volume (Å ³)	6976.8(12)	2285.44(16)
Z	4	2
Density (calcd mg/m3)	1.183	1.371
Abs coeff (mm-1)	0.284	2.391
F(000)	2716	968
Wavelength	0.71073	0.71073
θ range for data collection (°)	1.25 to 27.59	3.071 to 27.564
h, k, l ranges collected	$-17 \le h \le 16$	$-15 \le h \le 15$
	$-31 \le k \le 27$	$-17 \le k \le 17$
	$-29 \le l \le 29$	$-19 \le l \le 19$
# Reflns collected	16122	10531
Refinement method	Full-matrix least- squares on F ²	Full-matrix least-squares on F ²
R_1^{a}	0.0455	0.0200
$wR_{2^{b}}$	0.1075	0.0535
Goodness-of-fit on <i>F2</i> ^c	1.017	1.216

Compound	$A.3 \cdot C_4 H_{10}O$	A.4 · C ₇ H ₈
Molecular formula	$C_{44}H_{62}N_8P_2Hf,$ ($C_4H_{10}O$)	$\begin{array}{c} C_{44}H_{62}ClN_2P_2Sc,\\ (C_7H_8) \end{array}$
Formula weight	1017.56	928.37
Temperature (K)	100	100
Crystal system	Monoclinic	Monoclinic
Space group	P 1 2 ₁ /c 1	P 1 2 ₁ /c 1
Cell constants:		
a (Å)	11.0207(9)	12.3351(7)
b (Å)	16.1978(14)	22.9883(12)
c (Å) Alpha Agle Beta Angle Gamma Angle	27.094(2) 90 93.365(4) 90	17.4009(9) 90 103.888(2) 90
Volume (ų)	4828.2(7)	4790.0(4)
Z	4	4
Density (calcd mg/m3)	1.400	1.287
Abs coeff (mm-1)	2.270	0.284
F(000)	2104	1984
Wavelength	0.71073	0.71073
θ range for data collection (°)	1.851 to 27.524	2.99 to 27.49

Table A.2. Crystallographic Data of compounds **A.3-A.4**.

<i>h, k, l</i> ranges collected	$-14 \le h \le 14$ $-21 \le k \le 21$ $-25 \le l \le 34$	$-16 \le h \le 16$ $-29 \le k \le 29$ $-22 \le l \le 22$	
# Reflns collected	10932	11026	
Refinement method	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²	
R_1^{a}	0.0316	0.0835	
$wR_{2^{b}}$	0.0670	0.1358	
Goodness-of-fit on <i>F2^c</i>	1.088	1.170	



Figure A.4. Molecular structure of complex **A.5** showing thermal ellipsoids at the 50% probability level. All H-atoms and one molecule of toluene have been omitted for clarity.



Figure A.5. Molecular structure of complex **A.6** showing thermal ellipsoids at the 50% probability level. All H-atoms and one molecule of toluene have been omitted for clarity.



Figure A.6. Molecular structure of complex **A.7** showing thermal ellipsoids at the 50% probability level. All H-atoms have been omitted for clarity.



Figure A.7. Molecular structure of complex **A.8** showing thermal ellipsoids at the 50% probability level. All H-atoms have been omitted for clarity.

Compound	A.5	A.6 · C ₇ H ₈
Molecular formula	$C_{44}H_{62}N_5P_2Sc$	C ₄₈ H ₇₃ SiN ₂ P ₂ Sc, (C ₇ H ₈)
Formula weight	767.88	905.20
Temperature (K)	100	100
Crystal system	Monoclinic	Triclinic
Space group	P 1 2 ₁ /c 1	P -1

Table A.3. Crystallographic Data of compounds
 A.5-A.6.

