

Oxidatively Induced Abstraction Reactions. A Synthetic Approach to Low-Coordinate and Reactive Early Transition Metal Complexes Containing Metal–Ligand Multiple Bonds

DANIEL J. MINDIOLA*

Department of Chemistry, Indiana University,
Bloomington, Indiana 47405

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ABSTRACT

A library of low-coordinate titanium and vanadium complexes containing terminal metal–ligand multiply bonded functionalities such as alkylidenes, alkylidynes, and imides have been prepared by one-electron oxidatively induced α -hydrogen abstraction reactions. In the case of the alkylidene motif, the nucleophilic nature of the M–C multiple bond permits subsequent reactions such as α -hydrogen migration to generate other rare functionalities such as phosphinidene–alkyl and imide–alkyls. Identifying and fine-tuning of the supporting ancillary ligand on the metal has allowed the isolation of kinetically stable titanium alkylidene and phosphinidene systems. The former is a key functionality to generate transient titanium alkylidynes, which readily engage in intermolecular C–H activation reactions of arenes and alkanes, and the ring-opening metathesis of aromatic substrates such as pyridines. In this Account, we describe several synthetic strategies to achieve reactive functionalities, functionalities that were previously portrayed as “incompatible” or “too kinetically reactive” with 3d early transition metals.

1. Introduction

High-oxidation-state transition metal alkylidenes are an important functionality to industrial processes such as cross-metathesis, ring-closing metathesis, ring-opening metathesis, ring-opening metathesis polymerization, acyclic diene metathesis polymerization, acetylene polymerization, and Wittig-type or group-transfer reactions. The increasing importance of metal alkylidene complexes has been manifested in several reviews¹ and highlights,² with the most prominent result being the 2005 Nobel Prize in Chemistry bestowed to Chauvin, Grubbs, and Schrock.³ Likewise, the closely related functionality, the alkylidyne, is now beginning to be applied in catalytic processes such as alkyne metathesis and polymerization reactions.⁴

Parallel to the metal–carbon double bond functionality is the isolobal nitrene group (:NR).⁵ As expected, the imide

functionality also assumes its rightful place alongside the M=C bond since such systems play pivotal roles in stoichiometric :NR group transfer,⁵ catalytic processes such as the intermolecular hydroamination of alkynes^{5,5–10} and alkenes,¹¹ hydrohydrazination,¹² aziridination,^{5a} multicomponent coupling reactions,¹³ guanylations,¹⁴ and recently carboamination,¹⁵ among other important transformations.^{5a} Unlike high-oxidation-state transition metal alkylidenes, the imide functionality is versatile, and on occasion it can behave as an ancillary ligand purely invoked in stabilizing reactive metal fragments during the catalytic cycle.^{5a,5h} Such a contrast between :CR₂ and :NR motifs can be partially blamed on the highly nucleophilic or “Schrock-like” nature of the alkylidene ligand when bound to a very electropositive metal. Hence, alkylidene complexes are often represented as $^+M-CR_2^- \leftrightarrow M=CR_2$, much like ylides resonate, while imides can be depicted as $^-M\equiv N^+R$ instead of $M=NR$.

In contrast to alkylidenes or imides, high-oxidation-state transition metal phosphinidenes continue to be a scant functionality.¹⁶ These systems have drawn popularity in the past decade given their ability to perform important transformations such as phospho-Staudinger or -Wittig-type reactions for the construction of low-coordinate phosphoorganic molecules.¹⁷ Specifically, d⁰ phosphinidene complexes are the “carbon copy”^{17b} of the Schrock-type alkylidenes since phosphorus is slightly more electropositive than carbon.

As a result, M–C, M–N, and M–P multiply bonded linkages are all important and related functionalities given their involvement in catalysis and group-transfer processes. Therefore, organometallic chemists are continuously discovering new synthetic routes to these motifs, especially in low-coordination environments since unsaturated organotransition metal complexes are inherently reactive and provide useful templates to study small molecule activation^{5c} and catalysis.^{5a,5g} In this Account, we will describe a series of synthetic methods to achieve these types of functionalities with the transition metals titanium and vanadium. Some subsequent reactivity involving these ligands will also be presented and discussed.

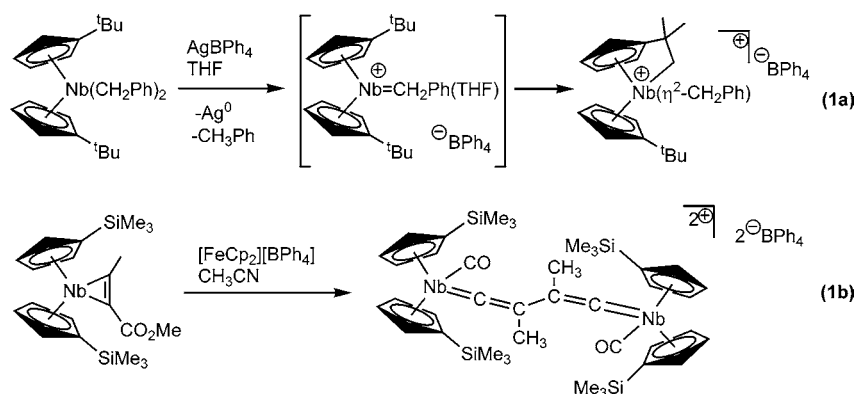
2. Accessing Low-Coordinate Early Transition Metal Complexes (Metal = Ti or V) Having Terminal Alkylidene Functionalities

Despite rapid growth of research in the area of high-valent metal alkylidenes,¹ far less attention has been applied to the synthesis and reactivity of terminal alkylidene complexes of 3d early transition metals. The rather low number of terminal alkylidene complexes of titanium is somewhat surprising since titanium alkylidenes generated in situ are utilized commonly as stoichiometric reagents in organic synthesis.¹⁸ So why are first row early transition metal alkylidenes so scarce? First, it is necessary to know how high-oxidation-state transition metal alkylidenes are commonly prepared, and second, it is important to

* E-mail: mindiola@indiana.edu.

