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What a Difference One Electron Makes! Generating Low-Coordinate Ti–C and V–C Multiply Bonded Frameworks through One Electron Oxidatively Induced α-Hydrogen Abstractions

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Keywords: Alkylidenes / Alkylidynes / Titanium / Vanadium / Hydrogen abstraction / Oxidation

Low-coordinate, high oxidation state titanium and vanadium complexes containing terminal metal–carbon multiply bonded functionalities have been prepared directly or indirectly through one electron oxidatively induced α-hydrogen abstraction reactions. This synthetic approach offers a mild entry to reactive M=C and M≡C motifs, and does not depend on external stimulants such as heat, light or base to promote the α-hydrogen-abstraction step. In addition, this strategic protocol avoids the use of powerful electrophiles, thus generating terminal and nucleophilic M–C multiple bonds in low-coordination environments. In some cases terminal alkylidenes containing β-hydrogen atoms can also be introduced through this route. This microreview surveys the synthesis and chemistry surrounding isolable titanium and vanadium complexes bearing terminal alkylidene and alkylidyne ligands. Particular emphasis will be placed on the synthesis of the high oxidation state M–C multiple bond.

Introduction

Metal–carbon multiple bonds are an important functionality given their utilization in important industrial processes such as metathesis, in particular cross-metathesis, ring-closing metathesis, ring-opening metathesis, ring-opening metathesis polymerization, acyclic diene metathesis polymerization, acetylene polymerization, and Wittig-type (alternatively referred to as group-transfer) reactions.[1] Seminal papers and reviews by Chauvin,[2] Grubbs,[3] and Schrock[4] exemplify both the fundamental and practical use of the M–C multiple bond. The combination of their efforts clearly portray how critical fundamental research addressing the bonding and structure of the M–C linkage can rapidly evolve into a more applied area of chemistry such as catalysis.[1,3,4] Consequently, a cascade of applications such as the synthesis of pharmaceutical fine chemicals, natural products, and the formation of polymers have evolved from a fundamental study involving the M–C multiple bond.[1,3,4] Not surprisingly, the contribution by Chauvin, Grubbs, and Schrock resulted in their winning of the 2005 Nobel Prize in Chemistry.[5]

Extensive reviews covering advances in the field of metal–carbon multiple bonds have been published,[3,4,6] with one of the most comprehensive reviews for high oxidation state transition-metal alkylidenes and alkylidynes being published in 2002 by R. R. Schrock.[4c] For this reason, we will limit our attention to the synthesis and chemistry of high oxidation state alkylidenes and alkylidynes of group 4 and 5 transition metals, since in recent years there has been a dramatic advancement in this group of elements.[4c] More specifically, we will discuss only compounds which have been fully characterized, and that invoke a nucleophilic or "Schrock-like" M–C multiply bonded linkage. We refer the reader to comprehensive reviews discussing the "in situ" preparation of alkylidenes.[1f,6] This microreview will focus on the synthesis, structure, and small-molecule chemistry invoking alkylidene and alkylidyne ligands of group 4 and 5 transition metals, in particular the lighter 3d congeners for each group. Catalytic reactions will not be covered in this review, nor the synthesis and chemistry of bridging alkylidenes or alkylidynes. Given the extensive literature covering this popular field, we apologize in advance for any omission of relevant work pertaining to the subject we are discussing.

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Synthesis of Group 4 and 5 High Oxidation State Alkylidenes

High oxidation state transition-metal alkylidenes are commonly prepared through an α-hydrogen-abstraction route with the first prototypical examples $(tBuCH_2)_3Ta{=}CHtBu$[7] and $(\eta^5\text{-}C_5H_5)_2Ta{=}CHCH_3$[8] being reported by Schrock. For instance, d^0 metal complexes containing an alkyl group can often be subjected to heat or light [Equation (1)], sterically imposing Lewis bases [Equation (2)], or Brønsted bases [Equation (3)] to assist in the α-hydrogen abstraction or deprotonation of the alkyl α-hydrogen.[4]

$$L_mM^n(CH_2R)_2 \xrightarrow{\Delta \text{ or } h\nu} L_mM^n{=}CHR + CH_3R \tag{1}$$

$$L_mM^n(CH_2R)_2 \xrightarrow{x\,PR_3} L_mM^n{=}CHR(PR_3)_x + CH_3R \tag{2}$$

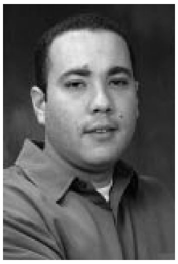
$$L_mM^n(CH_2R)X \xrightarrow{2\text{ Base}} L_mM^n{=}CHR(\text{Base}) + HX(\text{Base}) \tag{3}$$

In most cases, the Lewis base is often restricted to non-nucleophilic reagents such as bulky amides, neutral amines, phospha-ylides, in order to avoid displacement of the alkyl and subsequent redox chemistry from taking place.[4] In addition, the metal–alkyl ligand must lack β-hydrogen atoms, albeit with some exceptions, in order to avoid β-hydrogen-elimination or -abstraction pathways.[4] Alternate routes to the M=C linkage involve the in situ $2e^-$ reduction reactions of diazoalkanes, "CH_2" group-transfer reactions using phosphoranes such as $Ph_3P{=}CH_2$ [Equation (4)],[9] or two-electron reduction reactions to promote α-hydrogen elimination [Equation (5)].[10]

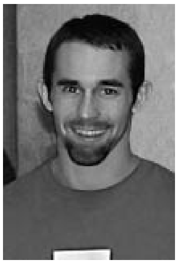
$$LM^n(LG) \xrightarrow{\text{"CHR"}} L_mM^{n+2}(CHR) + LG \tag{4}$$
LG = leaving group

$$LM^n(CH_2R)X_2 \xrightarrow[-2X^-]{x\,PR_3 \quad +2e^-} L_mM^n(CHR)(H)(PR_3)_x \tag{5}$$
X^- = halide or pseudohalide

Another elegant and rare transformation leading to alkylidene formation is the isomerization of terminal and 1,2-disubstituted olefins using low-valent metal centers [Equation (6)].[4c,11] The microscopic reverse, rearrangement of an alkylidene to an olefin, is not surprising given the intrinsic instability of β-hydrogen atoms with respect to the bound olefin. The latter rearrangement has been recognized as a potentially damaging side-reaction within the alkene metathesis cycle, but quite possibly, an important step in processes such as "alkane metathesis".[12] Recently, two new protocols to assemble low-coordinate metal–carbon multiple bonds have been reported. One applies a one-electron oxidation to promote the α-hydrogen abstraction [Equation



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 (East Lansing, Michigan, USA), and then completed a Ph.D. in chemistry from the Massachusetts Institute of Technology under the tutelage of Prof. C. C. Cummins (2000). Following an NIH and Ford postdoctoral fellowship under the direction of 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 (USA). His research interests include synthesis, reactivity, and mechanistic studies involving low-coordinate early transition metal complexes containing metal–ligand multiple bonds, in particular their development as synthons or catalysts for unusual organometallic transformations.



