

Intramolecular C–H Activation Reactions Derived from a Terminal Titanium Neopentylidene Functionality. Redox-Controlled 1,2-Addition and α -Hydrogen Abstraction Reactions

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Alkylation of the terminal neopentylidene titanium(IV) complex $(L_1)Ti=CH^tBu(OTf)$ ($L_1^- = [Ar]NC(Me)CHC(Me)N[Ar]$, $Ar = 2,6-(CHMe_2)_2C_6H_3$) with $LiCH_2SiMe_3$ resulted in formation of the alkylidene–alkyl species $(L_1)Ti=CH^tBu(CH_2SiMe_3)$ (**1**) in 82% yield. Compound **1** was fully characterized, and the molecular structure disclosed a four-coordinate titanium complex having significant α -hydrogen agostic interaction and possessing terminal alkylidene and alkyl functionalities. Attempts to alkylate $(L_1)Ti=CH^tBu(OTf)$ with KCH_2Ph in THF resulted in clean deprotonation of the methyl group attached to the β -carbon of the diketiminate ligand to form the four-coordinate titanium(IV) neopentylidene–tetrahydrofuran complex $(L_2)Ti=CH^tBu(THF)$ (**2**; $L_2^{2-} = [Ar]NC(Me)CH(CH_2)N[Ar]$, 64% isolated yield). Complex **2** was fully characterized and revealed a low-coordinate titanium(IV) in a C_1 environment, which is supported by a chelating bis-anilide ligand. Alkylation of the alkylidene derivative $(L_3)Ti=CH^tBu(OTf)$ ($L_3^- = [Ar]NC(tBu)CHC(tBu)N[Ar]$, $Ar = 2,6-(CHMe_2)_2C_6H_3$) with $LiCH_2SiMe_3$ or KCH_2Ph resulted in clean formation of $(L_3)Ti=CH^tBu(R)$ ($R = CH_2SiMe_3$ (**3**), CH_2Ph (**4**)). Complexes **3** and **4** were fully characterized, and the structure of **4** was determined by single-crystal X-ray diffraction studies. Complex **1** was found to decompose rapidly to several products, of which the titanacycle $Ti[2,6-(CMe_2)-(CHMe_2)C_6H_3]NC(Me)CHC(Me)N[2,6-(CMe_2)(CHMe_2)C_6H_3](CH_2Si(Me)_3)$ (**5**) and dimer $[Ti=NAr([Ar]NC(Me)CHC(\mu-CH_2)=CH^tBu)]_2$ (**6**) were formed. Complex **5** was prepared in better yield through an independent synthesis involving $Ti[2,6-(CMe_2)(CHMe_2)C_6H_3]NC(Me)CHC(Me)N[2,6-(CMe_2)(CHMe_2)C_6H_3](OTf)$ and $LiCH_2SiMe_3$. In THF complex **6** dissociated into the corresponding monomer $(^tBu)HC=C(CH_2)CHC(CH_3)N[Ar]Ti=NAr(THF)$ (**8**), quantitatively. Unlike complex **1**, complexes **3** and **4** are kinetically more stable to intramolecular Wittig-like and C–H abstraction reactions. It was also found that one-electron reduction of the four-coordinate titanium alkylidene complexes $(L_1)Ti=CH^tBu(OTf)$ and $(L_3)Ti=CH^tBu(OTf)$ afforded the Ti(III) metallacycles $([Ar]NC(R)CHC(R)N[2,6-(CHMe_2)(CH(CH_2)(Me))C_6H_3])TiCH_2^tBu$ (L_4^{2-} , $R = Me$ (**9**); L_5^{2-} , $R = ^tBu$ (**10**)), both resulting from 1,2-addition of the proximal isopropyl CH_3 group across the $Ti=CH^tBu$ bond. One-electron oxidation of **10** with $AgOTf$ promotes α -abstraction to generate back the alkylidene precursor $(L_3)Ti=CH^tBu(OTf)$. The redox-controlled 1,2-addition and α -abstraction reactions are specific only to the isopropyl methyl attached to the aryl group of the β -diketiminate ligand.

Introduction

The activation and functionalization of carbon–hydrogen bonds are important classes of reactions which have generated considerable attention in the field of organometallic chemistry. Selective functionalization of alkanes typically involves late-transition-metal catalysts composed of platinum,¹ and these systems often contain coordinately unsaturated metal centers.² One possible strategy to activate an inert C–H bond is to utilize transition-metal complexes containing metal–ligand multiple bonds. A clear illustration of this type of

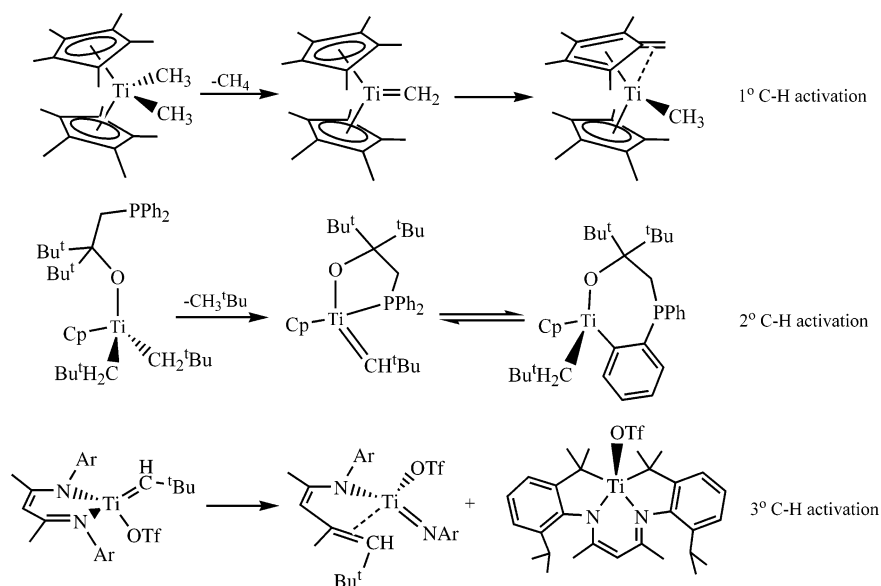
reaction is Theopold's putative $Co=O$ and $Co=NR$ systems, which can activate a C–H bond of the methyl group attached to a pyrazole arm of the Tp ligand.³ In contrast to the later metals, seminal work by Wolczanski and co-workers has shown

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Scheme 1



that low-coordinate group 4 complexes supported by sterically demanding ligands ($^t\text{Bu}_3\text{SiNH}^-$ and $^t\text{Bu}_3\text{SiO}^-$) can generate, through an α -abstraction process, three- and four-coordinate imido complexes capable of activating C–H bonds.⁴ Likewise, Bergman and co-workers have established that alkanes and sp^2 C–H bonds can be activated under mild conditions by zirconium bis(cyclopentadienide) imido systems.⁵ Girolami, Gibson, Hessen, and Legzdins have also established that unsaturated complexes having an alkylidene ligand can promote intermolecular C–H activation reactions.⁶

As opposed to intermolecular C–H activation reactions in group 4, Chirik and co-workers recently proposed that a transient titanium diphenylalkylidene species can activate, via an intramolecular reaction, two sp^3 C–H bonds from SiMe_3 groups attached to a Cp ring.^{7a} This type of reaction follows pioneering work by

Bercaw and co-workers on group 4 metals.^{7b,c} Previous work has also proposed that unsaturated and electron-deficient metal systems of group 4 alkylidenes can engage in intramolecular C–H activation reactions.⁸ One such transformation occurs by addition of one C–H bond of a phenyl group in a bulky (phenylphosphino)-alkoxide ligand across the double-bond system of a transient titanium–alkylidene species.^{8a}

Our interest in low-coordinate and early-transition-metal systems having metal–ligand multiple bonds⁹ stimulated the quest for group 4 complexes having the capability of activating rather inert and hindered C–H bonds. β -Diketiminates have become popular ligands in the past few years¹⁰ and are pivotal in the construction of reactive metal fragments. Such fragments are capable of activating innocent molecules such as N_2 ,¹¹ as well as inert C–H bonds.¹² In addition, the ligand has been demonstrated to kinetically stabilize low-coordinate and reactive metal–ligand multiple bonds.^{9,13} Recently, we discovered that four-coordinate titanium alkylidenes, when thermolyzed, can undergo facile C–H activation of two tertiary carbons.^{14,15} This work established a C–H bond cleavage reaction by which two methine groups are selectively activated under mild conditions.¹⁴ Scheme 1 depicts three distinct intramolecular reactions in which a reactive $\text{Ti}=\text{C}_{\text{alkylidene}}$ functionality becomes involved with primary,^{7b} secondary,^{8a} and tertiary¹⁴ C–H bonds.