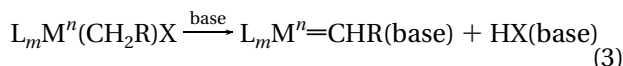
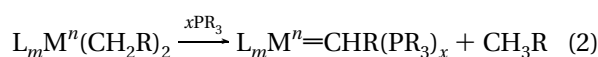
Daniel Mindiola was born in San Cristóbal, Venezuela, in 1974. In 1996, he received a B.S. degree in chemistry with honors from Michigan State University and then completed a Ph.D. in chemistry from the Massachusetts Institute of Technology under the guidance of Prof. C. C. Cummins (2000). Following a postdoctoral fellowship with Prof. G. L. Hillhouse at the University of Chicago, he then began his independent work in 2002 as an Assistant Professor at Indiana University in Bloomington, Indiana.

Scheme 1

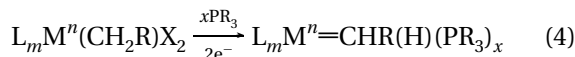


consider the trends in the periodic table between first row transition metals and second and third row congeners.

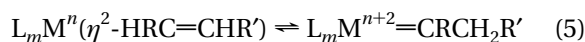
The most common method to prepare high-oxidation-state metal alkylidenes is by promoting α -abstraction or α -deprotonation reactions from metal alkyl complexes lacking β -hydrogens (eqs 1–3).¹ In order to promote the



α -hydrogen abstraction to yield high-oxidation-state metal alkylidenes, one must typically stimulate photochemically (eq 1), sterically (eq 2), or with a base (eq 3) the high-valent metal center.^{1,19,20} An elegant but rare approach to the terminal alkylidene functionality involves a two-electron reduction step, which promotes an α -hydrogen migration (eq 4).²¹ Last, olefin rearrangement to the d^0



alkylidene has also been documented (eq 5).²² Since first

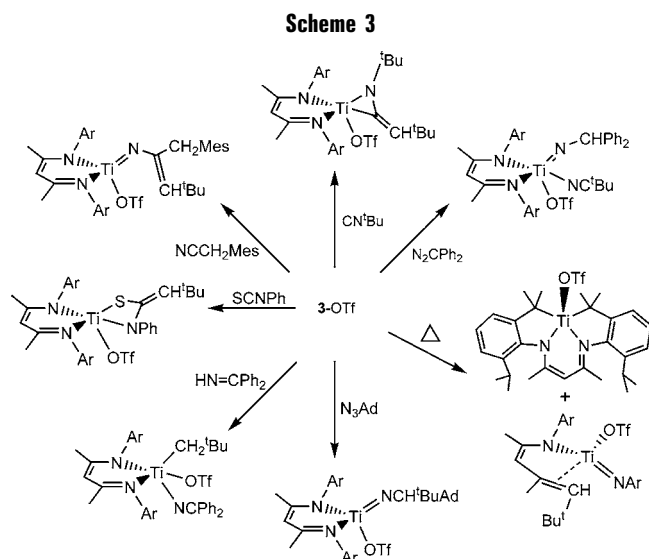
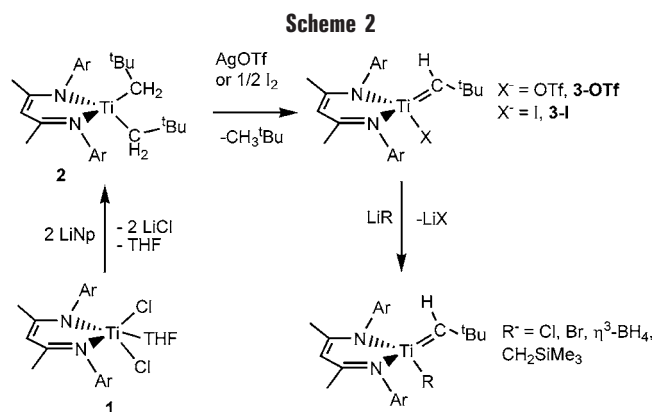


row early transition metals are far more readily reduced than the second and third row congeners, reduction reactions are far more common, hence limiting the alkylation step in the high-valent state. Unavoidably, this property makes dehydrohalogenation or α -hydrogen abstraction reactions much more common for the heavy congeners.

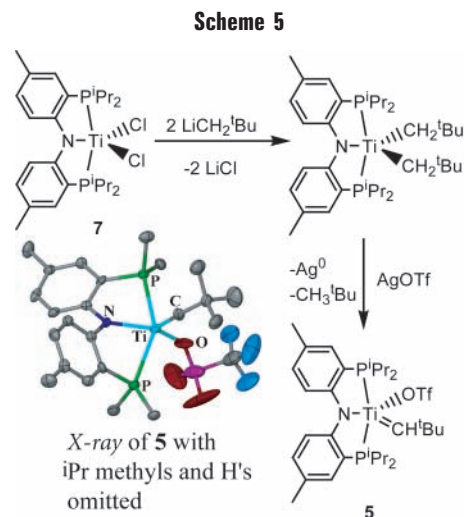
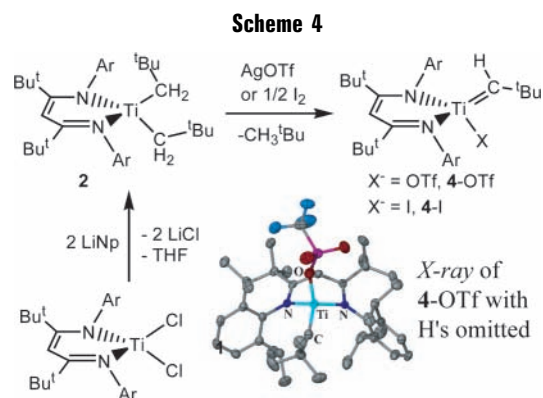
2a. Oxidatively Induced α -Hydrogen Abstraction Reactions. The entry into d^0 -metal alkylidenes is often restricted to α -H abstraction reactions where a good leaving group is generated (e.g., an alkane or a very weak conjugate acid). In addition, access to low-coordinate systems possessing this functionality can be difficult or limited, since formation of the metal–alkylidene bonds typically stems from a high-oxidation-state and coordinatively saturated complex (eqs 1–4). For this reason, an attractive entry to the assembly of low-coordinate systems