Brad Bailey was born in Clarkston, Michigan, USA on June 10th 1980. In 2002, he received his B.S. from the University of Michigan while working under Dr. David Curtis on the synthesis of polythiophenes for their use as conducting polymers. Brad is currently working under the supervision of Dr. Daniel Mindiola on the preparation of highly reactive terminal titanium alkylidenes and alkylidynes, and exploring the reactivity of these unusual motifs.

Falguni Basuli was born in Panskura a small town of Midnapore district of west Bengal, India, in 1972. After completing her Master's (M.Sc.) in chemistry from Vidyasagar University, she received her Ph.D. degree in 2001 from Jadavpur University, Kolkata, in synthetic inorganic chemistry under the supervision of Prof. Samaresh Bhattacharyya. In 2002 she joined Prof. Daniel J. Mindiola's group as a post-doctoral researcher at Indiana University, Bloomington, USA. She continues to work on the syntheses of early transition metal complexes containing metal–ligand multiple bonds (e.g. alkylidenes, alkylidynes, imides, and phosphanylidenes), as well as their reactivity towards different substrates.

(7)],[13] while the second method utilizes a highly reducing metal center to promote P–C bond rupture of a bound trimethylphosphane [Equation (8)].[14]

$$L_mM^n(\eta^2\text{-HRC=CHR}') \rightleftharpoons L_mM^{n+2}(\text{CRCH}_2\text{R}') \qquad (6)$$

$$L_mM^n(\text{CH}_2\text{R})_2 \xrightarrow[-A^0]{[A][X]} L_mM^{n+1}(\text{CHR})(\text{X}) + \text{CH}_3\text{R} \qquad (7)$$

$$L_mM^n[\text{P(CH}_3)_3] \longrightarrow L_mM^{n+2}(\text{CH}_2) + \text{HP(CH}_3)_2 \qquad (8)$$

The former synthetic strategy has been referred to as an oxidatively induced α-hydrogen abstraction.[13] One advantage to this process is that bis(alkyl) complexes composed of 3d elements such as Ti and V can be readily transformed to the high-valent alkylidene by a single-electron oxidation. Most notably, this protocol can generate low-coordinate complexes bearing terminal M=C linkages with substitutionally labile ligands or counter anions such as OTf^-, I^-, Br^-, Cl^-, and BPh_4^-. As a result, d^0 transition-metal alkylidenes prepared by this route are poised for a subsequent α-hydrogen abstraction or α-hydrogen deprotonation to generate the alkylidyne ligand. Another rare, but known method to generate the terminal alkylidene ligand involves the breaking of dimers (composed of bridging alkylidenes) with donor ligands such as phosphanes [Equation (9)].[15a]

$$[L_mM^n]_2(\mu_2\text{-CHR})_2 \xrightarrow{2\ \text{PR}_3} 2\ L_mM^n(\text{CHR})(\text{PR}_3) \qquad (9)$$

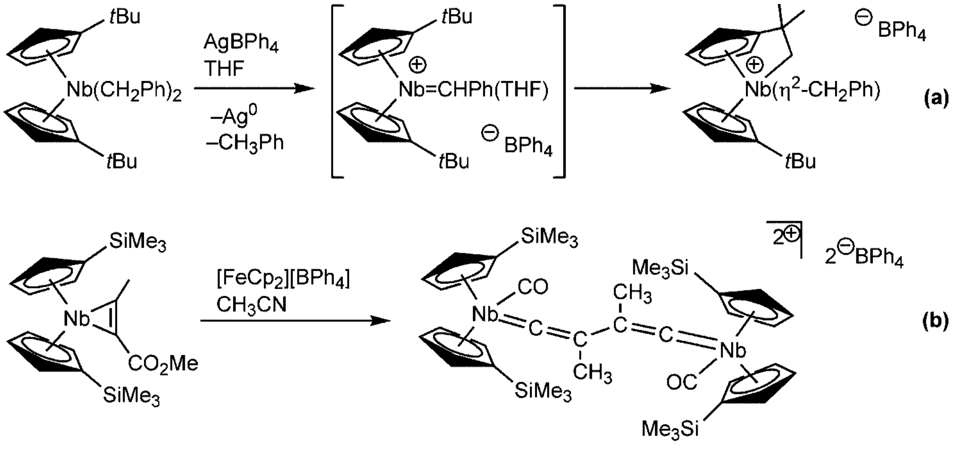
This same strategy can be used for Lewis acid decomplexation of heterobimetallic μ_2-alkylidene systems using strong donors such as HMPA.[15b]

Alkylidenevanadium and -titanium Complexes

Despite the extensive number of alkylidenetantalum complexes,[4] fewer examples exist for the lighter congener, Nb, while even less cases have been reported for V.[4,6] Table 1 lists high oxidation state alkylidene complexes for V (isolated) along with some diagnostic features. The lower number of V and Nb alkylidenes vs. those for tantalum, can arguably be correlated to the propensity of the former metals to generate low-valent oxidation states.

Theoretical studies by Nugent and co-workers have uncovered that the charge on the atom multiply bonded to the metal (e.g. imides, alkylidenes, oxo groups) decreases as we go up and to the right within the periodic table.[16] Consequently, high-valent Nb^{V} and V^{V} are more likely to be reduced by Grignard compounds or alkyllithium compounds as opposed to Ta^{V}. Hence, if one plans to incorporate the M=C linkage onto a lighter congener in a high oxidation state, then perhaps one should work retrosynthetically from the low-valent state by subsequent oxidation reactions. Gratifyingly, two examples for the later hypothesis have been reported (Scheme 1).[17,18] In 1995, McCamley and co-workers trapped a transient niobium alkylidene by a redox route.[17] Their studies described the one-electron oxidation of $\text{Nb}^{\text{IV}}(\eta^5\text{-C}_5\text{H}_4t\text{Bu})_2(\text{CH}_2\text{Ph})_2$ with AgBPh_4 to generate a Ag^0 mirror along with the kinetically unstable benzylidene salt $[\text{Nb}^{\text{V}}(\eta^5\text{-C}_5\text{H}_4t\text{Bu})_2(\text{CHPh})][\text{BPh}_4]$ (Scheme 1, a).[17] The latter intermediate underwent facile C–H activation reactions in toluene to afford the cyclometallated product (Scheme 1, a), but the mechanism of the C–H activation reaction was not discussed in this work. The second example involving one-electron oxidation to generate M=C linkages was reported by Otero and co-workers.[18] In their studies, one-electron oxidation of the Nb^{IV} alkyne $\text{Cp}'_2\text{Nb}[\eta^2\text{-MeOC(O)C}\equiv\text{CMe}]$ ($\text{Cp}' = \text{C}_5\text{H}_4\text{SiMe}_3$) with $[\text{FeCp}_2][\text{BPh}_4]$ generated a binuclear vinylidene complex (Scheme 1, b).[18] Albeit a fascinating transformation, the mechanism of the latter reaction remains unclear.