Cell constants:

14.9388(6)	10.6220(3)
12.6791(5)	12.5964(4)
23.0342(10) 90 96.544(2) 90	21.8807(8) 94.962(2) 97.273(2) 112.760(2)
4334.5(3)	2648.40(15)
4	2
1.177	1.135
0.279	0.258
1648	980
0.71073	0.71073
3.10 to 27.55	2.300 to 27.637
$-19 \le h \le 19$ $-16 \le k \le 15$ $-29 \le l \le 29$	$-13 \le h \le 13$ $-16 \le k \le 16$ $-28 \le l \le 28$
9978	12254
Full-matrix least- squares on F ²	Full-matrix least-squares on F ²
0.0432	0.0396
0.0885	0.0889
1.060	1.024
	14.9388(6) 12.6791(5) 23.0342(10) 90 96.544(2) 90 4334.5(3) 4 1.177 0.279 1648 0.71073 3.10 to 27.55 -19 $\leq h \leq 19$ -16 $\leq k \leq 15$ -29 $\leq l \leq 29$ 9978 Full-matrix least-squares on F ² 0.0432 0.0885 1.060

Compound	A.7	A.8
Molecular formula	$C_{45}H_{62}N_2O_3F_3P_2SCe$	$C_{46}H_{62}N_2O_2P_4Zr$
Formula weight	970.09	890.07
Temperature (K)	100(2)	100
Crystal system	Monoclinic	Monoclinic
Space group	P 2 ₁	P 1 2 ₁ /n 1
Cell constants:		
a (Å)	11.6652(4)	18.0417(4)
b (Å)	15.5102(5)	14.6108(4)
c (Å) Alpha Agle Beta Angle Gamma Angle	12.7746(5) 90 92.440(2) 90	19.8177(5) 90 98.9240(10) 90
Volume (Å ³)	2309.21(14)	5160.8(2)
Z	2	4
Density (calcd mg/m3)	1.395	1.146
Abs coeff (mm-1)	1.152	0.284
F(000)	1002	1872
Wavelength	0.71073	0.71073
θ range for data collection (°)	1.75 to 27.53	2.68 to 27.51

 Table A.4. Crystallographic Data of compounds A.7-A.8.

<i>h, k, l</i> ranges collected	$-15 \le h \le 15$ $0 \le k \le 20$ $0 \le l \le 16$	$-23 \le h \le 23$ $-18 \le k \le 19$ $-25 \le l \le 25$
# Reflns collected	5497	11884
Refinement method	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²
R_1^{a}	0.0435	0.0403
$wR_{2^{b}}$	0.1100	0.1015
Goodness-of-fit on <i>F2^c</i>	1.070	1.171



Figure A.8. Molecular structure of complex **A.9** showing thermal ellipsoids at the 50% probability level. All H-atoms, one molecule of **A.9** and one molecule of toluene have been omitted for clarity.



Figure A.9. Molecular structure of complex **A.10** showing thermal ellipsoids at the 50% probability level. All H-atoms and one molecule of toluene have been omitted for clarity.



Figure A.10. Molecular structure of complex **A.11** showing thermal ellipsoids at the 50% probability level. All H-atoms have been omitted for clarity.



Figure A.11. Molecular structure of complex **A.12** showing thermal ellipsoids at the 50% probability level. All H-atoms, disorder of the As atom, and disorder of one isopropyl group have been omitted for clarity.

Table A.5. Crystallographic Data of compounds A.9-A.10.

Compound	2(A.9) · C ₇ H ₈	A.10 · C ₇ H ₈
Molecular formula	2(C ₄₅ H ₆₅ N ₂ P ₂ V), (C ₇ H ₈)	$C_{44}H_{65}N_3P_2V$, (C_7H_8)
Formula weight	1585.87	841.00
Temperature (K)	100	100
Crystal system	Triclinic	Monoclinic
Space group	P -1	P 1 2 ₁ /c 1