possessing metal–ligand multiple bonds can be derived from a redox reaction where the low-valent metal is alkylated, then oxidized.²³ Oxidatively induced α -hydrogen abstraction reactions to generate reactive $\text{M}=\text{C}$ bonds can be traced back to the work by Cooper and co-workers (referred to as an H atom transfer).²⁴ However, it was not until 1995 that McCamley and co-workers trapped a transient niobium alkyldiene by a redox route.²⁵ Their studies described the one-electron oxidation of $\text{Nb}(\text{IV})-(\eta^5\text{-C}_5\text{H}_4\text{tBu})_2(\text{CH}_2\text{Ph})_2$ with AgBPh_4 to generate a Ag^0 mirror along with the kinetically unstable benzylidene $[\text{Nb}(\text{V})(\eta^5\text{-C}_5\text{H}_4\text{tBu})_2(\text{CHPh})][\text{BPh}_4]$ salt.²⁵ The latter intermediate underwent facile C–H activation reactions in toluene to afford the cyclometallated product (Scheme 1a). The mechanism of the C–H activation reaction was not discussed in their work. A similar process involving one-electron oxidation to generate $\text{M}=\text{C}$ linkages was reported by Otero and co-workers.²⁶ In their work, one-electron oxidation of the $\text{Nb}(\text{IV})$ alkyne $\text{Cp}'_2\text{Nb}(\eta^2\text{-MeOC}(\text{O})\text{C}\equiv\text{CMe})$ ($\text{Cp}' = \text{C}_5\text{H}_4\text{SiMe}_3$) with $[\text{FeCp}_2][\text{BPh}_4]$ generated a binuclear vinylidene complex (Scheme 1b).²⁶ Unfortunately, the mechanism of this reaction remains to be clarified. Work by Cooper, McCamley, and Otero suggested, tantalizingly, that high-valent metal–carbon multiple bonds could be assembled under a one-electron oxidation pathway, provided a good leaving group was generated in the process. Could similar reactions be applied to the lighter congeners of group 4 and 5 transition metals? Of particular interest was the seminal work reported by Budzelaar²⁷ and Theopold²⁸ on redox active and stable early transition metal d^x ($x = 1\text{--}3$) complexes having metal alkyl ligands. These complexes contain first row transition metals prone to one-electron oxidation, where the leaving group would be an entropically and thermodynamically favorable product like an alkane.

2b. Synthesis of Low-Coordinate Titanium Alkylidenes. The protocol to prepare low-coordinate and terminal titanium alkylidene complexes involved a modification of the synthesis of $(\text{nacnac})\text{TiCl}_2$ ($\text{nacnac}^- = [\text{Ar}]\text{NC}(\text{Me})\text{CHC}(\text{Me})\text{N}[\text{Ar}]$, $\text{Ar} = 2,6\text{-(CHMe}_2)_2\text{C}_6\text{H}_3$), reported previously by Budzelaar and co-workers.²⁷ We chose the sterically encumbering nacnac^- ligands given their precedent to generate low-coordination environments.²⁹ Following Budzelaar's procedure, we recrystal-

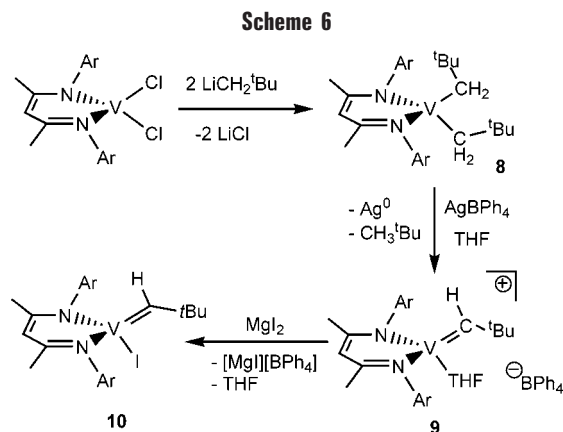


lized the THF base adduct (nacnac)TiCl₂(THF) (**1**) from toluene in 70% yield as dark green blocks. Ether solutions of **1** react smoothly with 2 equiv of LiCH₂tBu to afford emerald green solutions of (nacnac)Ti(CH₂tBu)₂ (**2**), which resulted in formation of dark blocks in excellent yield.³⁰ When complex **2** was treated with AgOTf or 1/2 equiv of I₂, a rapid color change from green to red brown was observed concurrent with formation of the alkylidene complexes (nacnac)Ti=CHtBu(X) (X⁻ = OTf, **3-OTf**, 89%; X⁻ = I, **3-I**, 61%) as evaluated by ¹H and ¹³C NMR spectroscopic methods (Scheme 2).^{30,31} Compounds **3-OTf** and **3-I** display C_s symmetry in solution and have a C_α resonance centered at δ ≈ 271–272 ppm with a J_{CH} coupling constant of 90–85 Hz. The latter parameters are consistent with these systems having a terminal alkylidene functionality where there is significant α-hydrogen agostic interaction with the low-coordinate metal center. The low-coordination number in **3-OTf** and **3-I** was also confirmed by single-crystal crystallographic studies.^{30,31} We speculate that complexes **3-OTf** and **3-I** are formed from the putative five-coordinate and d⁰ intermediate (nacnac)-Ti(CH₂tBu)₂(X),³² which then undergoes smooth α-hydrogen abstraction to form the Ti=C linkage. The labile pseudohalide group in **3-OTf** can be exchanged readily for Cl⁻, Br⁻, BH₄⁻, and ⁻CH₂SiMe₃ to afford other alkylidene analogues thereby creating a new class of titanium alkylidene complexes (Scheme 2).³¹ In addition to trans-