Schwartz and co-workers are likely the first group to report the synthesis and characterization (NMR spectroscopic data) of group 4 alkylidenes $\text{Cp}_2\text{M=CHR(PR}_3)$ (M = Ti and Zr).[9d,15b] Their seminal work was followed-up by Bickelhaupt and co-workers in 1986.[15a] However, it was not until 1992 that Krüger and co-workers structurally characterized the d^0 Ti=C bonded complex (PMe_3)-



Scheme 1.

Table 1. Terminal alkylidenevanadium and -titanium complexes (see also ref.[13,15,32,36–41]).

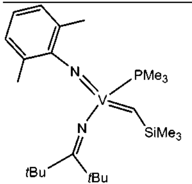
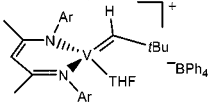
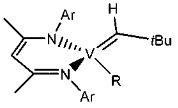
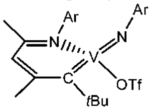
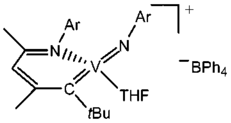
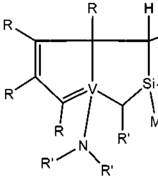
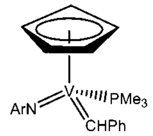
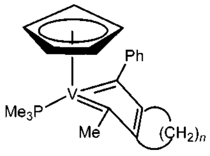
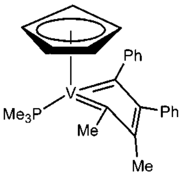
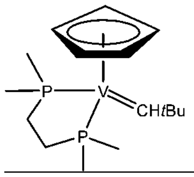
Complex	^{13}C NMR δ (ppm); J_{C-H} (Hz)	M=C Bond length (Å)	Ref.
Vanadium			
	302	1.860(2)	[32c]
 Ar = $2,6\text{-}(CHMe_2)_2C_6H_3$		1.795(3)	[13e]
 Ar = $2,6\text{-}(CHMe_2)_2C_6H_3$ R = I, CH_2SiMe_3		R = I, 1.787(3); R = CH_2SiMe_3, 1.791(6)	[13e,13f]
 Ar = $2,6\text{-}(CHMe_2)_2C_6H_3$	320	1.899(7)	[13f]
 Ar = $2,6\text{-}(CHMe_2)_2C_6H_3$	323		[13f]
 R' = Me_3Si R = Ph	319	1.876(7)	[32f]
 Ar = $2,6\text{-}(CHMe_2)_2C_6H_3$	304	1.922(6)	[32e]
 n = 3, 4	259.6 (n = 3), 263.4 (n = 4)		[32b]
	273 and 257	1.891(3) [V–C(Ph)] 1.884(3) [V–C(Me)]	[32b,32g]
	260	1.809(3)	[32a]

Table 1. *(Continued)*

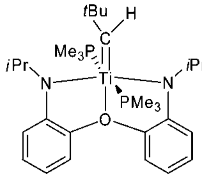
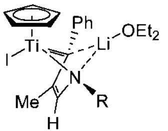
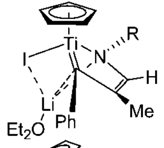
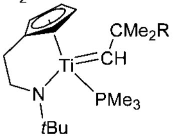
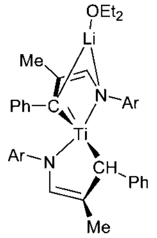
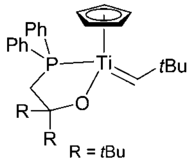
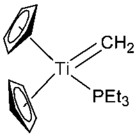
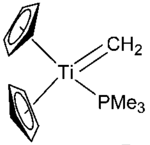
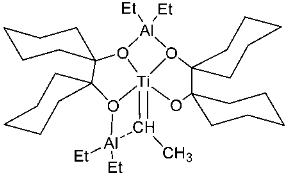
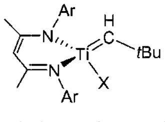
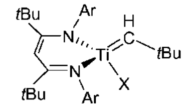
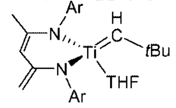
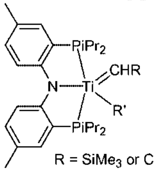
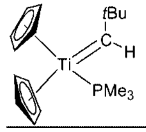
Complex	^{13}C NMR δ (ppm); J_{C-H} (Hz)	M=C Bond length (Å)	Ref.
Titanium			
	229; 80	1.884(4)	[36]
	245	1.958(3)	[37]
	245	1.979(3)	[37]
 R = Me or Ph	251; 83		[38]
 Ar = $2,6\text{-}(CHMe_2)_2C_6H_3$	236	1.978(3)	[39]
 R = tBu	287; 92	1.911(3)	[40]
	287		[15b]
	285		[15a]
		1.933(6)	[41]
 X = OTf, BH_4, Cl, Br, I, CH_2TMS Ar = $2,6\text{-}(CHMe_2)_2C_6H_3$	267–274; 85–95	1.826–1.855	[13a–c]

Table 1. *(Continued)*

Complex	^{13}C NMR δ (ppm); J_{C-H} (Hz)	M=C Bond length (Å)	Ref.
 X = OTf, I, CH_2SiMe_3, CH_2Ph Ar = 2,6-$(CHMe_2)_2C_6H_3$	254–260; 88–92	1.822–1.852	[13b–c]
 Ar = 2,6-$(CHMe_2)_2C_6H_3$	254; 93	1.86(1)	[13c]
 R = $SiMe_3$ or CMe_3 R' = CH_2CMe_3, CH_2SiMe_3, Ph, OTf	260–311; 86–99	1.790(5)–1.883(4)	[13d, 27]
	313; 110		[42]

$Cp_2Ti=C=C=TiCp_2(PMe_3)$ [Ti=C, 2.051(2) Å].[19] In 1993, Fryzuk and co-workers[20] reported the synthesis and structural elucidation of the first mononuclear and terminal alkylidene [η^5-C_5H_3-1,3-$(SiMe_2CH_2PiPr_2)_2$]Zr=CHPh(Cl). Not surprisingly, alkylidene complexes of group 4 are often represented as $^+M–CR_2^- \leftrightarrow M=CR_2$, much like ylides resonate. This feature explains why common reagents such as Tebbe's complex[21] are much more stable than Lewis acid free and terminal alkylidenes. Table 1 depicts isolable titanium complexes bearing a terminal alkylidene ligand along with diagnostic features.