Cell constants:

a (Å)	12.8064(4)	12.3507(5)
b (Å)	15.8450(5)	22.9606(12)
c (Å) Alpha Agle Beta Angle Gamma Angle	24.9106(8) 78.8440(10) 76.1570(10) 89.1890(10)	17.1614(7) 90 105.021(2) 90
Volume (ų)	4812.5(3)	4700.3(4)
Z	2	4
Density (calcd mg/m3)	1.094	1.188
Abs coeff (mm-1)	0.304	0.316
F(000)	1708	1812
Wavelength	0.71073	0.71073
θ range for data collection (°)	3.01 to 27.52	2.93 to 27.52
<i>h, k, l</i> ranges collected	$-16 \le h \le 14$ $-20 \le k \le 20$ $-32 \le l \le 32$	$-16 \le h \le 16$ $-29 \le k \le 29$ $-22 \le l \le 22$
# Reflns collected	22167	10803
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
R_1^{a}	0.0438	0.0370
$wR_{2^{b}}$	0.0917	0.0862
Goodness-of-fit on <i>F2^c</i>	1.016	1.033

Compound	A.11	A.12	
Molecular formula	$C_{34}H_{61}Si_2NOPSc$	$C_{46}H_{66}AsN_2O_3Sc$	_
Formula weight	631.94	814.88	
Temperature (K)	100	100	
Crystal system	Orthorhombic	Monoclinic	
Space group	F d d 2	C 1 2/c 1	
Cell constants:			
a (Å)	29.3058(12)	37.919(3)	
b (Å)	52.144(2)	11.2713(9)	
c (Å) Alpha Agle Beta Angle Gamma Angle	9.9572(4) 90 90 90	20.8687(13) 90 91.866(3) 90	
Volume (ų)	15215.9(11)	8914.4(11)	
Z	16	8	
Density (calcd mg/m3)	1.103	1.214	
Abs coeff (mm-1)	0.323	0.941	
F(000)	5504	3472	
Wavelength	0.71073	0.71073	
θ range for data collection (°)	1.562 to 27.499	2.421 to 27.547	

Table A.6. Crystallographic Data of compounds **A.11-A.12**.

<i>h, k, l</i> ranges collected	$-38 \le h \le 37$ $-67 \le k \le 67$ $-12 \le l \le 12$	$-49 \le h \le 49$ $-14 \le k \le 14$ $-21 \le l \le 26$
# Reflns collected	8733	10164
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
R_1^{a}	0.0357	0.0300
$wR_{2^{b}}$	0.0815	0.0753
Goodness-of-fit on <i>F2^c</i>	1.035	1.038



Figure A.12. Molecular structure of complex **A.13** showing thermal ellipsoids at the 50% probability level. All H-atoms have been omitted for clarity.



Figure A.13. Molecular structure of complex **A.14** showing thermal ellipsoids at the 50% probability level. All H-atoms and disorder of a Cl have been omitted for clarity.



Figure A.14. Molecular structure of complex **A.15** showing thermal ellipsoids at the 50% probability level. All H-atoms have been omitted for clarity.



Figure A.15. Molecular structure of complex **A.16** showing thermal ellipsoids at the 50% probability level. All H-atoms and two molecules of toluene have been omitted for clarity. Note that a structure of **A.19** has not been included since this is the same complex, with ether bound to the sodium cation as opposed to 1,4-dioxane.

Compound	A.13	A.14
Molecular formula	$C_{53}H_{75}N_2O_2Sc$	$\begin{array}{c} C_{49.75}H_{67}Cl_{0.25}N_{3}\\ O_{0.75}P_{0.75}Ti \end{array}$
Formula weight	1340.18	799.05
Temperature (K)	100	100
Crystal system	Orthorhombic	Monoclinic
Space group	$P 2_1 2_1 2_1$	P 1 2 ₁ /c 1

Table A.7. Crystallographic Data of compounds **A.13-A.14**.

Cell constants:

a (Å)	10.7359(6)	19.4614(12)
b (Å)	21.1753(12)	13.1209(8)
c (Å) Alpha Agle Beta Angle Gamma Angle	21.1934(12) 90 90 90 90	20.1591(13) 90 110.724(2) 90
Volume (ų)	4818.0(5)	4814.6(5)
Z	4	4
Density (calcd mg/m3)	1.126	1.102
Abs coeff (mm-1)	0.193	0.252
F(000)	1776	1720
Wavelength	0.71073	0.71073
θ range for data collection (°)	3.042 to 27.575	3.17 to 27.52
<i>h, k, l</i> ranges collected	$-13 \le h \le 13$ $-27 \le k \le 27$ $-27 \le l \le 26$	$-25 \le h \le 25$ $-17 \le k \le 17$ $-26 \le l \le 26$
# Reflns collected	11107	11066
Refinement method	Full-matrix least- squares on F ²	Full-matrix least-squares on F ²
$R_{1^{\mathrm{a}}}$	0.0669	0.0470
$wR_{2^{b}}$	0.1107	0.0986
Goodness-of-fit on F2 ^c	1.063	1.081