metallation reactions, complex **3-OTf** can also engage in Wittig-like, acid–base, and intramolecular C–H activation rearrangements (Scheme 3 displays a pinwheel of reactivity for **3-OTf**).^{30,31,33} To block these decomposition pathways from occurring, we prepared Ti(III) precursors supported by more robust ancillary ligands such as nacnac^{tBu-} ([Ar]NC(tBu)CHC(tBu)N[Ar], Ar = 2,6-(CHMe)₂C₆H₃) and PNP⁻ (N[2-P(CHMe)₂-4-methylphenyl]₂).³⁴ As a result, kinetically stable titanium alkylidene complexes such as (nacnac^{tBu})Ti=CHtBu(X) (X⁻ = OTf, **4-OTf**; X⁻ = I, **4-I**), and (PNP)Ti=CHtBu(OTf) (**5**) can also be prepared via the one-electron oxidatively induced α-hydrogen abstraction protocol but using instead the precursors (nacnac^{tBu})TiCl₂ (**6**) and (PNP)TiCl₂ (**7**) (Schemes 4 and 5, respectively). It is important to note that attempts to integrate the neopentylidene functionality directly onto Ti(IV) led to a myriad of products. Hence, in order to avoid reduction pathways in the alkylation process, one must first alkylate a lower-valent Ti^{III} precursor and then oxidize by one-electron to promote the α-hydrogen abstraction. We have determined that both bulky alkyl groups and large coordinating anions are needed in order to promote steric crowding and subsequent α-hydrogen abstraction.³²

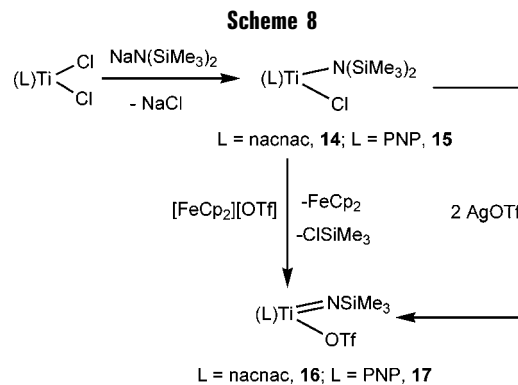
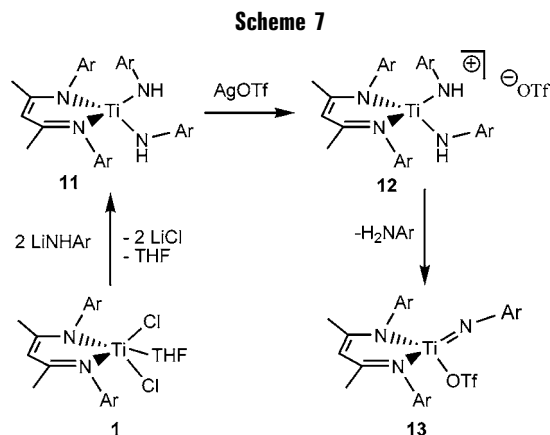
2c. Synthesis of Low-Coordinate Vanadium Alkylidenes. Our recent strategy to prepare the first four-coordinate titanium neopentylidene via an oxidatively induced α-abstraction reaction³⁰ motivated us to pursue other 3d transition metals that lacked such a motif.^{35,36} Unlike titanium, vanadium displays more di-



verse redox chemistry; hence oxidation states ranging from +2 to +5 are commonly allowed. Using Budzelaar's precursor (nacnac)VCl₂²⁷ and 2 equiv of LiCH₂^tBu, we prepared the *bis*-neopentyl complex (nacnac)V(CH₂^tBu)₂ (**8**) in 80% yield as dark brown needles (Scheme 6).³⁶ One-electron oxidation of **8** with AgBPh₄ generated a Ag⁰ mirror concurrent with the vanadium(IV) alkylidene complex [(nacnac)V=CH^tBu(THF)][BPh₄] (**9**) in 74% yield (Scheme 6). By anion exchange with MgI₂, the neutral vanadium(IV) alkylidene (nacnac)V=CH^tBu(I) (**10**) can be readily prepared.³⁶ Cationic and neutral complexes such as **9** and **10** are paramagnetic and therefore display EPR spectra consistent with a doublet ground state and reveal coupling to the vanadium center ($I = 7/2$, 99.6%).³⁶ Molecular structures for each system reveal α -H agostic interactions taking place with the d¹-metal center. More importantly, the d¹ nature of these systems prevents α -H migration from occurring. Compounds **9** and **10** are also reactive, inasmuch as thermolysis of each lead to THF dehydrogenation or Wittig-like rearrangement, respectively.³⁶