Synthesis of Group 4 and 5 High Oxidation State Alkylidynes

High oxidation state alkylidyne transition-metal complexes are far more rare than the corresponding alkylidenes, in particular for the early transition metals prior to group 6.[4c] This fact is not surprising because most d^0 alkylidynes are commonly prepared from alkylidenes by an α-hydrogen abstraction or deprotonation reaction [Equation (10)].

$$L_mM^n(CHR)(LG) \longrightarrow LM^n(CR) + H(LG) \qquad (10)$$

Some elegant but rare entries to the terminal alkylidyne functionality invoke two-electron reduction of an alkyl group to promote α,α′-dehydrogenation and elimination of H_2 [Equation (11)],[11f] or α-hydrogen elimination of a reduced alkylidene–metal complex to generate the alkylidyne–hydride product [Equation (12)].[10,11f]

$$L_mM^n(CH_2R) \longrightarrow L_mM^{n+2}(CR) + H_2 \qquad (11)$$

$$L_mM^n(CHR)(X)_2 \xrightarrow[-2X^-]{x\,PR_3} L_mM^n(CR)(H)(PR_3)_x \qquad (12)$$

If one includes group 6 alkylidynes, other elegant entries would be methine (CH) group transfer to a low-valent metal center [Equation (13)],[22] trimethylsilyl migration of η^2-vinyl groups [Equation (14)],[23] and alkyne or nitrile metathesis with $W_2^{(III,III)}$ dimers [Equation (15)].[24]

$$L_mM^n + \text{"CH"} \longrightarrow L_mM^{n+3}(CH) \qquad (13)$$

$$L_mM^n(\eta^2\text{-}H_2CCSiMe_3) \xrightarrow{\Delta} L_mM^n(CCH_2SiMe_3) \qquad (14)$$

$$\underset{X\,=\,N\text{ or }CR}{L_mM^n{\equiv}M^nL_m + XCR} \longrightarrow L_mM^{n+3}(X) + L_mM^{n+3}(CR) \qquad (15)$$

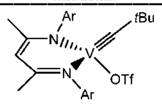
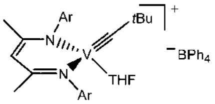
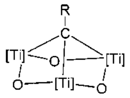
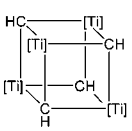
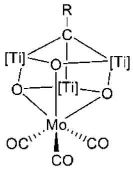
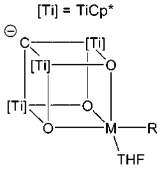
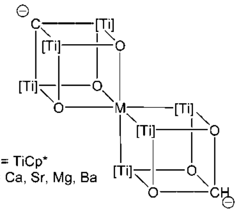
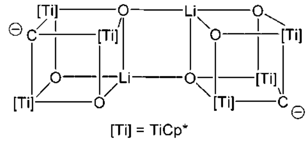
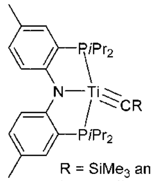
An extensive description of protocols to achieve group 6 M≡C linkages have been reported, and we refer the reader to this work.[6h] However, prior to group 6 transition metals, M≡CR linkages are far more scarce.[4c] As mentioned previously, our group has developed a novel technique applying one-electron oxidation to promote α-hydrogen abstraction. This strategy can also be applied to alkylidene(alkyl) species of vanadium(IV) thus giving rise to the first example of an alkylidynevanadium complex [Equation (16)].[13f]

$$L_mM^n(CHR)(R') \xrightarrow[-A^0]{[A][X]} L_mM^{n+1}(CR)(X) + HR' \qquad (16)$$

Schrock and co-workers reported the first examples of group 5 alkylidynes, which were composed of tantalum(V),[10b,25] but it was not until 2004 that Mindiola and co-workers[13f] reported the only examples of alkylidynevanadium(V) complexes (both in neutral and cationic forms). The latter complexes are derived from two subsequent one-electron oxidation and α-H abstraction steps commencing from a bis(alkyl)vanadium(III) precursor (vide infra). Table 2 compiles a list of terminal alkylidynevanadium complexes.

Not surprisingly, isolable and terminal group 4 alkylidynes are unknown.[4c] Mena and co-workers have reported μ_3-bridging alkylidynes of titanium where the hybridization at the α-C is best described as sp^3.[26] Very recently however, transient titanium(IV) complexes bearing terminal alkylidynes can be smoothly generated, mechanistically studied, and also trapped with various substrates (vide infra).[27] Interestingly, the latter alkylidyne precursors have been indirectly derived from a one electron oxidatively induced α-hydrogen abstraction. Table 2 compiles a list of well-defined alkylidynetitanium complexes.

Table 2. Terminal alkylidynevanadium and -titanium complexes.[13,26,27]

Complex	^{13}C NMR δ (ppm); J_{C-H} (Hz)	M≡C Bond length (Å)	Ref.
Vanadium			
 Ar = 2,6-(CHMe$_2$)$_2$C$_6$H$_3$	375	1.674(2)	[13f]
 Ar = 2,6-(CHMe$_2$)$_2$C$_6$H$_3$	374	1.696(3)	[13f]
Titanium			
 R = Me, H [Ti] = TiCp*	383 (R = H) and 402 (R = Me)	For R = Me: C–Ti1 = 2.117(4), C–Ti' = 2.127(5)	[26a]
 [Ti] = TiCp*	491	2.052(7)	[26b]
 R = Me, H [Ti] = TiCp*	410 (R = H) and 434 (R = Me)	R = CH$_3$: C–Ti1 = 2.13(5), C–Ti2 = 2.12(2), C–Ti3 = 2.10(2)	[26c]
 [Ti] = TiCp* M = Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba R = THF for group I and N(TMS)$_2$ or Cp* for Group II	577–598	For M = Ca: C–Ti1 = 1.959(5), C–Ti2 = 1.966(4), C–Ti3 = 1.965(4)	[26d]
 [Ti] = TiCp* M = Ca, Sr, Mg, Ba		For M = Ca: C–Ti1 = 1.923(6), C–Ti' = 2.123(9) For M = Sr: C–Ti1 = 1.966(2), C–Ti2 = 1.971(2), C–Ti3 = 1.972(3) For M = Mg: C–Ti = 2.06(4), C–Ti' = 2.00(1)	[26d]
 [Ti] = TiCp*		C–Ti1 = 2.067(6), C–Ti2 = 2.050(6), C–Ti3 = 2.047(6)	[26e]
 R = SiMe$_3$ and CMe$_3$ Intermediate		1.749 (computed) for R = CMe$_3$	[27]

Oxidatively Induced α-Hydrogen Abstraction to Prepare M–C Multiple Bonds of Ti and V.

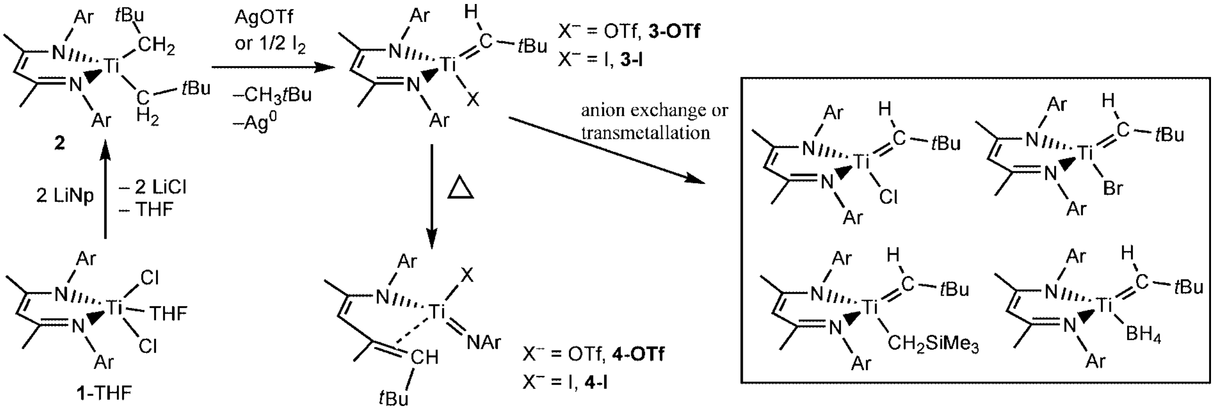
a. Synthesis of Alkylidenetitanium Complexes