Compound	A.15	A.16 · 2(C ₇ H ₈)
Molecular formula	$C_{49}H_{67}N_3Ti$	C94H132Na2O10 N4V2, 2(C7H8)
Formula weight	745.95	1810.16
Temperature (K)	100	100
Crystal system	Triclinic	Monoclinic
Space group	P -1	P 1 2 ₁ /n 1
Cell constants:		
a (Å)	10.550(6)	18.6749(11)
b (Å)	11.374(6)	12.8690(8)
c (Å) Alpha Agle Beta Angle Gamma Angle	19.835(10) 96.16(3) 100.11(2) 110.32(3)	22.0623(13) 90 107.066(3) 90
Volume (Å ³)	2161(2)	5068.7(5)
Z	2	2
Density (calcd mg/m3)	1.147	1.186
Abs coeff (mm-1)	0.234	0.251
F(000)	808	1944
Wavelength	0.71073	0.71073
θ range for data collection (°)	3.12 to 27.69	2.32 to 27.44

Table A.8. Crystallographic Data of compounds A.15-A.16.

<i>h, k, l</i> ranges collected	$-13 \le h \le 13$ $-14 \le k \le 14$ $-25 \le l \le 25$	$-24 \le h \le 23$ $0 \le k \le 16$ $0 \le l \le 28$
# Reflns collected	10100	11604
Refinement method	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²
R_1^{a}	0.0979	0.0574
$wR_{2^{b}}$	0.2254	0.1389
Goodness-of-fit on <i>F2^c</i>	1.144	1.049



Figure A.16. Molecular structure of complex **A.17** showing thermal ellipsoids at the 50% probability level. All H-atoms and one molecule have been omitted for clarity.



Figure A.17. Molecular structure of complex **A.18** showing thermal ellipsoids at the 50% probability level. All H-atoms and one molecule of diethyl ether have been omitted for clarity.



Figure A.18. Molecular structure of complex **A.20** showing thermal ellipsoids at the 50% probability level. All H-atoms and have been omitted for clarity.

Compound	A.17	A.18 · C ₄ H ₁₀ O
Molecular formula	$C_{42}H_{58}F_3N_2O_4SV$	$C_{63}H_{94}As_3N_4O_2V_2$, (C4H ₁₀ O)
Formula weight	794.90	1672.04
Temperature (K)	100	100
Crystal system	Tetragonal	Monoclinic
Space group	P 4 ₁	P 1 2 ₁ /c 1
Cell constants:		
a (Å)	12.2806(6)	23.2303(19)
b (Å)	12.2806(6)	13.8748(12)
c (Å) Alpha Agle Beta Angle	27.8404(15) 90 90	25.097(2) 90 116.676(4)
Gamma Angle	90	90
Volume (Å ³)	4198.7(5)	7228.1(11)
Z	4	4
Density (calcd mg/m3)	1.257	1.232
Abs coeff (mm-1)	0.341	1.664
F(000)	1688	2812
Wavelength	0.71073	0.71073

Table A.9. Crystallographic Data of compounds **A.17-A.18**.

θ range for data collection (°)	2.927 to 27.475	2.47 to 27.60
<i>h, k, l</i> ranges collected	$-15 \le h \le 15$ $-15 \le k \le 15$ $-36 \le l \le 36$	$-30 \le h \le 30$ $-18 \le k \le 17$ $-32 \le l \le 32$
# Reflns collected	9642	16545
Refinement method	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²
R_1^{a}	0.0513	0.0506
$wR_{2^{b}}$	0.0786	0.1254
Goodness-of-fit on F2 ^c	1.027	1.027

Table A.10. Crystallographic Data of compounds **A.19-A.20**.