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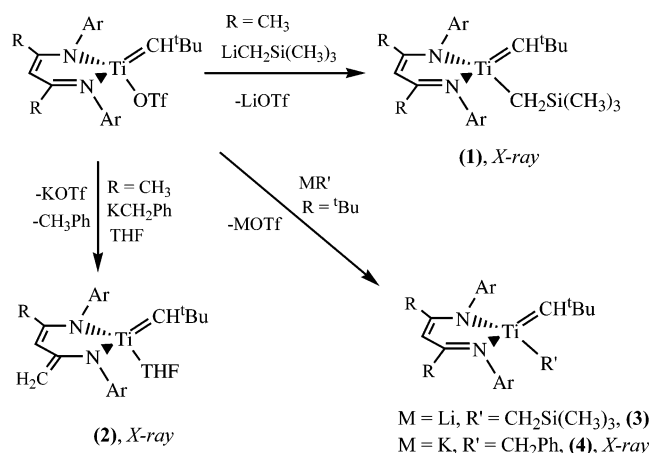
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Scheme 2



The present work describes the pursuit of titanium alkylidynes as well as three-coordinate titanium alkylidenes via a family of four-coordinate titanium alkylidene species. In the process we discovered that the Ti=CH^tBu unit can activate 1° and 3° C–H bonds. Hence, one-electron reduction of Ti(IV) alkylidene complexes leads to 1,2-addition of a 1° C–H bond to generate a Ti(III) metallacycle, while one-electron oxidation of such a metallacycle can regenerate the four-coordinate titanium(IV) neopentylidene precursor via an oxidatively induced α -hydrogen abstraction reaction. Low-coordinate titanium alkylidenes and reversible 1,2-addition and α -abstraction reactions of C–H bonds which appear to be redox controlled will also be described.

Results and Discussion

A pentane solution of the four-coordinate titanium alkylidene complex (L₁)Ti=CH^tBu(OTf) (L₁[−] = [Ar]NC-

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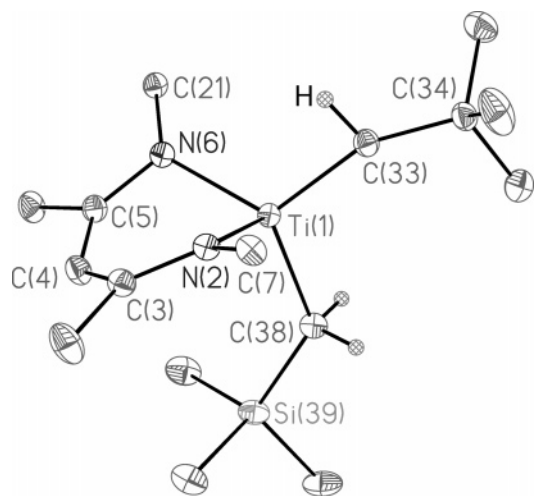


Figure 1. Perspective view of **1** with thermal ellipsoids at the 50% probability level. Hydrogens, with the exception of α -hydrogens, and aryl groups on the β -diketiminate, with the exception of ipso carbons C(7) and C(21), have been omitted for clarity. The α -hydrogens on C(33) and C(38) were located and refined isotropically. Table 1 lists pertinent metrical parameters.

(Me)CHC(Me)N[Ar], Ar = 2,6-(CHMe₂)₂C₆H₃) reacts rapidly with LiCH₂Si(CH₃)₃ at −35 °C to yield the titanium alkylidene–alkyl species (L₁)Ti=CH^tBu(CH₂SiMe₃) (**1**) as dark red blocks in 82% yield (Scheme 2). Solutions of **1** must be worked up rapidly in order to avoid significant decomposition (vide infra). ¹H and ¹³C NMR spectra of isolated samples of **1** display features consistent with the molecule retaining C_s symmetry in solution. A C_α resonance centered at δ 271 with a J_{C-H} coupling constant of 99 Hz was diagnostic of this complex having a terminal alkylidene functionality.^{9a,16–18} No α -hydrogen abstraction or migration occurred during the alkylation reaction, and the neopentylidene functionality is thus conserved in complex **1**. The J_{C-H} coupling values from the ¹³C NMR spectral data suggest significant α -hydrogen agostic interaction with the electron-deficient metal center.^{17,18} In addition, the ¹H NMR Ti=CH_α resonance in **1** was located at 5.05 ppm and differentiated from the CH_γ resonance for the Nacnac[−] backbone using HMQC NMR methods.¹⁹ To the best of our knowledge, compound **1** represents the first example of a relatively stable titanium system containing both terminal alkylidene and alkyl functionalities.

Single crystals of **1** were grown from pentane at −35 °C, and the molecular structure is depicted in Figure 1. The structure of **1** reveals a low-coordinate titanium center in a tetrahedral environment, having terminal alkylidene and alkyl functionalities and displaying C_s symmetry in the solid state. As with other four-coordinate neopentylidene complexes prepared by our group, complex **1** also possesses a short Ti=C bond

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Table 1. Selected Metrical Parameters for the Four-Coordinate Titanium Alkylidene Structures **1**, **2**, and **4**^a

	1	2	4
Ti=C _α	Ti(1)–C(33) = 1.855(4)	Ti(1)–C(33) = 1.86(1)	Ti(1)–C(39) = 1.852(6)
Ti–N _a	Ti(1)–N(2) = 2.058(1)	Ti(1)–N(2) = 1.993(8)	Ti(1)–N(2) = 2.031(2)
Ti–N _α	Ti(1)–N(6) = 2.046(1)	Ti(1)–N(6) = 1.942(9)	Ti(1)–N(6) = 2.064(2)
Ti–X _α	Ti(1)–C(38) = 2.126(4)	Ti(1)–O(38) = 2.130(8)	Ti(1)–C(44) = 2.162(6)
Ti–H _α (agostic)	Ti(1)–H = 2.02(3)	n/a	Ti(1)–H = 1.96(8)
C _α –H _α	C(33)–H = 0.93(3)	n/a	C(39)–H = 0.99(8)
N _α –C _β (N-ligand)	N(2)–C(3) = 1.331(8)	N(2)–C(3) = 1.42(2)	N(2)–C(3) = 1.355(9)
N _α –C _β (N-ligand)	N(6)–C(5) = 1.348(8)	N(6)–C(5) = 1.48(2)	N(6)–C(5) = 1.331(9)
C _β –C _γ (N-ligand)	C(3)–C(4) = 1.418(9)	C(3)–C(4) = 1.39(3)	C(3)–C(4) = 1.401(2)
C _β –C _γ (N-ligand)	C(5)–C(4) = 1.407(2)	C(5)–C(4) = 1.51(3)	C(5)–C(4) = 1.426(2)
Ti–C _α –C _β	Ti(1)–C(33)–C(34) = 158.3(1)	Ti(1)–C(33)–C(34) = 161.7(8)	Ti(1)–C(39)–C(40) = 165.5(2)
C _α –Ti–X _α	C(33)–Ti(1)–C(38) = 108.58(6)	C(33)–Ti(1)–O(38) = 104.9(4)	C(39)–Ti(1)–C(44) = 112.72(7)
N _α –Ti–N _α	N(2)–Ti(1)–N(6) = 93.66(5)	N(2)–Ti(1)–N(6) = 101.5(4)	N(2)–Ti(1)–N(6) = 94.84(5)
C _α –Ti–N _α	C(33)–Ti(1)–N(2) = 106.48(5)	C(33)–Ti(1)–N(2) = 115.7(4)	C(39)–Ti(1)–N(2) = 114.44(6)
C _α –Ti–N _α	C(33)–Ti(1)–N(6) = 116.03(5)	C(33)–Ti(1)–N(6) = 114.4(4)	C(39)–Ti(1)–N(6) = 104.16(6)
X _α –Ti–N _α	C(38)–Ti(1)–N(2) = 111.61(5)	O(38)–Ti(1)–N(2) = 107.2(3)	C(44)–Ti(1)–N(2) = 119.70(7)
X _α –Ti–N _α	C(38)–Ti(1)–N(6) = 118.93(5)	O(38)–Ti(1)–N(6) = 113.3(3)	C(44)–Ti(1)–N(6) = 107.79(6)
Ti–N _α –C _{ipso}	Ti(1)–N(2)–C(7) = 126.46(9)	Ti(1)–N(2)–C(7) = 133.3(6)	Ti(1)–N(2)–C(7) = 128.0(1)
Ti–N _α –C _{ipso}	Ti(1)–N(6)–C(21) = 132.13(9)	Ti(1)–N(6)–C(21) = 126.7(6)	Ti(1)–N(6)–C(27) = 122.92(9)
Ti–C _α –H _α	Ti(1)–C(33)–H = 86(6)	n/a	Ti(1)–C(39)–H, 81(1)
Ti–N _α –C _β	Ti(1)–N(2)–C(3) = 112.14(9)	Ti(1)–N(2)–C(3) = 107.9(6)	Ti(1)–N(2)–C(3) = 105.71(9)
Ti–N _α –C _β	Ti(1)–N(6)–C(5) = 107.74(9)	Ti(1)–N(6)–C(5) = 115.9(6)	Ti(1)–N(6)–C(5) = 111.19(9)
N _α –C _β –C _γ	N(2)–C(3)–C(4) = 122.5(3)	N(2)–C(3)–C(4) = 125.8(9)	N(2)–C(3)–C(4) = 120.7(3)
N _α –C _β –C _γ	N(6)–C(5)–C(4) = 124.0(2)	N(6)–C(5)–C(4) = 113.7(9)	N(6)–C(5)–C(4) = 119.4(3)
C _β –C _γ –C _β	C(3)–C(4)–C(5) = 130.2(3)	C(3)–C(4)–C(5) = 134(1)	C(3)–C(4)–C(5) = 134.2(4)