An attractive entry towards 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. Accordingly, the protocol to prepare low-coordinate and terminal alkylidenetitanium complexes involved the use of a d^1 precursor complex (nacnac)TiCl$_2$ (**1**) {nacnac$^-$ = [ArNC(Me)]$_2$CH, Ar = 2,6-(CHMe$_2$)$_2$C$_6$H$_3$}, reported previously by Budzelaar.[28] The β-diketiminate ancillary ligand, nacnac$^-$, was chosen given its precedence to generate low-coordination environments in both early- and late metal complexes.[29] Hence, the THF base adduct of **1** can be readily alkylated with 2 equiv. of LiCH$_2$*t*Bu to afford the bis(alkyl)titanium(III) complex (nacnac)Ti(CH$_2$*t*Bu)$_2$ (**2**) in excellent yield.[13a] This compound is remarkably stable to heat, but when treated with oxidants such as AgOTf or I$_2$, the four-coordinate alkylidene complexes (nacnac)Ti=CH*t*Bu(X) [X$^-$ = OTf, (**3**)–OTf; X$^-$ = I, (**3**)–I] are readily obtained (Scheme 2).[13a,13b] Complex **3** displays ^{1}H and ^{13}C NMR spectroscopic signatures consistent with C_s symmetry in solution. The alkylidene C$_\alpha$ resonance is centered at δ ca. 271–272 ppm with a J_{CH} coupling constant of 95–85 Hz. The latter parameters are consistent with these molecules having a terminal alkylidene functionality in which there is a significant α-hydrogen agostic interaction with the metal center.[4c] The low-coordination number of **3** was confirmed by single-crystal X-ray crystallographic studies.[13a,13b] Conveniently, anion exchange or transmetallation in compounds such as **3**-OTf is facile (Scheme 2), thus giving rise to a family of alkylidenes where X$^-$ can be varied from halides (Cl and Br), to alkyl groups (CH$_2$SiMe$_3$), to a borohydride (η^3-BH$_4$). These alkylidenes have been thoroughly characterized, but all these compounds are kinetic products inasmuch as they can undergo intramolecular C–H activation transformations[13a] or intramolecular Wittig-like rearrangements to afford compounds such as **4**-OTf and **4**-I (Scheme 2 shows only the Wittig-like conversion of **3**-X to **4**-X, where X$^-$ = OTf or I).[13a,13b] However, the intramolecular Wittig-like rearrangement can be readily blocked by replacing the β-methyl groups on the β-diketiminate NCCCN framework with *t*Bu.[28] As a result, kinetically stable alkylidenetitanium complexes such as (^{tBu}nacnac)Ti=CH*t*Bu(X) (X$^-$ = OTf, **5**–OTf; X$^-$ = I, **5**–I; ^{tBu}nacnac$^-$ = [Ar]NC(*t*Bu)]$_2$CH) can also be prepared from the corresponding bis(alkyl) precursor (^{tBu}nacnac)Ti(CH$_2$*t*Bu)$_2$ (**6**) (Scheme 3).[13b] Structural and spectroscopic features for **5** are similar to those observed for **3**. With the bulkier ^{tBu}nacnac$^-$ framework, one can also incorporate the isobutylidene ligand onto titanium by oxidizing precursors such as (^{tBu}nacnac)Ti(CH$_2$*i*Pr)$_2$ (**7**) with AgOTf (Scheme 3).[30] This implies that oxidatively induced α-hydrogen abstraction is the preferred pathway as opposed to the more common β-hydrogen elimination and α-hydrogen abstraction themes. Although isolable, complex (^{tBu}nacnac)Ti=CH*i*Pr(OTf) (**8**) is a kinetic product since solutions decompose gradually over 24 h at 25 °C to afford the product (η^2-H*i*PrC=C(*t*Bu)CHC(*t*Bu)N[Ar])Ti=NAr-(OTf) (**9**): a complex resulting from an intramolecular Wittig-like rearrangement.[30] Despite complex **8** having *t*Bu groups to block the intramolecular [2+2]cycloaddition, the alkylidene functionality is apparently far less crowded and therefore more prone to group-transfer processes (Scheme 3).

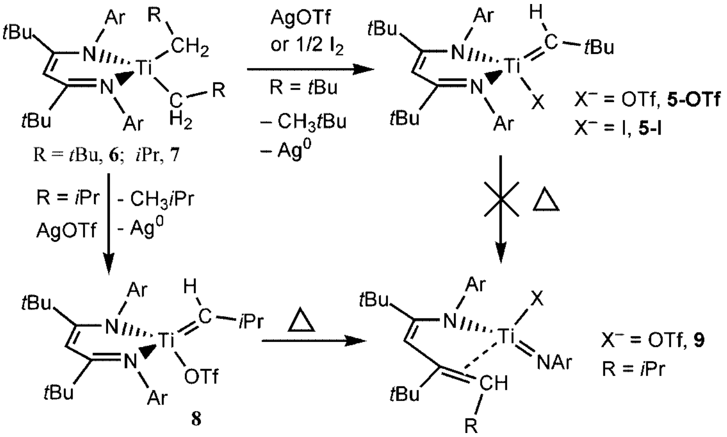
Oxidatively induced α-hydrogen abstraction is a versatile process because terminal titanium alkylidene ligands can be readily assembled utilizing another ancillary ligand framework such as PNP (PNP = N[2-P(CHMe$_2$)$_2$-4-methylphenyl]$_2^-$).[31] PNP as an ancillary support provides a "hybrid type" coordination environment where both a hard amide and two soft phosphane donors are oriented in a meridional geometry. In addition, this ancillary support is impervious to intramolecular Wittig-like rearrangements often observed with sterically imposing β-diketiminate ligands.[13] Consequently, both (trimethylsilylmethylidene)- and (neopentylidene)titanium (PNP)Ti=CHR(OTf) (**10**: R = SiMe$_3$, **11**: R = *t*Bu),[13d] as well as isobutylidene (PNP)-Ti=CH*i*Pr(OTf) (**12**)[30] complexes can be constructed with this robust and rigid pincer system (Figure 1 shows their synthesis along with their corresponding X-ray structures). Unlike **3**, **5**, and **8**, compounds **10**–**12** display weaker α-hydrogen agostic interactions (J_{C-H} = 85–99 Hz), presumably due to the greater coordination number at titanium. Distinct from **8**, complex **12** is remarkably stable despite having a less hindered and terminal alkylidene with a β-hydrogen.[30] This demonstrates that alkyl reagents that commonly reduce, such as *i*Bu$^-$, can be easily transformed into never-before seen isobutylidene "M=CH*i*Pr" functionalities on titanium. Compounds like **12** might offer an excellent opportunity to study the reverse: alkylidene to olefin conversion (vide supra).

b. Synthesis of Alkylidenevanadium Complexes

Our success in preparing the first four-coordinate neopentylidenetitanium by an oxidatively induced α-abstraction reaction[13] motivated us to pursue other 3d transition metals, which lack such a motif. Unlike titanium, vanadium displays more diverse redox chemistry, which could result in more redox couples as opposed to the more general one-electron oxidation observed with Ti^{3+}. Terminal alkylidene



Scheme 2.