3. Synthesis of M–N Multiply Bonded Systems

3a. Oxidatively Induced α -Hydrogen Abstraction Reactions to Prepare Low-Coordinate Titanium Imides. The synthesis of **3** stimulated the pursuit of an analogous titanium imide complex. Intuitively, NH abstraction should be more facile than C–H, especially since metal–imide formation is thermodynamically more favorable than M=C given the ability of imides to form a pseudo M \equiv NR linkage with an early transition metal. The dichloride precursor (nacnac)TiCl₂(THF)³⁰ reacts readily with 2 equiv of LiNHAr to afford the *bis*-anilido titanium(III) complex (nacnac)Ti(NHAr)₂ (**11**) in 92% yield (Ar = 2,6-ⁱPr₂C₆H₃, Scheme 7).³⁹ Chemical oxidation of **11** with AgOTf caused a color change from green to orange-red concomitant with formation of a Ag⁰ mirror. Immediate workup of the reaction afforded the *bis*-anilido triflate salt [(nacnac)Ti(NHAr)₂][OTf] (**12**) in 71% yield (Scheme 7).³⁷ Complex **12** is remarkably stable as a solid, but solutions of **12** slowly transform to the four-coordinate titanium imide (nacnac)-Ti=NAr(OTf) (**13**) and H₂NAr, and the former can be isolated as red prisms in 67% yield (Scheme 7).³⁷ Unlike complex **2**, which displays an irreversible oxidative wave

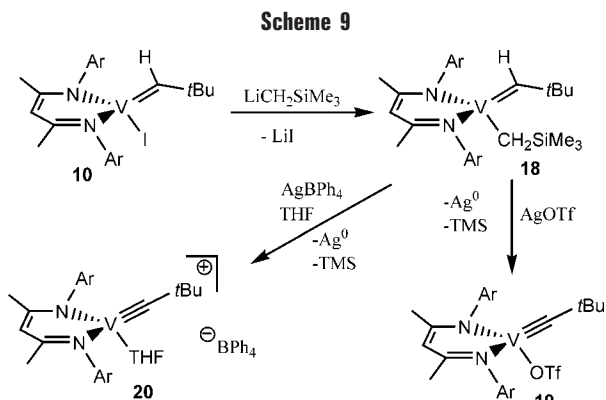


at -0.90 V (referenced vs FeCp₂/FeCp₂⁺ in THF/TBAH, TBAH = [Bu₄N][PF₆]) for the Ti(III)/Ti(IV) couple, complex **11** revealed a *reversible* oxidation wave at -0.89 V for the Ti(III)/Ti(IV) couple, thus suggesting that one-electron oxidation is not the rate-determining step for this type of transformation.

3b. Oxidatively Induced Trimethylsilyl Abstraction Reactions. If Ti=N preparation concurrent with N–H bond formation (H₂NAr being a leaving group) are the favored products resulting from the one-electron oxidation, then perhaps other products, in addition to aniline, could be envisioned as great leaving groups. When a THF solution of the Ti(III) hexamethyldisilazide complexes (nacnac)TiCl(N(SiMe₃)₂) (**14**) or (PNP)TiCl(N(SiMe₃)₂) (**15**), both prepared from 1 equiv of NaN(SiMe₃)₂ and the corresponding dichloride precursor (Scheme 8), is treated with [FeCp₂][OTf], oxidation rapidly occurs to generate the silylimides (nacnac)Ti=NSiMe₃(OTf) (**16**) and (PNP)Ti=NSiMe₃(OTf) (**17**), along with ClSiMe₃ and FeCp₂ (Scheme 8).³⁸ Separation of the silylimide is readily achieved by fractional crystallization. Alternatively, the Ti(III) precursors **14** and **15** can be treated with 2 equiv of AgOTf to yield complexes **16** or **17** in isolated yields greater than 76% (Scheme 8).³⁸ We believe Ag⁺ not only acts as an oxidant but partakes in the salt metathesis of Cl[−] for OTf[−].

4. Synthesis of M \equiv C Multiply Bonded Systems

4a. Preparing Low-Coordinate Vanadium Alkylidyne by Two One-Electron α -Hydrogen Abstraction Reactions. Terminal alkylidyne ligands in groups 4 and 5 transition metals are far more limited when compared to the alkyl-