^a X represents –CH₂Si(CH₃)₃ for **1**, THF for **2**, and –CH₂Ph for **4**. Bond distances are reported in Å and bond angles in deg.

length of 1.855(4) Å,^{9a,16,17,18c,20} In the structure of **1**, the *tert*-butyl group is along the σ -plane bisecting the N–Ti–N plane and is oriented syn with respect to the –CH₂SiMe₃ ligand. The Ti=C_αH_α hydrogen was located and refined isotropically, and its position indicated interaction with the metal center (Ti–H_α = 2.02(3) Å; Table 1). Consequently, the C_α–H_α distance follows the reciprocal trend and becomes much longer as a result of α -hydrogen agostic interaction with the titanium center (Table 1). As expected, the Ti=C_α–C_β angle (158.3(1)°) is obtuse and significantly different from that for the Ti–C_α–Si_β angle of the alkyl group (129.78(8)°). Selected metrical parameters are displayed in Table 1, and crystal data for **1** are shown in Table 2.

The choice of alkylating agent and solvent are critical, inasmuch as attempts to alkylate (L₁)Ti=CH^tBu(OTf) with KCH₂Ph in THF do not lead to formation of (L₁)Ti=CH^tBu(CH₂Ph). Instead of alkylation, deprotonation of the methyl group attached to the β -carbon on the Nacnac[–] ligand occurs to afford the four-coordinate titanium(IV) neopentylidene–tetrahydrofuran complex (L₂)Ti=CH^tBu(THF) (**2**) (L₂^{2–} = [Ar]NC(Me)CH(CH₂)N–[Ar]) in 64% yield (Scheme 2). Similar reactions have

been reported for titanium imides^{9d} and Ge²¹ complexes bearing this type of ligand. Previous work has also demonstrated that deprotonation of the Me group attached to the β -carbon on a β -diketiminate can often lead to unprecedented binding of the ligand.²² Diagnostic features for complex **2** include the observation (by ¹H NMR spectra) of two inequivalent protons for the β -carbon methylene group centered at 3.64 and 3.25 ppm. The two resonances were correlated to the sp²-hybridized carbon at 83.0 ppm via HMQC experiments (*J*_{C–H} = 161 Hz).¹⁹ A result from the methyl being deprotonated is the loss of symmetry from C_s to C₁, which explains the spectroscopic observation of four inequivalent isopropyl groups on the supporting N-ligand. The alkylidene C_α resonance was centered at δ 254 with a *J*_{C–H} coupling constant of 93 Hz. As observed in **1**, the *J*_{C–H} coupling from the ¹³C NMR spectral data suggests an α -hydrogen agostic interaction taking place in **2**. Coordination of THF is also observed in both the ¹H and ¹³C NMR spectra of **2**. Interestingly, the ¹H NMR spectrum of **2** displays four diastereotopic methylene protons for the bound THF (see the Experimental Section). Complex **2** does not dissociate THF readily to generate the three-coordinate species (L₂)Ti=CH^tBu. Hence, solvent appears to play a significant role in the formation and stability of **2**. In fact, efforts to generate three-coordinate alkylidene species such as [(L₁)Ti=CH^tBu]⁺ have also been unsuccessful, since (L₁)Ti=CH^tBu(OTf) fails to react with salts such as Na[B(3,5-(CF₃)₂C₆H₃)₄] and Li[B(C₆F₅)₄]. Unlike (L₁)Ti=CH^tBu(OTf) or **1**, compound **2** is remarkably stable. Only upon extensive thermolysis (10 h, 40 °C) will complex **2** undergo significant decomposition. It thus appears obvious that the transformation of the β -diketiminate ligand to an imine-free, bis-anilide system in **2** prohibits

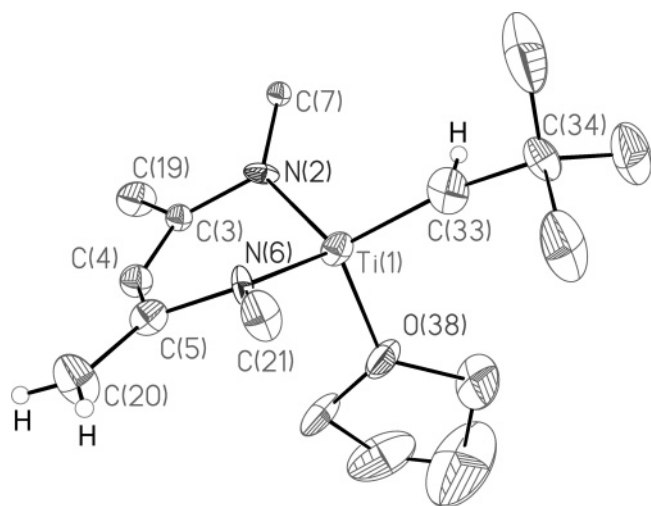
(20) Group 4 terminal alkylidenes are scarce, and few have been structurally characterized: (a) Fryzuk, M. D.; Mao, S. S. H.; Zaworotko, M. J.; MacGillivray, L. R. *J. Am. Chem. Soc.* **1993**, *115*, 5336–5337. (b) Fryzuk, M. D.; Duval, P. B.; Mao, S. S. H.; Zaworotko, M. J.; MacGillivray, L. R. *J. Am. Chem. Soc.* **1999**, *121*, 2478–2487. (c) Fryzuk, M. D.; Duval, P. B.; Patrick, B. O.; Rettig, S. J. *Organometallics* **2001**, *20*, 1608–1613. (d) Barger, P. T.; Santarsiero, B. D.; Armantrout, J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5178–5186. (e) Cheon, J.; Rogers, D. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1997**, *119*, 6804–6813. (f) Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mahtab, R. J. *J. Chem. Soc., Chem. Commun.* **1978**, 604–606. (g) Rice, G. W.; Ansell, G. B.; Modrick, M. A.; Zentz, S. *Organometallics* **1983**, *2*, 154–157. (h) Meinhardt, J. D.; Anslyn, E. V.; Grubbs, R. H. *Organometallics* **1989**, *8*, 583–589. (i) Gilliom, L. R.; Grubbs, R. H. *Organometallics* **1986**, *5*, 721–724. (j) Hartner, F. W., Jr.; Schwartz, J.; Clift, S. M. *J. Am. Chem. Soc.* **1983**, *105*, 640–641. (k) Weng, W.; Yang, L.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2004**, *23*, 4700–4705. Attempts to prepare group 4 alkylidene species have been reported: (l) Wengrovius, J. H.; Schrock, R. R. *J. Organomet. Chem.* **1981**, *205*, 319–327.