Scheme 3.

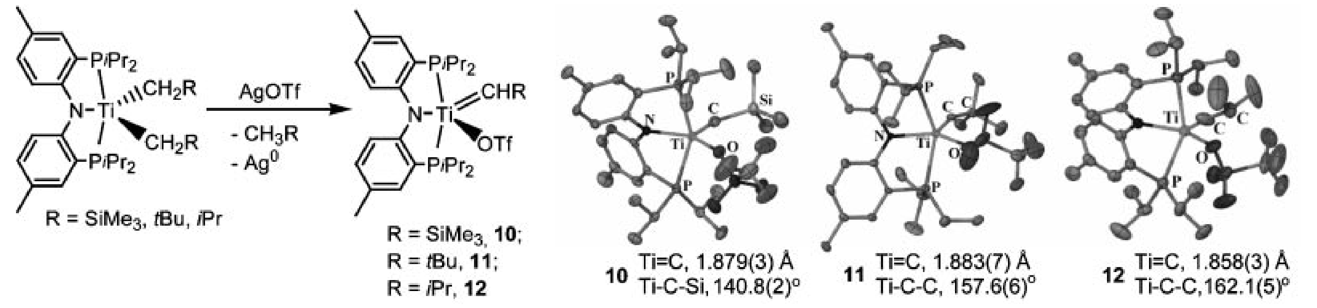
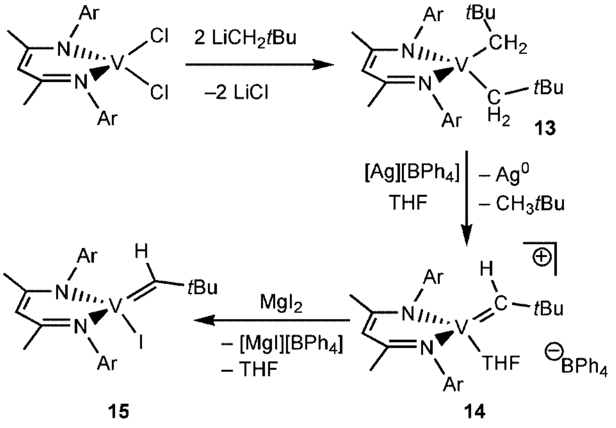


Figure 1. Synthesis of the terminal alkylidenetitanium(IV) complexes **10**–**12**. Single-crystal X-ray structures are displayed to the right with H atoms omitted for clarity. Selected metrical parameters are displayed under each structure.

complexes of vanadium are rare,[32] with the first example being reported by Teuben and co-workers, namely CpV=CH*t*Bu(dmpe) [dmpe = bis(dimethylphosphanyl)ethane].[32a] For us, alkylating Budzelaar's precursor (nacnac)-VCl_2[28] with 2 equiv. of $LiCH_2tBu$ afforded the bis-neopentyl complex (nacnac)$V(CH_2tBu)_2$ (**13**) as dark brown needles. Subsequent one-electron oxidation with $AgBPh_4$ generated a Ag^0 mirror along with the alkylidenevanadium(IV) complex [(nacnac)V=CH*t*Bu(THF)][BPh_4] (**14**) (Scheme 4).[13e] Complex **14** can readily disproportionate, but anion exchange using MgI_2 (or I_2) yielded the much more stable alkylidenevanadium(IV) (nacnac)V=CH*t*Bu(I) (**15**).[13e] Not only is the neutral complex **15** far more stable than the corresponding cation, but the I^- ligand can also be readily substituted (vide infra). Compounds **14** and **15** are d^1 paramagnets as well as EPR active. More specifically, these compounds display an 8-line hyperfine coupling pattern resulting from coupling of the unpaired electron to the vanadium center (I = 7/2, 99.6%, Figure 2).[13e] Single-crystal X-ray diffraction analysis for each system reveal four-coordinate vanadium complexes bearing a terminal neopentylidene ligand with short V=C distances [**14**, 1.795(3) Å; **15**, 1.787(3) Å], obtuse V=C–C angles [**14**, 159.8(4)°; **15**, 158.7(3)°], and in each case an α-H agostic interaction with the d^1-metal center.



Scheme 4.

c. Synthesis of Alkylidynetitanium Complexes

Terminal alkylidynetitanium complexes are unknown, and the only isolable examples reported in the literature are μ^3-alkylidynes restricted to cubane Ti^{IV}_4 clusters.[26] In 2004, Ozerov and co-workers reported remarkably stable alkylidene(alkyl)zirconium complexes of the type (PNP)-$Zr=CHR(CH_2R)$ (R = Ph or *p*-tolyl), which were prepared by α-hydrogen abstraction through thermolysis of the corresponding tris(alkyl) species.[33] However, α-hydrogen abstraction for the latter complex was not reported. Inspired by their work, we reasoned whether analogous Ti^{IV} derivatives could undergo not one, but two α-hydrogen abstractions given the more congested environment for the Ti^{4+} center. Our hypothesis proved fruitful inasmuch as four-co-

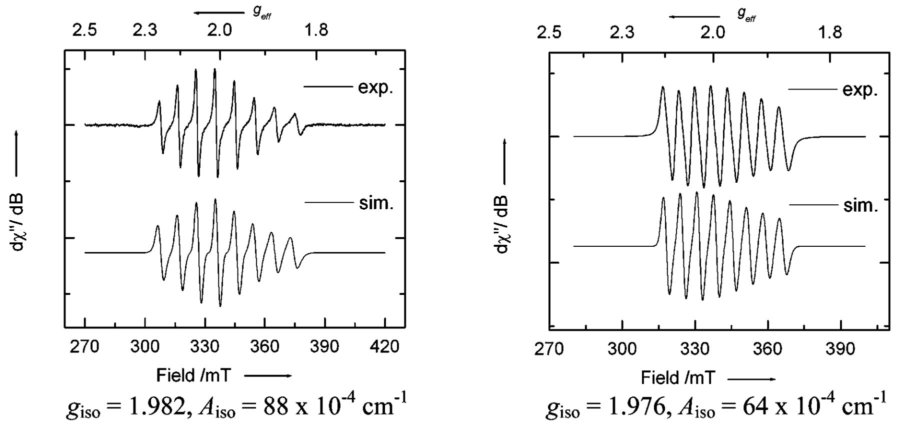
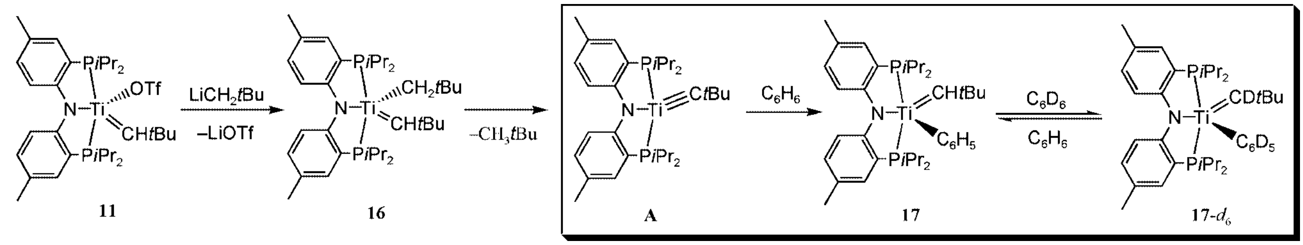