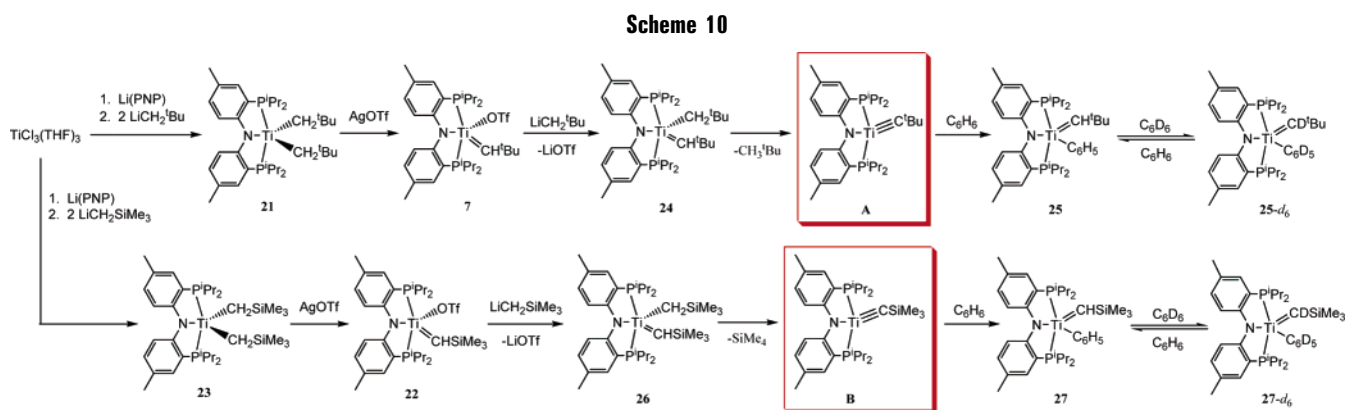


idene functionality.¹ Lippard and Protasiewicz reported the Fischer-carbyne complex $(\text{CO})(\text{dmpe})_2\text{V}=\text{COSiPh}_3$ ($\text{V}=\text{C}$, 1.754(8) Å),³⁹ but it was not until recently that d^0 , 3d transition metals alkylidyne of group 5 could be prepared.⁴⁰ Given our ability to generate four-coordinate vanadium(IV) alkylidenes, it was thought that alkylation of such species followed by one electron oxidation, should in principle promote another α -hydrogen abstraction to furnish the $\text{V}=\text{C}$ linkage in a high-valent state. In view of that hypothesis, the four-coordinate neopentylidene complex **10** can be readily alkylated with $\text{LiCH}_2\text{SiMe}_3$ to afford the neopentylidene-alkyl species $(\text{nacnac})\text{V}=\text{CH}^t\text{Bu}(\text{CH}_2\text{SiMe}_3)$ (**18**) in good yield (Scheme 9).⁴⁰ Complex **18** exhibits a solution magnetic moment of 1.90 μ_B , and the EPR spectrum is in accordance with a $\text{V}(\text{IV})$ radical center. As hypothesized, one-electron oxidation of **18** with AgOTf or AgBPh_4 yielded the neutral $(\text{nacnac})\text{V}=\text{C}^t\text{Bu}(\text{OTf})$ (**19**) or cationic $[(\text{nacnac})\text{V}=\text{C}^t\text{Bu}(\text{THF})][\text{BPh}_4]$ (**20**) four-coordinate alkylidyne complexes in 59% and 65% yield, respectively (Scheme 9).⁴⁰ Interestingly, our strategy to prepare first row d^0 metal alkylidyne from vanadium alkylidenes contrasts Schrock's two-electron reduction reactions of high-valent alkylidenes to prepare $\text{Ta}=\text{C}$ linkages. The latter process has been referred to as an α -H elimination, a 1,2-H migration, or an α -dehydrogenation.²⁰

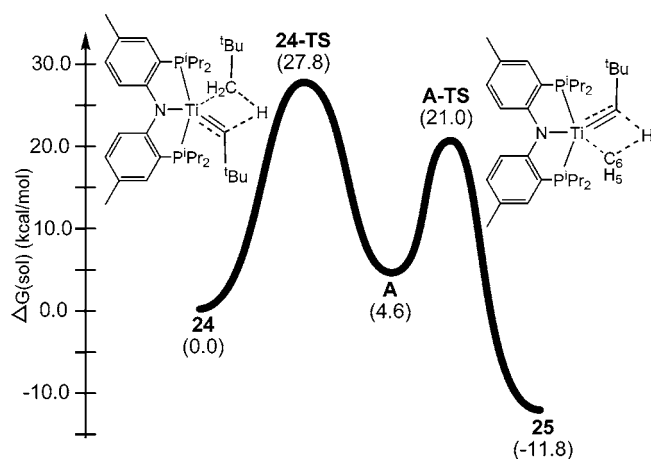
4b. Preparing Low-Coordinate Titanium Alkylidyne by α -Hydrogen Abstraction Reactions. The broad range of oxidation states for vanadium allows us to carry out two one-electron oxidation/one α -hydrogen abstraction processes in the sequence $\text{V}(\text{III}) \rightarrow \text{V}(\text{IV}) + e^- + \text{H}^+ \rightarrow \text{V}(\text{V}) + e^- + \text{H}^+$ (alternatively referred to as proton-coupled electron transfer, PCET)⁴¹ to generate the $\text{V}=\text{C}$ linkage.

However, this could not be the case for titanium, since the $\text{Ti}(\text{III}) \rightarrow \text{Ti}(\text{IV}) + e^- + \text{H}^+$ process is only plausible. Despite this redox limitation, our one-electron oxidatively induced α -hydrogen abstraction allows for not only $\text{M}=\text{C}$ bond formation but also incorporation of a labile group for subsequent transmetalation with a sterically imposing base to promote another α -hydrogen abstraction. Unfortunately, attempts to trap titanium alkylidyne via α -hydrogen abstraction from precursors such as $(\text{nacnac})\text{-Ti}=\text{CH}^t\text{Bu}(\text{OTf})$ or $(\text{nacnac}^t\text{Bu})\text{-Ti}=\text{CH}^t\text{Bu}(\text{OTf})$ and a bulky base have proven unsuccessful given the propensity of the β -diketiminate ligand to undergo multiple transformations.^{31,33} Frustrated by these observations, we decided to examine other titanium alkylidene systems that were more kinetically stable. For this reason, we focused our attention to the PNP pincer-type framework, $\text{N}[2\text{-P}(\text{CHMe}_2)_2\text{-4-methylphenyl}]_2^-$, developed by Ozerov and Liang.⁴² In 2004, Ozerov and co-workers reported the zirconium alkylidene alkyl complexes $(\text{PNP})\text{Zr}=\text{CHR}(\text{CH}_2\text{R})$ ($\text{R} = \text{Ph}$ or p -tolyl). These systems were readily prepared from the thermolysis of the corresponding trisalkyl systems $(\text{PNP})\text{-Zr}(\text{CH}_2\text{R})_3$.^{42a} As a result, we pursued similar systems with Ti, since steric hindrance at the smaller Ti^{4+} ion should favor another α -hydrogen abstraction to furnish the desired $\text{Ti}=\text{C}$ linkage. The d^1 precursor to the alkylidene **7**, $(\text{PNP})\text{Ti}(\text{CH}_2^t\text{Bu})_2$ (**21**) (vide supra), can be conveniently prepared from a "one-pot" synthesis of $\text{Li}(\text{PNP})$ and $\text{TiCl}_3(\text{THF})_3$, followed by the addition of 2 equiv of LiCH_2^tBu .³⁴ In order to promote α -abstraction and form **7**, complex **21** is oxidized with AgOTf to generate a Ag^0 mirror and alkylidene **7** quantitatively (vide supra, Scheme 5).³⁴ Likewise, the trimethylsilyl alkylidene derivative $(\text{PNP})\text{-Ti}=\text{CHSiMe}_3(\text{OTf})$ (**22**) can be alternatively prepared from $(\text{PNP})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2$ (**23**) and AgOTf .⁴³