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Table 2. Summary of Crystallographic Data and Structure Refinement Details for Complexes **1**, **2**, **4**, and **6**·C₅H₁₂

	1	2	4	6 ·C ₅ H ₁₂
formula	C ₃₈ H ₆₂ N ₂ SiTi	C ₃₈ H ₅₈ N ₂ OTi	C ₄₇ H ₇₀ N ₂ Ti	C ₇₃ H ₁₁₂ N ₄ Ti ₂
fw	622.89	606.76	710.95	1141.47
space group	<i>P</i> 1	<i>P</i> 3 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1
<i>a</i> (Å)	9.9829(7)	29.025(4)	13.0516(9)	9.158(3)
<i>b</i> (Å)	10.3129(8)	29.025(4)	22.653(7)	13.307(4)
<i>c</i> (Å)	10.5462(8)	12.170(2)	14.487(2)	14.680(4)
α (deg)	105.068(2)	90.00	90.00	80.214(7)
β (deg)	94.188(2)	90.00	98.217(2)	81.987(7)
γ (deg)	113.742(2)	120.00	90.00	72.650(7)
<i>V</i> (Å ³)	940.1(2)	8879(2)	4239.2(6)	1675.3(8)
<i>Z</i>	1	9	4	1
<i>D</i> _{calcd}	1.100	1.021	1.114	1.131
linear abs coeff	0.286	0.244	0.234	0.281
<i>F</i> (000)	340	2970	1552	622
cryst color, solvent	brown-red, pentane	red-orange, hexane	brown-red, hexane	orange, pentane
cryst form	block	prism	cleaved fragment	needle
cryst size (mm)	0.35 × 0.30 × 0.25	0.24 × 0.26 × 0.30	0.30 × 0.30 × 0.25	0.25 × 0.08 × 0.02
θ range (lattice, deg)	2.28–30.01	2.14–26.91	2.16–27.53	2.00–27.57
index ranges	–14 ≤ <i>h</i> ≤ 14, –14 ≤ <i>k</i> ≤ 14, –14 ≤ <i>l</i> ≤ 14	–36 ≤ <i>h</i> ≤ 36, –12 ≤ <i>k</i> ≤ 36, –15 ≤ <i>l</i> ≤ 14	–16 ≤ <i>h</i> ≤ 12, –27 ≤ <i>k</i> ≤ 29, –18 ≤ <i>l</i> ≤ 18	–11 ≤ <i>h</i> ≤ 11, –17 ≤ <i>k</i> ≤ 17, –19 ≤ <i>l</i> ≤ 19
no. of rflns collected	25 640	30 989	30 675	18 020
no. of unique rflns, <i>F</i> > 4σ(<i>F</i>)	10 411	23 806	9739	7683
no. of obsd rflns	10 047	6962	6637	2489
<i>R</i> _{int}	0.0469	0.2267	0.0632	0.2364
final <i>R</i> indices (<i>I</i> > 2σ(<i>I</i>))	<i>R</i> 1 = 0.0355, w <i>R</i> 2 = 0.0871	<i>R</i> 1 = 0.1062, w <i>R</i> 2 = 0.1909	<i>R</i> 1 = 0.0378, w <i>R</i> 2 = 0.0792	<i>R</i> 1 = 0.0682, w <i>R</i> 2 = 0.0848
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0369, w <i>R</i> 2 = 0.0885	<i>R</i> 1 = 0.2936, w <i>R</i> 2 = 0.2629	<i>R</i> 1 = 0.0617, w <i>R</i> 2 = 0.0847	<i>R</i> 1 = 0.1244, w <i>R</i> 2 = 0.2371
GOF on <i>F</i> ²	1.035	0.870	0.872	0.740

**Figure 2.** Perspective view of **2** with thermal ellipsoids at the 50% probability level. Hydrogens, with the exception of the α -hydrogen and hydrogens on C(20), have been omitted for clarity. Aryl groups on the β -diketiminato, with the exception of ipso carbons C(7) and C(21), have also been omitted for clarity. Table 1 lists pertinent metrical parameters.

the intramolecular Wittig-like transformation previously encountered with (L₁)Ti=CH^tBu(OTf).^{9a,14}

Single crystals of **2** suitable for X-ray diffraction studies were grown from a saturated hexane solution cooled to –35 °C. Relevant metrical parameters and crystal data for the structure of **2** are listed in Tables 1 and 2, respectively. The molecular structure of **2** displays a rare four-coordinate titanium–alkylidene complex supported by a chelating bis-anilide ligand (Figure 2). Intensity statistics and systematic absences suggested the structure of **2** to be in the noncentrosymmetric, trigonal space group *P*3₁. Although the molecular

structure of **2** is of poor quality (several different crystals were examined, and all were badly split with large mosaic character), the connectivity was unambiguously confirmed. In addition, three crystallographically independent but chemically equivalent molecules of **2** were confined in the asymmetric unit. In the molecular structure of **2** the dianionic nature of the ligand is supported clearly by the short Ti–N_{anilide} bond lengths (1.942(9) and 1.993(8) Å), which are different from typical Ti^{IV}–N_{Nacnac} distances observed in four-coordinate alkylidenes (the Ti–N distance can range between 2.03 and 2.06 Å).^{9a,14} In the dianionic bis-anilide system the N–C β distances are considerably longer than those reported for the Nacnac[–] ligand.^{9a,21} Other structural parameters worth noting are the short Ti=C bond of 1.86(1) Å and the rather obtuse T–C α –C β angle (161.7–(8)°). The latter characteristic is consistent with a Ti–H α -agostic interaction occurring in **2**.^{18c} Judging from the orientation of the neopentyl *tert*-butyl group, the α -hydrogen appears to reside along the NCCCN plane and not along the σ -plane bisecting N–Ti–N. This feature is in sharp contrast to the four-coordinate titanium alkylidene system (L₁)Ti=CH^tBu(OTf), which contains the neopentyl *tert*-butyl group along the σ -plane bisecting N–Ti–N and oriented syn with respect to the triflate ligand.^{9a} We should not, however, rely heavily on metrical parameters in the crystal structure of **2**, due to the poor data quality.

Realizing that (L₃)Ti=CH^tBu(OTf)¹⁴ lacks Me groups in the β -carbon position that are prone to deprotonation (L₃[–] = [Ar]NC(^tBu)CHC(^tBu)N[Ar]), we carried out alkylation reactions of this complex in pursuit of much more stable titanium alkylidene–alkyl species. Accordingly, alkylation of the sterically hindered alkylidene

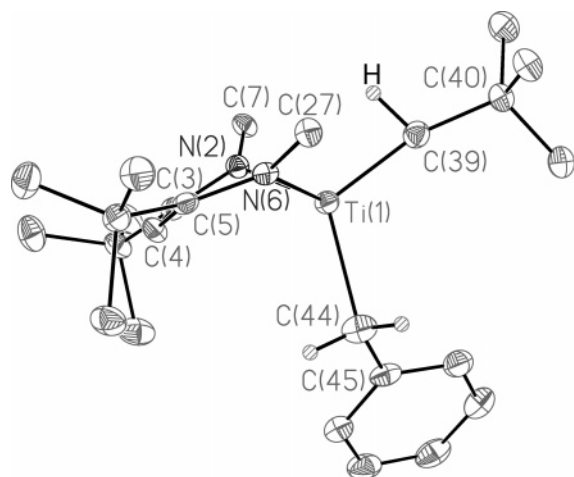
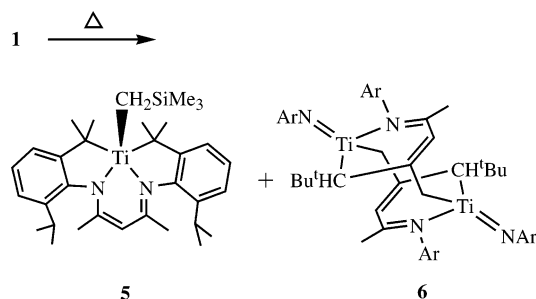


Figure 3. Perspective view of **4** with thermal ellipsoids at the 50% probability level. Hydrogens, with the exception of α -hydrogens, and aryl groups on the β -diketiminate, with the exception of ipso carbons C(7) and C(27), have been omitted for clarity. The α -hydrogens on C(39) and C(44) were located and refined isotropically. Table 1 lists pertinent metrical parameters.