Figure 2. X-Band isotropic EPR spectra of complexes **14** (left) and **15** (right) in a 0.1 mM toluene solution.

ordinate alkylidynetitanium complexes can be readily generated by α-hydrogen abstraction reactions utilizing precursors such as **10** and **11**.[27] Accordingly, when complex **11** is treated with $LiCH_2t$Bu in pentane at low temperatures, the neopentylidene–neopentyltitanium complex (PNP)Ti=CH-*t*Bu(CH_2tBu) (**16**) can be obtained upon rapid work-up of the reaction mixture (Scheme 5). Complex **16** reacts rapidly with benzene at 27 °C within 11.9 hours (4.5 half lives) to afford (PNP)Ti=CH*t*Bu(C_6H_5) (**17**) quantitatively.[27] The combination of high-level density functional theory (DFT), labeling, and kinetic studies have demonstrated that complex **16** first undergoes α-H abstraction concomitant with elimination of CH_3tBu, to afford a transient alkylidynetitanium intermediate (PNP)Ti≡C*t*Bu (**A**), which experiences 1,2 addition of the benzene C–H bond across the reactive Ti≡C*t*Bu linkage to provide **17** (Scheme 5). The reaction energy profile for the C–H activation of benzene has been probed using high-level DFT calculations and is depicted in Figure 3.[27] The post rate-determining step suggests that the reverse process (liberation of benzene to generate alkylidyne, **17** → **A**), is associated with a barrier of 32.8 kcal/mol. In fact, this theoretical prediction can be experimentally proven under elevated temperature conditions. For example, complex **17**-d_6 can undergo clean conversion to **17** in C_6H_6 (95 °C, 48 hours), and vice-versa, thus linking intermediate **A** to complex **17** in the reaction profile.[27] This paradigm is particularly interesting because complex **17** can potentially be a synthon of **A** (albeit slow), in benzene, at ca. 95–120 °C. We have also found another alkylidyne source. Compound **10** can also be alkylated with $LiCH_2SiMe_3$ to afford (PNP)Ti=$CHSiMe_3(CH_2SiMe_3)$ (**18**). Compound **18** has been shown to generate the transient alkylidyne (PNP)Ti≡$CSiMe_3$ (**B**) in C_6H_6, albeit at higher temperatures, to afford the phenyl derivative (PNP)-Ti=$CHSiMe_3(C_6H_5)$ (**19**) (Scheme 6). As observed with **17**, thermolysis of **19** in C_6D_6 also leads to complete conversion to **19**-d_6, thus consistent with **19** being in equilibrium (at higher temperatures) with the alkylidyne intermediate **B**.[27]



Scheme 5.

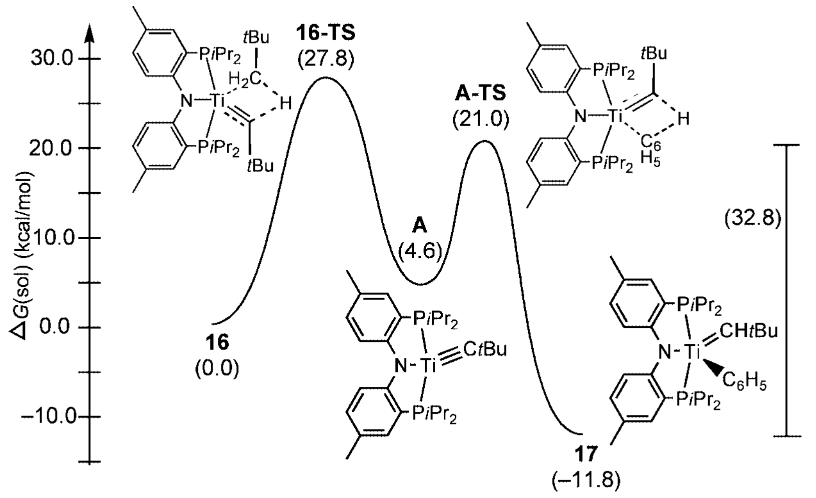
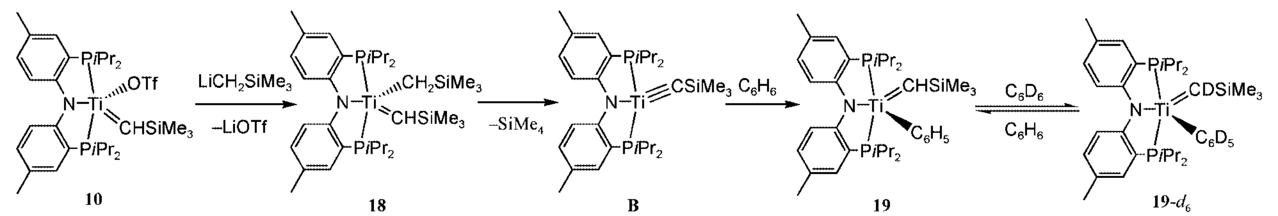


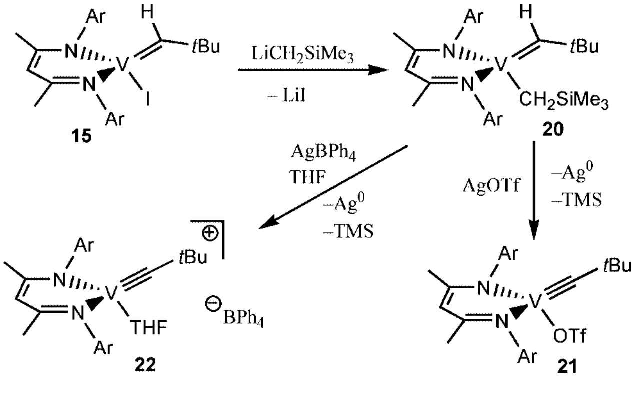
Figure 3. Reaction profile for the **15** → **16** conversion, whereby intermediate **A** is generated. The two transition-state geometries (**TS**) are depicted below.