Compound	$A.19 \cdot C_4 H_{10}O$	A.20	
Molecular formula	C94H136N4Na2O8V2, (C4H10O)	$C_{56}H_{88}NaO_6V$	
Formula weight	1672.04	931.19	
Temperature (K)	100	100	
Crystal system	Monoclinic	Triclinic	
Space group	C 1 2/c 1	P -1	
Cell constants:			
a (Å)	36.652(2)	12.3920(6)	
b (Å)	17.2092(10)	12.8040(6)	

c (Å) Alpha Agle Beta Angle Gamma Angle	30.9582(18) 90 101.272(2) 90	20.1562(10) 77.459(2) 81.957(2) 66.426(2)
Volume (Å ³)	19150.2(19)	2856.3(2)
Z	8	2
Density (calcd mg/m3)	1.160	1.083
Abs coeff (mm-1)	0.260	0.225
F(000)	7216	1012
Wavelength	0.71073	0.71073
θ range for data collection (°)	3.02 to 27.55	2.47 to 27.55
<i>h, k, l</i> ranges collected	$-47 \le h \le 47$ $-22 \le k \le 22$ $-40 \le l \le 40$	$-16 \le h \le 14$ $-16 \le k \le 16$ $-26 \le l \le 26$
# Reflns collected	22110	12804
Refinement method	Full-matrix least-squares on F ²	Full-matrix least- squares on F ²
R_1^{a}	0.0643	0.0441
$wR_{2^{b}}$	0.1287	0.1152
Goodness-of-fit on F2 ^c	1.091	1.071



Figure A.19. Molecular structure of complex **A.21** showing thermal ellipsoids at the 50% probability level. All H-atoms one molecule of toluene have been omitted for clarity.



Figure A.20. Molecular structure of complex **A.22** showing thermal ellipsoids at the 50% probability level. All H-atoms, aryl isopropyl groups, and one molecule of hexane have been omitted for clarity.



Figure A.21. Molecular structure of complex **A.23** showing thermal ellipsoids at the 50% probability level. All H-atoms, aryl isopropyl groups, and three molecules of toluene have been omitted for clarity.



Figure A.22. Molecular structure of complex **A.24** showing thermal ellipsoids at the 50% probability level. All H-atoms and one molecule of ether (including ether disorder and isorder of an aryl group) have been omitted for clarity.

Table A.11. Crystallographic Data of compounds
 A.21-A.22.

Compound	A.21 · C ₇ H ₈	$A.22 \cdot C_6H_{14}$
Molecular formula	C ₄₇ H ₅₆ N ₃ OPCo, (C ₇ H ₈)	C ₆₄ H ₁₀₂ Fe ₂ Li ₂ N ₄ O ₂ , (C ₆ H ₁₄)
Formula weight	860.98	1171.24
Temperature (K)	100	100
Crystal system	Monoclinic	Monoclinic
Space group	P 1 2 ₁ /n 1	C 1 2/c 1
Cell constants:		
a (Å)	10.2812(3)	24.3513(8)
b (Å)	23.7199(8)	12.2438(5)
--	--	--
c (Å) Alpha Agle Beta Angle Gamma Angle	19.8291(7) 90 103.725(2) 90	25.8541(13) 90 116.724(2) 90
Volume (Å ³)	4697.6(3)	6885.1(5)
Z	4	4
Density (calcd mg/m3)	1.217	1.130
Abs coeff (mm-1)	0.440	0.465
F(000)	1836	2552
Wavelength	0.71073	0.71073
θ range for data collection (°)	2.72 to 27.56	2.87 to 27.51
<i>h, k, l</i> ranges collected	$-12 \le h \le 13$ $-30 \le k \le 30$ $-25 \le l \le 25$	$-30 \le h \le 31$ $-15 \le k \le 15$ $-33 \le l \le 33$
# Reflns collected	10814	7918
Refinement method	Full-matrix least- squares on F ²	Full-matrix least-squares on F ²
$R_{1^{\mathrm{a}}}$	0.0340	0.0518
$wR_{2^{b}}$	0.0790	0.1364
Goodness-of-fit on <i>F2^c</i>	1.022	1.054

Table A.12. Crystallographic Data of compounds A.23-A.24.