$(L_3)Ti=CH^tBu(OTf)^{14}$ with $LiCH_2SiMe_3$ or KCH_2Ph affords in excellent yield the alkylidene-alkyl complexes $(L_3)Ti=CH^tBu(R)$ ($R = CH_2SiMe_3$ (**3**), 89%; $R = CH_2Ph$ (**4**), 72% yield; Scheme 2). Diagnostic features for **3** and **4** include a ^{13}C NMR resonance for the alkylidene carbon centered at 261 and 254 ppm, respectively. The coupling constant for the $C_\alpha-H_\alpha$ component for both systems was found to be ~ 88 Hz, which is in accord with the titanium centers engaging significantly with the α -hydrogen via an agostic interaction. Both systems retain C_s symmetry in solution, and the J_{C-H} values also compare well with those of the alkylidene-alkyl derivative **1**. Single-crystal X-ray diffraction studies were carried out for complex **4**, and the molecular structure is shown in Figure 3. Although the molecular structure of **4** resembles that of complex **1** ($Ti=C = 1.852(6)$ Å, $Ti-H = 1.96(8)$ Å, $C-H = 0.99(8)$ Å), the steric bulk offered by the flanking aryl groups is more significant in **4** than in **1**. Steric bulk arises from the encumbering tBu group on the β -carbon position, which pushes the aryl groups closer to the metal. This feature is clearly reflected by the $Ti-N-C_{ipso}$ angles in **4** ($128.0(1)$ and $122.92(9)^\circ$) vs those observed in **1** ($127.3(9)$ and $126.1(9)^\circ$). The steric hindrance induced by L_3^- is presumably the main factor governing the kinetic stability of **4**. Another significant structural aspect worth mentioning in the molecular structure of **4** is deviation of the titanium metal center from the NCCCN plane. Steric encumbrance pushes the metal center further out of the mean plane defined by NCCCN. Hence, complex **4** displays a greater degree of deviation (~ 1.053 Å) vs complex **1** (~ 1.027 Å). This feature has been observed with the d^0 -scandium bis-alkyl species $(L_3)ScR_2$ prepared by Piers and co-workers, in which the Sc atom sits 1.1–1.3 Å out of the NCCCN plane.²³ The “out of plane” structural features have been linked to bonding

Scheme 3



considerations involving in-plane orbitals of σ -symmetry in the β -diketiminate ligand or from steric contributions involving the maximum bite angle of the ligand and size of the metal ion.^{23,24} Table 1 lists relevant metrical parameters, while Table 2 reports crystallographic data for **4**.

Our recent discovery of four-coordinate vanadium alkylidyne complexes stimulated the pursuit of an isoelectronic titanium-alkylidyne system.^{9h} It was found, however, that complexes **3** and **4** are both kinetic products and that such species decompose gradually in solution. Gentle heating of **3** or **4** ($30-40^\circ C$) leads to a myriad of products, as evidenced by 1H NMR spectroscopy. Addition of THF, PMe_3 , p -(dimethylamino)pyridine, and $O=PMe_3$ to complex **3** or **4** results in decomposition to multiple products. In fact, treatment of **3** with $[PPN][OTf]$ ²⁵ ($PPN^+ = \text{bis}(\text{triphenylphosphoranylidene})\text{ammonium}$) does not result in a reaction to promote α -abstraction to produce the hypothetical alkylidyne-ate complex $[PPN][(L_3)Ti\equiv C^tBu(OTf)]$.

Since complex **1** decomposes rapidly in solution (vide supra), we decided to examine the nature of the compounds generated. It was found that complex **1** transformed to several products, from which the titanacycle $Ti[2,6-(CMe_2)(CHMe_2)C_6H_3]NC(Me)CHC(Me)N[2,6-(CMe_2)(CHMe_2)C_6H_3](CH_2SiMe_3)$ (**5**) and the dimer $[Ti=NAr([Ar]NC(Me)CHC(\mu-CH_2)=CH^tBu)]_2$ (**6**) were isolated (Scheme 3). Examination of the volatiles of the reaction mixture revealed both $SiMe_4$ and CMe_4 to be produced. The connectivity in complex **5** was confirmed via an independent synthesis (vide infra), while the degree of aggregation of complex **6** was established by single-crystal X-ray diffraction studies (Figure 4).

Formation of a complex such as **5** is uncommon, since previous work has documented C–H abstraction of the supporting Nacnac[−] ligand in the ortho aryl positions, in the substituents on the β -carbon of the backbone, and in 1° carbons attached to groups in the ortho aryl positions.^{10,22,23a} In general, C–H activation of 1° carbons in the 2,6-dialkyl substituents on the aryl rings is often encountered for the Nacnac[−] ligand used in the present study.^{12,23a} The C–H activation of both the methine and methyl groups of the isopropyl of Nacnac[−] (L_1^-) via reductive elimination of a $Pt(IV)$ species and subsequent oxidative addition leading to formation of

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(25) $[PPN][OTf]$ was prepared by addition of a THF solution of $AgOTf$ to a THF solution of $[PPN]Cl$. The precipitate was filtered and washed with THF and Et_2O . The solids were extracted with CH_2Cl_2 and filtered to remove $AgCl$, and the filtrate was dried under reduced pressure to afford pure product.

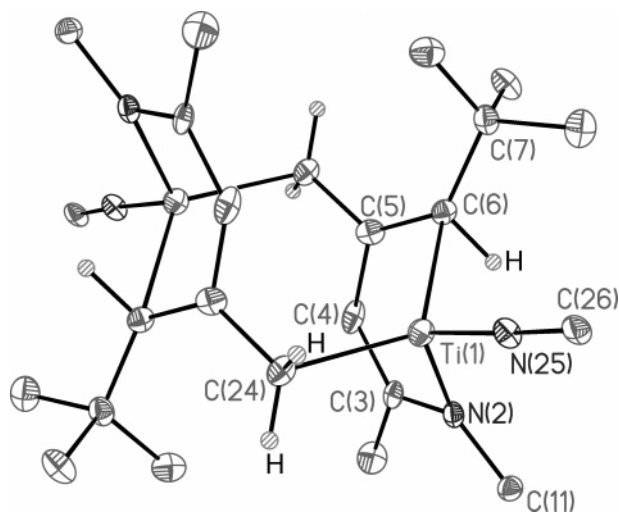
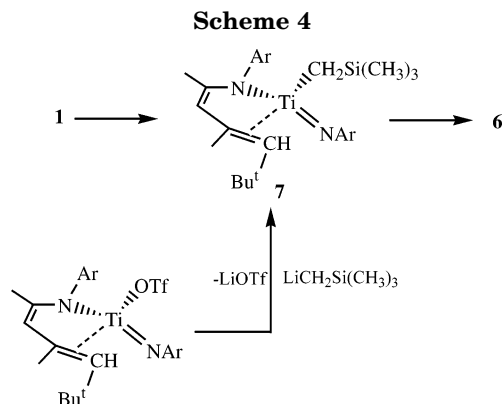


Figure 4. Perspective view of complex **6** with thermal ellipsoids at the 50% probability level. Hydrogens, with the exception of α -hydrogens, have been omitted for clarity. Aryl groups on the β -diketiminato nitrogens, with the exception of ipso carbons C(26) and C(11), and solvent have also been omitted for clarity. The α -hydrogens were located and refined isotropically. Selected bond lengths (Å) for **6**: Ti(1)–N(25), 1.732(4); Ti(1)–N(2), 1.994(4); Ti(1)–C(6), 2.209(5); Ti(1)–C(24), 2.253(5); Ti(1)–C(5), 2.661(5); Ti(1)–C(3), 2.665(5); Ti(1)–H, 2.16(4); N(2)–C(3), 1.366(5); N(2)–C(11), 1.433(6); C(3)–C(4), 1.393(7); C(4)–C(5), 1.454(6). Selected angles (deg) for **6**: N(25)–Ti(1)–N(2), 111.9(7); N(25)–Ti(1)–C(6), 106.9(7); N(2)–Ti(1)–C(6), 94.7(7); N(25)–Ti(1)–C(24), 105.4(8); C(26)–N(25)–Ti(1), 173.8(4).

an isopropenyl(hydrido)platinum(II) complex has also been reported.^{12a–c} Our work establishes a C–H activation reaction by which two methine groups are selectively cleaved under room-temperature conditions.¹⁵ Although **5** is formed in poor yields, synthetic access to this complex is easily achieved (87% isolated yield) by direct treatment of the known titanacycle Ti[2,6-(CMe₂)-(CHMe₂)C₆H₃]NC(Me)CHC(Me)N[2,6-(CMe₂)-(CHMe₂)-C₆H₃](OTf)¹⁴ with LiCH₂SiMe₃ in Et₂O. ¹H and ¹³C NMR spectra are consistent with complex **5** retaining C_s symmetry in solution, and spectral features are analogous to the those of the Ti[2,6-(CMe₂)-(CHMe₂)-C₆H₃]NC(Me)CHC(Me)N[2,6-(CMe₂)-(CHMe₂)-C₆H₃](OTf)¹⁴ precursor.