Alkylation of **7** with LiCH_2^tBu in pentane allows for clean isolation of the titanium neopentylidene-neopentyl complex $(\text{PNP})\text{Ti}=\text{CH}^t\text{Bu}(\text{CH}_2^t\text{Bu})$ (**24**) (Scheme 10). Complex **24** is a highly reactive complex inasmuch as it transforms in benzene at 27 °C over 11.9 h (4.5 half-lives) to $(\text{PNP})\text{Ti}=\text{CH}^t\text{Bu}(\text{C}_6\text{H}_5)$ (**25**) quantitatively.⁴³ Combining high-level density functional theory (DFT), labeling, and kinetic studies, we demonstrate that complex **23** first undergoes α -H abstraction concomitant with elimination of CH_3^tBu to afford the titanium alkylidyne intermediate $(\text{PNP})\text{Ti}=\text{C}^t\text{Bu}$ (**A**), which embarks on an intermolecular



Scheme 11

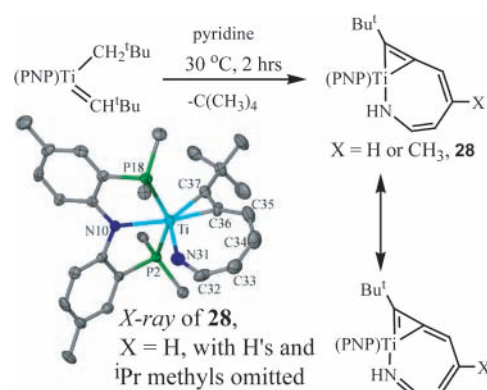


1,2-addition of the benzene C–H bond across the reactive Ti≡C linkage to provide **25**. The energy profile for the C–H activation reaction is depicted in Scheme 11.⁴³ Interestingly, the C–H and C–D activation steps of benzene are reversible, since **25-d₆** undergoes clean conversion to **25** in C₆H₆ (80 °C, 48 h) and vice-versa, thus linking intermediate **A** to **25** in the reaction profile (Scheme 11).⁴³ In fact, the proposed reaction energy profile in Scheme 9 suggests that the reverse step of the C–H activation, that is, **25** → **A**, is associated with a barrier of 32.8 kcal/mol, which could be quite possible to overcome under elevated temperature conditions (*vide supra*). The titanium alkylidyne synthon **24** can activate multiple C–H bonds in SiMe₄ to afford (PNP)Ti=CHSiMe₃(CH₂SiMe₃) (**26**) quantitatively, a complex that can be independently prepared from **22** and LiCH₂SiMe₃ in pentane (Scheme 10). As observed with **24**, benzene solutions of **26** gradually react with C₆H₆, albeit more slowly (40 °C, 24 h), to afford the alkylidene phenyl derivative (PNP)Ti=CHSiMe₃(C₆H₅) (**27**) (Scheme 10). Exchange with C₆D₆ is also observed with **27** to generate the isotopomer (PNP)Ti=CDSiMe₃(C₆D₅), (**27**-d₆). Hence, the possibility of transient titanium alkylidynes (**A** or (PNP)Ti≡CSiMe₃ (**B**)) makes it reasonable to propose this set of reactions.⁴³ Complex **24** is a synthon to **A**, consequently activating the C–H bonds of other inert substrates such as alkanes and fluoroarenes.⁴⁴ Most notably, intermediate **A** can ring-open pyridines⁴⁵ at room temperature to afford azametallacyclic frameworks such as **28** (Scheme 12).⁴⁶

5. Accessing Low-Coordinate Early Transition Metal Complexes (M = V or Ti) Having Terminal Phosphinidene Functionalities

The polarized nature of the M=C bond renders titanium and vanadium alkylidene functionalities exceedingly nucleophilic, thus readily engaging in α -hydrogen migration or deprotonation reactions of primary phosphides and amides. Schrock and co-workers applied this strategy to prepare tungsten alkylidene–imide or alkylidene–oxo complexes via an α -hydrogen migration route.⁴⁷ For us, this same protocol allowed the incorporation of the unusual terminal phosphinidene functionality^{16,17} onto