Compound	A.23 · 3(C ₇ H ₈)	$A.24 \cdot C_4 H_{10}O$

Molecular formula	C ₅₈ H ₈₆ Fe ₂ N ₄ , 3(C ₇ H ₈)	C ₄₇ H ₅₇ N ₂ ClPFe, (C ₄ H ₁₀ O)
Formula weight	1227.40	846.33
Temperature (K)	100	100
Crystal system	Monoclinic	Triclinic
Space group	C 1 2/c 1	P -1
Cell constants:		
a (Å)	21.3473(5)	12.7941(4)
b (Å)	15.1676(4)	12.8930(4)
c (Å) Alpha Agle Beta Angle Gamma Angle	23.3801(5) 90 108.1760(10) 90	16.3940(5) 74.557(2) 80.329(2) 66.304(2)
Volume (Å ³)	7192.4(3)	2381.16(13)
Z	4	2
Density (calcd mg/m3)	1.232	1.180
Abs coeff (mm-1)	1.133	0.443
F(000)	2656	906
Wavelength	0.71073	0.71073
θ range for data collection (°)	2.71 to 27.51	2.41 to 27.53
<i>h, k, l</i> ranges collected	$-27 \le h \le 27$ $-19 \le k \le 19$ $-30 \le l \le 30$	$-16 \le h \le 16$ $-16 \le k \le 16$ $-21 \le l \le 21$
# Reflns collected	8304	11009

Refinement method	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²
R_{I}^{a}	0.0309	0.0363
$wR_{2^{b}}$	0.0777	0.0940
Goodness-of-fit on F2 ^c	1.019	1.098



Figure A.23. Molecular structure of complex **A.25** showing thermal ellipsoids at the 50% probability level. All H-atoms and aryl isopropyl groups have been omitted for clarity.



Figure A.24. Molecular structure of complex **A.26** showing thermal ellipsoids at the 50% probability level. All H-atoms have been omitted for clarity.

 Table A.13. Crystallographic Data of compounds A.25-A.26.

Compound	A.25	A.26
Molecular formula	$C_{60}H_{88}Cl_3N_4O_2Ti_2$	$C_{38}H_{54}ClN_4OTi$
Formula weight	1099.49	666.20
Temperature (K)	100	100
Crystal system	Monoclinic	Triclinic
Space group	P 1 2 ₁ /n 1	P -1
Cell constants:		
a (Å)	12.4716(4)	12.7913(5)
b (Å)	20.9467(6)	13.1174(5)
c (Å) Alpha Agle Beta Angle Gamma Angle	23.2127(7) 90 103.869(2) 90	14.6262(6) 80.497(2) 82.922(2) 63.6750(10)

Volume (Å ³)	5887.3(3)	2165.94(15)
Z	4	2
Density (calcd mg/m3)	1.240	1.021
Abs coeff (mm-1)	0.440	0.288
F(000)	2348	714
Wavelength	0.71073	0.71073
θ range for data collection (°)	1.327 to 27.526	2.98 to 27.57
<i>h, k, l</i> ranges collected	$-16 \le h \le 16$ $-26 \le k \le 27$ $-30 \le l \le 30$	$-16 \le h \le 13$ $-17 \le k \le 17$ $-19 \le l \le 19$
# Reflns collected	13563	9997
Refinement method	Full-matrix least- squares on F ²	Full-matrix least-squares on F ²
R_{I}^{a}	0.0366	0.0382
$wR_{2^{b}}$	0.0803	0.0850
Goodness-of-fit on F2 ^c	1.007	1.039

 a R1 = (|Fo| - |Fc|) / |Fo|. b wR2 = [[w(Fo2 - Fc2)2] / [w(Fo2)2]]1/2. c Goodness-of-fit

 = [[w(Fo2 - Fc2)2]/Nobservns Nparams)]1/2, all data.