The second product generated from the thermolysis of **1** was complex **6**. Formation of complex **6** likely occurs through an intramolecular Wittig-like reaction to give the imido species (H^tBuC=C(Me)CHC(Me)N[Ar]Ti=NAr(CH₂SiMe₃) (**7**) (Scheme 4), which then undergoes deprotonation of the methyl group attached to the β -carbon of the L₁[−] ligand. We favor an intra- vs intermolecular rearrangement, since the complex (L₁)Ti=CH^t-Bu(OTf) also transforms via an analogous mechanism.¹⁴ The second step in the formation of **6** is rather unusual, in the sense that deprotonation of the methyl group occurs preferably over migratory insertion of the olefinic group into the Ti–CH₂SiMe₃ bond. The latter type of reaction has been invoked in the transformation of terminal titanium phosphinidenes supported by the present L₁[−] system.^{9b} Upon deprotonation of the β -CH₃ group, C_s symmetry in the ligand in complex **6** is expected to be disrupted. LDI-MS of complex **6** is consistent with a dimer being generated (see the



Experimental Section). However, attempts to collect ¹H NMR spectra of **6** were hampered by its insolubility in solvents such as benzene, toluene, and CH₂Cl₂. Complex **6** does dissolve gradually in THF, but the combination of ¹H, ¹³C NMR, and HMQC¹⁹ experiments in addition to single-crystal X-ray diffraction studies revealed that a novel complex was generated upon solvation (vide infra).¹⁹

To probe whether an intermediate such as **7** was a precursor to **6**, we prepared complex **7** independently and thermolyzed it. Accordingly, alkylation of the known complex (H^tBuC=C(Me)CHC(Me)N[Ar]Ti=NAr(OTf)^{9a} with LiCH₂SiMe₃ in pentane cleanly forms **7** in 83% yield as red blocks (Scheme 4). ¹H and ¹³C NMR spectra are analogous to those of the triflate-precursor derivative (H^tBuC=C(Me)CHC(Me)N[Ar]Ti=NAr(OTf).^{9a} The terminal olefinic carbon and hydrogen were located by ¹H and ¹³C NMR at 2.43 and 131.6 ppm, respectively. In addition, the J_{C–H} coupling of 123 Hz for the terminal olefinic CH indicates that substantial α -hydrogen agostic interaction occurs in solution.²⁶ Single crystals of **7** suitable for X-ray diffraction analysis were grown from pentane at −35 °C, and crystal data for the molecular structure of **7** are reported in Table 3. The molecular structure of **7** reveals a titanium center supported by an amide–diene, an imido, and an alkyl ligand (Figure 5). The titanium center in complex **7** interacts strongly with the olefinic carbons (Ti(1)–C(6), 2.260(2) Å; Ti(1)–C(5), 2.563(2) Å), and there is proximity to the β - and γ -carbons of the NCCCC ring (Figure 5). The α -hydrogen was located and refined isotropically, and its position suggests significant interaction with the metal center (Ti–H, 2.10(9) Å). The low J_{C–H} value for the terminal CH group coupled with the strong agostic interaction observed in the crystal structure could indicate significant rehybridization of the terminal carbon. Similar α -hydrogen agostic interactions have been reported for 1-aza,1,3-diene ligands coordinated to titanium.²⁶ In fact, previous work has determined that the molecular structures of the derivatives (H^tBuC=C(Me)CHC(Me)N[Ar]Ti=NAr(X) (X[−] = OTf, I, η^2 -BH₄) also engage in α -agostic interactions.¹⁴ Upon thermolysis, complex **7** generates complex **6** (confirmed by LDI MS), albeit not cleanly (Scheme 4). Deprotonation of the methyl group attached to the β -carbon of the Nacnac[−] ligand has been reported previously,^{9d,21,22} but given the

(26) Similar spectroscopic features have been suggested for 1-aza-1,3-diene ligands containing α -hydrogens which are bonded to titanium: Scholz, J.; Kahlert, S.; Gohl, H. *Organometallics* **1998**, *17*, 2876–2884.

Table 3. Summary of Crystallographic Data and Structure Refinement Details for Complexes 7–10

	7	8	9	10
formula	C ₃₈ H ₆₂ N ₂ SiTi	C ₃₈ H _{58.46} N ₂ O ₂ Ti	C ₃₄ H ₅₁ N ₂ Ti	C ₄₀ H ₆₃ N ₂ Ti
fw	622.89	607.23	535.67	619.82
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	19.030(5)	12.9907(8)	8.977(3)	12.140(1)
<i>b</i> (Å)	11.355(1)	19.171(1)	15.620(5)	17.375(4)
<i>c</i> (Å)	18.246(5)	15.3903(9)	23.026(8)	17.852(4)
α (deg)	90.00	90.00	90.00	90.00
β (deg)	108.729(3)	106.712(2)	99.198(8)	96.395(2)
γ (deg)	90.00	90.00	90.00	90.00
<i>V</i> (Å ³)	3733.8(6)	3671.0(4)	3187(9)	3742.1(5)
<i>Z</i>	4	4	4	4
<i>D</i> _{calcd}	1.108	1.099	1.116	1.100
linear abs coeff	0.288	0.262	0.291	0.256
<i>F</i> (000)	1360	1322	1164	1356
cryst color, solvent	ruby red, hexane	pale orange, Et ₂ O	green, hexane	dark green, pentane
cryst form	diamond shape	plates	cleaved fragment	diamond shape
cryst size (mm)	0.28 × 0.28 × 0.23	0.25 × 0.25 × 0.25	0.25 × 0.20 × 0.20	0.25 × 0.25 × 0.12
θ range (lattice, deg)	2.12–27.53	2.10–30.06	2.22–27.60	2.06–27.53
index ranges	–17 ≤ <i>h</i> ≤ 24, –14 ≤ <i>k</i> ≤ 14, –23 ≤ <i>l</i> ≤ 23	–18 ≤ <i>h</i> ≤ 18, –26 ≤ <i>k</i> ≤ 27, –21 ≤ <i>l</i> ≤ 21	–11 ≤ <i>h</i> ≤ 11, –20 ≤ <i>k</i> ≤ 20, –30 ≤ <i>l</i> ≤ 29	–15 ≤ <i>h</i> ≤ 15, –22 ≤ <i>k</i> ≤ 22, –23 ≤ <i>l</i> ≤ 20
no. of rflns collected	20 961	99 525	70 591	66 446
no. of unique rflns, <i>F</i> > 4σ(<i>F</i>)	8538	10 731	7384	8628
no. of obsd rflns	4168	5592	3434	5942
<i>R</i> _{int}	0.0805	0.1079	0.2015	0.0755
final <i>R</i> indices (<i>I</i> > 2σ(<i>I</i>))	<i>R</i> 1 = 0.0445, w <i>R</i> 2 = 0.0676	<i>R</i> 1 = 0.0425, w <i>R</i> 2 = 0.0843	<i>R</i> 1 = 0.0483, w <i>R</i> 2 = 0.0913	<i>R</i> 1 = 0.0441, w <i>R</i> 2 = 0.1055
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1031, w <i>R</i> 2 = 0.0820	<i>R</i> 1 = 0.1019, w <i>R</i> 2 = 0.1006	<i>R</i> 1 = 0.1122, w <i>R</i> 2 = 0.1323	<i>R</i> 1 = 0.0708, w <i>R</i> 2 = 0.1134
GOF on <i>F</i> ²	0.714	0.856	0.815	0.947

formation of multiple byproducts in such a thermolysis of **7**, it is difficult to ascertain whether an insertion reaction is also taking place.

Interestingly, it was found that compound **6** is insoluble in most common organic solvents except for THF (vide supra). In fact, the dimeric nature of **6** is not conserved in THF solutions, inasmuch as ¹H and ¹³C NMR spectra are consistent with a novel product being generated. As suggested by NMR spectral data, complex **6** appears to transform quantitatively and gradually to the monomer (H₂C=C(CH^tBu)CHC(Me)N[Ar]Ti=NAr(THF) (**8**) (Scheme 5). The nature of the monomer was established by a combination of ¹H and ¹³C NMR spectra as well as HMQC¹⁹ NMR experiments (see the Experimental Section). We propose that THF promotes heterolytic Ti–C bond cleavage in **6** to generate a conjugated species such as (tBuHC=C(CH₂)CHC(Me)N[Ar]Ti=NAr(THF), which rapidly isomerizes to form **8** (Scheme 5). It is very likely that rotation about the C_β–C_γ bond containing the allyl motif occurs for steric reasons. Single crystals of **8** were grown from Et₂O at –35 °C, and the structure is depicted in Figure 5. Crystal data for the molecular structure of **8** are reported in Table 3. The structure of complex **8** depicts a monomeric titanium system possessing an anilide–alkyl–diene ligand system, which results from THF coordination and Ti–C bond cleavage (Figure 5). There is disparity in the C–C linkages within the NCCCC motif, which is evident from the C=C bond lengths (Figure 5). The NCCCC ring is far from being planar, which is reflected by the dihedral angle defined by the atoms C(6)–C(5)–C(4)–C(3) (29.1(3) °C). X-ray data suggest that no α-H agostic interactions are present, thus indicating that the NC–CCC ligand system in **8** is best described as a chelating amide–alkyl with a diene motif. In that respect, complex **8** is remarkable in that it represents a rare example of a low-coordinate titanium imido and alkyl complex. As a result, complex **8** is exceedingly unstable at room temperature (as a solid or in solution), decomposing to a myriad of products.