Scheme 6.

d. Synthesis of Vanadium Alkylidynes

In 1991, Lippard and Protasiewicz reported the only example of a terminal V≡C linkage, namely the Fischer carbyne (CO)(dmpe)$_2$V≡COSiPh$_3$ [V≡C, 1.754(8) Å].[34] However, it was not until recently that the first examples of alkylidynes d^0, 3d transition metal complexes of group 5 were reported.[13f] This achievement was in part possible given our access to low-coordinate alkylidenevanadium complexes having labile ligands, namely compounds **14** and **15**.[13e] Accordingly, the four-coordinate neopentylidene complex **15** can be readily alkylated with LiCH$_2$SiMe$_3$ to afford the neopentylidene(alkyl) species (nacnac)V=CH*t*Bu(CH$_2$SiMe$_3$) (**20**) (Scheme 7). Complex **20** exhibits an EPR spectrum and a solution magnetic moment in accordance with a V^{IV} radical center,[13f] and when oxidized with AgOTf or AgBPh$_4$, the neutral (nacnac)V≡C*t*Bu(OTf) (**21**) or cationic [(nacnac)V≡C*t*Bu(THF)][BPh$_4$] (**22**) neopentylidynes can be readily obtained, respectively (Scheme 7).[13f] ^{1}H NMR spectra are consistent with **21** and **22** retaining C_s symmetry in solution, while the combination of ^{13}C (*δ*: **21**, 375 ppm; **22**, 374 ppm)[7] and ^{51}V (**21**: δ = –882 ppm, **22**: δ = –956 ppm) NMR spectra unambiguously confirms the presence of a terminal neopentylidynevanadium(V) functionality.[13f] In contrast to Schrock's two-electron reduction reactions of high-valent 5d metals to form Ta≡C linkages (vide supra),[10] our work involves two, one electron oxidatively induced α-hydrogen abstraction steps to prepare vanadium alkylidynes. While compounds **21** and **22** are remarkably stable at room temperature, they remain kinetic products from the reaction, since extensive thermolysis at ca. 80 °C results in quantitative conversion to the imidovanadium complex supported by the chelating amido–vinyl ligand, (*t*BuC=C(Me)CHC(Me)N[Ar])V=NAr(OTf) (**23**) and [(*t*BuC=C(Me)CHC(Me)N[Ar])V=NAr(THF)][BPh$_4$] (**24**). Compounds **23** and **24** are best described as azametalacyclohexatriene systems resulting from an intramolecular cross-metathesis transformation involving an azametalacyclobutene transition state **21-TS** (Figure 4).[13f] The conversion **21** → **23** in C$_7$D$_8$ was determined to be first-order in vanadium with activation parameters $\Delta S^‡$ = –6(3) cal/mol·K, $\Delta H^‡$ = 25.4(3) kcal/mol. Formation of **23** was also found to be independent of solvent (C$_7$D$_8$ vs. [D$_8$]THF), which rules out dissociative or associative mechanisms from playing a role in this transformation.[13f] A similar transformation was observed for the analogous alkylidenetitanium systems bearing the same β-diketiminate ligand framework (vide supra).[13a,13b]



Scheme 7.

Conclusions and Future Outlook

In this microreview we have compiled a series of synthetic strategies that incorporate the terminal alkylidene and alkylidyne ligands onto the early transition metal series. One particular method which we have focused our attention to has been a reaction denoted "oxidatively induced α-hydrogen abstraction". This protocol combines a one-electron oxidation step with Schrock's seminal α-hydrogen abstraction method. One-electron oxidation does not only promote α-hydrogen abstraction, but also generates metal–carbon multiple bonds in low-coordination environments while in-

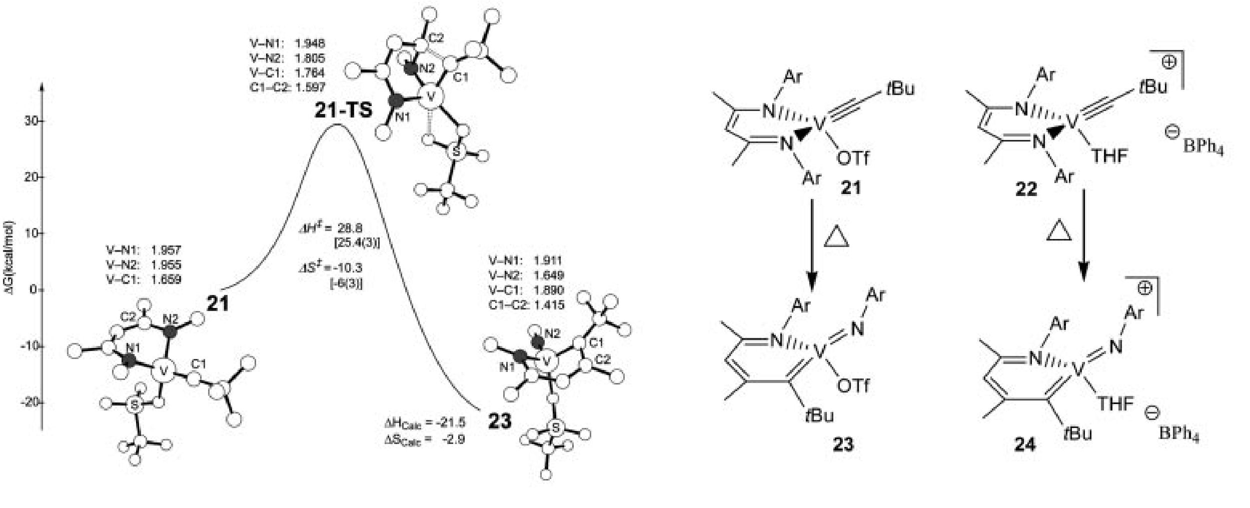


Figure 4. Transformation of the alkylidynevanadium complexes. The reaction coordinate for **21** → **23** is shown to the left with computed enthalpic values for the transition state (**21-TS**) and **23**. Calculated structural features for the cores of **21**, **21-TS**, and **23** are also displayed.

corporating labile ligands such as OTf^-, I^-, or BPh_4^-. This feature unavoidably places these compounds along a cascade of other reactions which will ultimately lead to other novel functionalities. For example, terminal alkylidyne ligands can be incorporated onto titanium by an α-hydrogen abstraction pathway, while alkylidynevanadium complexes can be generated by a subsequent one-electron α-hydrogen abstraction reaction stemming from the alkylidene(alkyl) V^{IV} precursor. In addition, the polarized nature of the $M=C$ bond renders alkylidenetitanium and -vanadium functionalities exceedingly nucleophilic thus readily engaging in α-hydrogen migration or deprotonation reactions of primary phosphides to generate novel functionalities such as terminal phosphanylidenetitanium and -vanadium complexes.[13d,35] Fine tuning of the ancillary support has created kinetically robust systems capable of undergoing interesting intermolecular reactions such as C–H activation. The chemistry surrounding high-oxidation $M=C$ and $M{\equiv}C$ linkages for group 4 and 5 metals is an immature, yet emerging field in organotransition metal chemistry despite the first alkylidenetantalum being reported by Schrock in the early 70's.[7,8]

With these synthetic strategies now available to generate a library of $M=C$ and $M{\equiv}C$ linkages, we are now in position to probe these reactive functionalities and hopefully, pull alongside with the prototypical group 6 alkylidene/alkylidyne reagents commonly used today in catalysis.

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