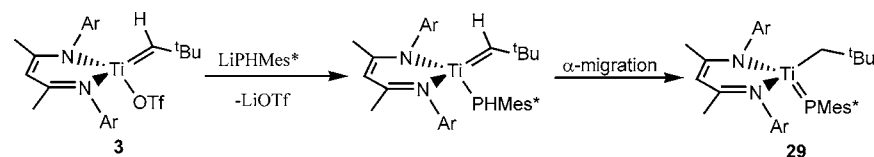
Scheme 12



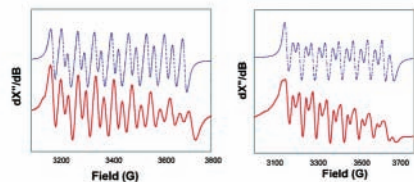
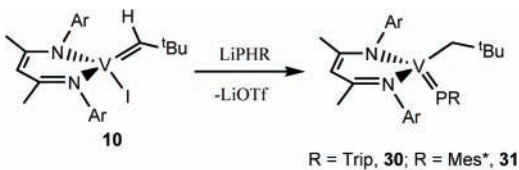
low-coordinate 3d metals composed of both titanium(IV) and vanadium(IV). When the titanium alkylidene **3** is treated with LiPHMes* (Mes* = 2,4,6-*t*Bu₃C₆H₂), the terminal phosphinidene complex (nacnac)Ti=PMes*(CH₂^{*t*}Bu) (**29**) can be obtained in 78% (Scheme 13).⁴⁸ Formation of **29** is proposed to occur via transmetalation of LiPHMes* with **3** to furnish a putative neopentylidene–phosphide (nacnac)Ti=CH^{*t*}Bu(PHMes*) intermediate, which rapidly undergoes α -H-migration to form the Ti=P linkage. The ³¹P NMR solution spectrum of complex **29** reveals two resonances at 242 and 216 ppm consistent with two phosphinidene species.⁴⁸ The observation of these two isomers could occur for steric reasons or by deviation of the “Ti=Par” fragment up and down from the imaginary NCCCN ligand plane. A similar fluxional process has been observed in four-coordinate scandium species supported by the same ligand.⁴⁹ The molecular structure of **29** displayed a four-coordinate titanium–phosphinidene complex possessing a short Ti=P bond (2.1831(4) Å)⁴⁸ and a linear Ti=P–C_{ipso} angle (164.44(5)°). This value is much shorter than Pauling’s predicted bond length of 2.288 Å for a Ti=P double bond.⁵⁰ Complex **29** is thermally unstable but undergoes rapid low-temperature reactions with CN^{*t*}Bu or cummulenes such as N₂CPh₂ to generate η^2 -(*N,C*)-phosphaazallene and phosphonylimide complexes, respectively.⁵¹ Unfortunately, the thermal instability of **29** has prevented us from further probing the reactive nature of the Ti=P linkage. If steric encumbrance at P is reduced to a *c*-C₆H₁₁ or Trip (Trip = 2,4,6-*i*Pr₃C₆H₂), the hypothetical phosphinidene intermediate generated from an α -hydrogen migration step is far too kinetically unstable and readily undergoes a series of intramolecular transformations such as phospho-Staudinger and phospho-alkene insertion reactions to generate the phosphine-based complex ([Ar]NC(Me)CHC(Me)P[CH₂^{*t*}Bu])Ti=NAr(OEt₂) (R⁻ = Cy or Trip).⁴⁸ The intermediates along the transformation pathway to the phosphine have been observed via low-temperature ³¹P and ³¹P{¹H} NMR studies.

As opposed to titanium phosphinidenes, α -hydrogen migration utilizing vanadium alkylidene precursors also leads to terminal phosphinidene assembly. Consequently, complex **10** reacts rapidly with LiPHR (R = Trip or Mes*) to produce the terminal vanadium phosphinidene alkyls (nacnac)V=PR(CH₂^{*t*}Bu) (Scheme 14; R = Trip, **30**; R =

Scheme 13

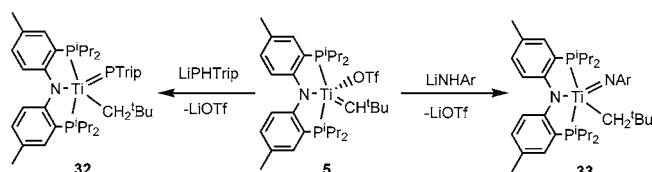


Scheme 14



EPR spectra of complexes 30 and 31

Scheme 15



Mes*, 31). Solution magnetic measurements of 30 and 31 are consistent with a d^1 V(IV) radical species, and the room-temperature X-band EPR spectra (Scheme 14) display a 16-line pattern resulting from hyperfine coupling of the unpaired electron to vanadium ($A_{\text{iso}} \approx 70$ G) and superhyperfine coupling to P ($I = 1/2$, 100%, $A_{\text{iso}} \approx 40$ G).⁵² Solid-state structural studies of these phosphinidene compounds depict short vanadium–phosphorus multiple bonds (30, 2.174(4) Å; 31, 2.1602(6) Å). Both structural features and high-level DFT studies suggest these radical species to be stabilized not only kinetically but via a pseudo-Jahn–Teller effect of second order.^{52,53} α -Hydrogen migration appears to be a general process since systems such as 5 also undergo Ti=P bond formation when treated with LiPHTrip to afford (PNP)Ti=P(Trip)(CH₂tBu) (32) (Scheme 15).³⁴ Primary amides such as LiNHAr can also be transmetalated with 5 to furnish the imide–alkyl functionalities in the complex (PNP)Ti=NAr(CH₂tBu) (33) via an α -hydrogen migration step (Scheme 15).³⁴

6. Conclusions

Oxidizing the appropriate titanium(III) or vanadium(III) systems by one-electron promotes an α -abstraction (H or trimethylsilyl) to afford Ti=C, Ti=N, and V=C linkages. In the case of vanadium, two-electron oxidation steps ultimately lead to V \equiv C bond formation. One-electron oxidation not only promotes α -hydrogen abstraction but also allows incorporation of labile ligands. This characteristic

unavoidably results in a cascade of other functionalities being derived from the nucleophilic M=C bond (alkylidyne, phosphinidene, and imides), which we are now beginning to probe. Despite extensive work in this area, synthetic chemists will inexorably seek pathways to achieve novel metal–ligand multiple-bonded species, given their involvement in catalysts, as biological mimics, or as ancillary ligands. Novel metal–ligand multiply bonded archetypes of unprecedented reactivity will continuously flourish as long as synthetic chemists seek tactical pathways to generate them.

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