Recognizing that three-coordinate species of group 4 can activate inert C–H bonds,⁴ we pursued the one-electron reduction of the alkylidene–triflate complex (L₁)Ti=CH^tBu(OTf) with KC₈ in THF. It was observed that solutions of (L₁)Ti=CH^tBu(OTf) rapidly changed from brown to green and then gradually to brown. Examination of the reaction mixture by ¹H NMR spectra revealed several products along with starting material. However, it was found that the one-electron reduction improves if the reaction is carried out in toluene with a small trace of THF or PMe₃. Workup of the persisting green solution afforded several paramagnetic products, of which the titanium(III) metallacycle–alkyl complex (L₄)Ti(CH₂^tBu) (**9**; L₄^{2–} = [Ar]NC(Me)CHC(Me)N[2,6-(CHMe₂)(CH(CH₂)(Me))C₆H₃]) could be isolated as a crude powder (Scheme 6). Rapid decomposition and significant contamination of **9** with other products precluded satisfactory characterization via spectroscopic assessment techniques (EPR, Evans, elemental analysis). However, a few single crystals of **9** were grown from the reaction mixture, and X-ray data confirmed the proposed connectivity (Figure 6 lists selected metrical parameters, and Table 3 lists crystallographic and refinement data for the molecular structure of **9**). Although crystals were found to be badly split and twinned, the molecular structure of **9** reveals a Ti(III) metallacycle resulting from C–H activation of the nearby isopropyl methyl group. In the molecular structure of **9** there is a slight disorder, with 7.3% of the site having an alternate Ti position. The azametallacyclohexene ring generated in **9** results from 1,2-addition of the C–H bond across the putative titanium(III)–alkylidene species “(L₁)Ti=CH^tBu”, which was generated from the one-electron reduction of (L₁)Ti=CH^tBu(OTf). The molecular structure of **9** also reveals ring strain, which is evident from the torsion angle defined by the atoms N(6)–C(21)–C(22)–C(30) (–171.5(2)°). 1,2-Addition of the proximal C–H bond across the Ti=C bond was not surprising, since the putative “(L₁)Ti=CH^tBu” is three-coordinate and contains a radical centered at

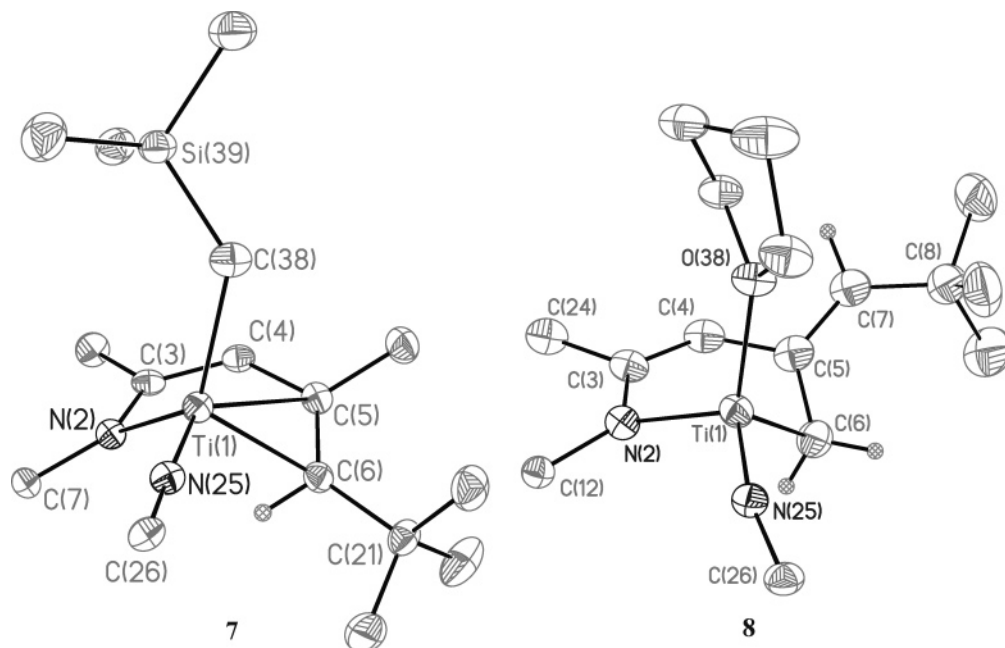
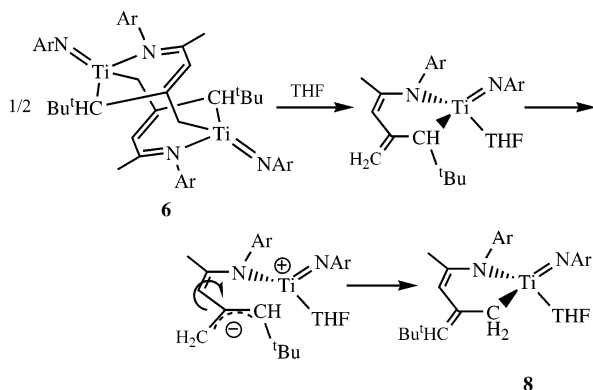
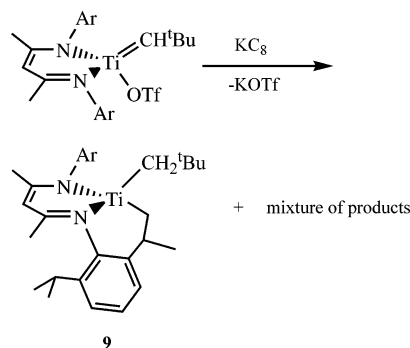


Figure 5. Perspective views of complexes **7** and **8** with thermal ellipsoids at the 50% probability level. Hydrogens, with the exception of the α -hydrogens on C(6) and C(7) (complex **8**), have been omitted for clarity. Aryl groups on the β -diketiminato nitrogens, with the exception of those located in carbons C(7) and C(26) for complex **7** and C(26) and C(12) for complex **8**, have also been omitted for clarity. Disorder involving a diethyl ether is present at the THF site of complex **8** but was easily modeled. Selected bond lengths (Å) for **7**: Ti(1)–N(25), 1.725(9); Ti(1)–N(2), 2.032(8); Ti(1)–C(6), 2.260(2); Ti(1)–C(5), 2.563(2); Ti(1)–C(4), 2.704(2); Ti(1)–C(3), 2.671(2); Ti(1)–H, 2.10(9); Ti(1)–C(38), 2.130(3); N(2)–C(3), 1.350(3); N(2)–C(7), 1.436(3); C(3)–C(4), 1.393(3); C(4)–C(5), 1.440(3); C(5)–C(6), 1.381(3); C(6)–C(21), 1.528(3); N(25)–C(26), 1.398(3). Selected angles (deg) for **7**: N(25)–Ti(1)–N(2), 112.09(8); N(25)–Ti(1)–C(6), 109.12(9); N(25)–Ti(1)–C(38), 107.91(10); N(2)–Ti(1)–C(6), 91.18(8); N(2)–Ti(1)–C(38), 122.03(9); Ti(1)–N(25)–C(26), 174.3(7); N(2)–C(3)–C(4), 120.7(2); C(3)–C(4)–C(5), 131.0(2); C(4)–C(5)–C(6), 126.0(2); C(5)–C(6)–Ti(1), 85.9(5); C(5)–C(6)–C(21), 129.2(2); Ti(1)–C(38)–Si(39), 130.9(5). Selected bond lengths (Å) for **8**: Ti(1)–N(25), 1.720(4); Ti(1)–N(2), 1.952(4); Ti(1)–C(6), 2.121(9); Ti(1)–O(38), 2.055(1); Ti(1)–C(5), 2.589(7); N(2)–C(3), 1.411(2); N(2)–C(12), 1.428(2); N(25)–C(26), 1.395(2); C(3)–C(4), 1.353(2); C(3)–C(24), 1.502(3); C(4)–C(5), 1.471(3); C(5)–C(7), 1.370(3); C(5)–C(6), 1.463(3). Selected angles (deg) for **8**: Ti(1)–N(25)–C(26), 167.9(2); Ti(1)–N(2)–C(3), 109.1(1); Ti(1)–C(6)–C(5), 90.6(1); O(38)–Ti(1)–N(25), 105.37(6); O(38)–Ti(1)–N(2), 114.39(5); O(38)–Ti(1)–C(6), 119.21(7); C(6)–Ti(1)–N(2), 93.49(7); C(6)–Ti(1)–N(25), 111.68(7); N(25)–Ti(1)–N(2), 112.74(6); N(2)–C(3)–C(4), 122.8(7); C(3)–C(4)–C(5), 129.9(7); C(4)–C(5)–C(6), 117.5(7); C(4)–C(5)–C(7), 116.6(7); C(6)–C(5)–C(7), 125.7(9).

Scheme 5



Scheme 6



the Ti=C bond. Theoretical studies on the four-coordinate titanium alkylidene (L_1)Ti=CH^tBu(OTf) have established that the HOMO is mostly of Ti=C π character, while the LUMO consists of L_1 π^* augmented with π^* character in the Ti=C bond.¹⁴ Hence, the one-electron reduction of (L_1)Ti=CH^tBu(OTf) would likely populate the Ti=C π^* orbital, thus giving rise to a Ti=C-centered radical. Analogous metallacycles have been reported in the thermolysis of (L_1)ScR₂ systems studied by Piers and co-workers.^{23a} In the context of late-transition-metal complexes, the intramolecular cleavage of C–H bonds

in the Nacnac[−] ligand has been invoked in intermolecular alkane activation.¹²

Given the precedent for L_1^- to undergo transformations,^{9d,10b} our inability to isolate complex **9** in good yield, and the lack of experimental data not conclusive for the identity of such species, we proceeded to carry out the one-electron reduction of the kinetically stable alkylidene complex (L_3)Ti=CH^tBu(OTf).¹⁴ Accordingly, reduction of (L_3)Ti=CH^tBu(OTf) with KC₈ or Li^tBu affords the ^tBu–titanacycle derivative of **9**, namely (L_5)Ti(CH₂^tBu) (**10**; L_5^{2-} = [Ar]NC(^tBu)CHC(^tBu)N[2,6-(CHMe₂)(CH(CH₂)(Me))C₆H₃]) as dark green crystals from pentane at −35 °C (Scheme 7). The use of Li^tBu as a reductant improves tremendously the yield of **10**

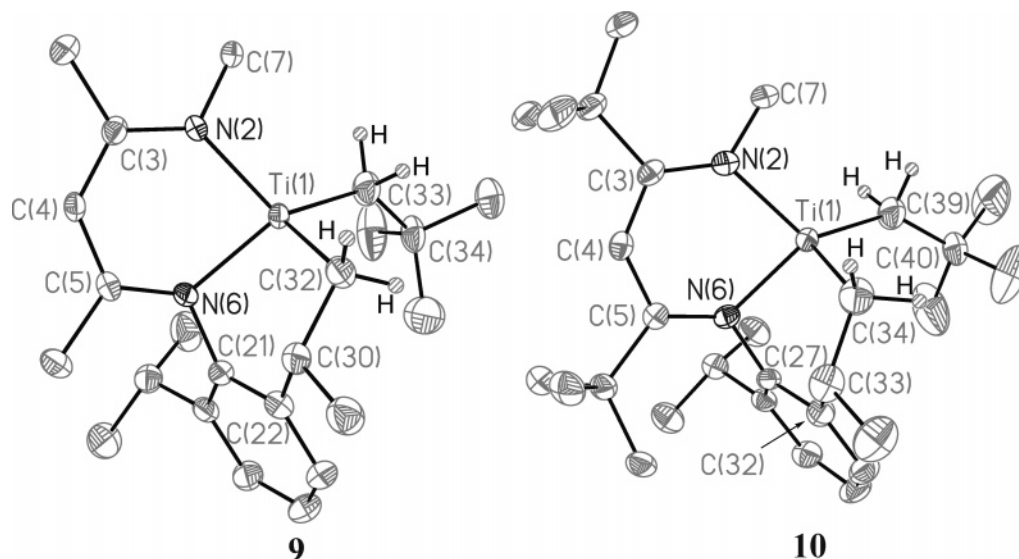
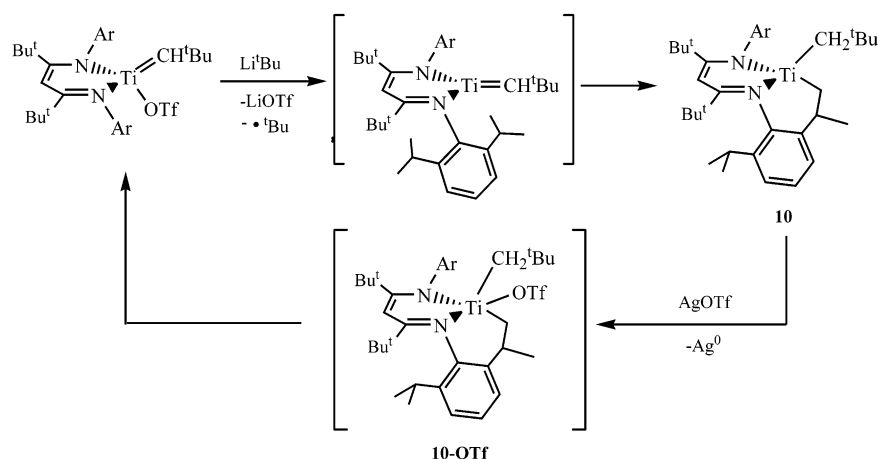


Figure 6. Perspective views of the titanacycles **9** and **10**, with thermal ellipsoids at the 50% probability level. Hydrogens, with the exception of α -hydrogens, have been omitted for clarity. Aryl groups on the β -diketiminate nitrogens, with the exception of the C(7) ipso carbons, have also been omitted for clarity. The α -hydrogens were located and refined isotropically. There is a disorder present with the titanium atom in the structure for complex **10** and appears shifted to the other side of the plane defined by the atoms N(2), N(6), and C(39). Selected bond lengths (Å) for **9**: Ti(1)–N(2), 1.988(2); Ti(1)–N(6), 2.009(2); Ti(1)–C(33), 2.124(3); Ti(1)–C(32), 2.167(3); Ti(1)–H(on C(33)), 2.27(3); N(2)–C(3), 1.357(3); C(3)–C(4), 1.390(4); C(4)–C(5), 1.396(4); C(5)–N(6), 1.349(3). Selected angles (deg) for **9**: Ti(1)–C(33)–C(34), 135.6(2); Ti(1)–C(32)–C(30), 111.1(2); Ti(1)–N(2)–C(3), 131.5(7); N(2)–Ti(1)–N(6), 86.06(9); Ti(1)–N(6)–C(5), 130.0(8); C(33)–Ti(1)–C(32), 107.7(3); Ti(1)–N(6)–C(21), 105.5(6); Ti(1)–N(2)–C(7), 107.0(5); N(2)–C(3)–C(4), 121.0(2); C(4)–C(5)–N(6), 120.9(2); N(6)–C(21)–C(22), 116.9(2); C(21)–C(22)–C(30), 119.3(2); C(22)–C(30)–C(32), 109.2(2). Selected bond lengths (Å) for **10**: Ti(1)–N(2), 2.021(4); Ti(1)–N(6), 2.004(4); Ti(1)–C(39), 2.143(2); Ti(1)–C(34), 2.173(2); Ti(1)–H(on C(39)), 2.27(3); N(2)–C(3), 1.351(2); C(3)–C(4), 1.390(2); C(4)–C(5), 1.407(2); C(5)–N(6), 1.340(2). Selected angles (deg) for **10**: Ti(1)–C(39)–C(40), 138.0(5); Ti(1)–C(34)–C(33), 111.2(3); Ti(1)–N(2)–C(3), 130.1(1); N(2)–Ti(1)–N(6), 87.05(6); Ti(1)–N(6)–C(5), 130.2(1); C(39)–Ti(1)–C(34), 109.4(9); Ti(1)–N(6)–C(27), 100.6(1); Ti(1)–N(2)–C(7), 100.3(1); N(2)–C(3)–C(4), 119.8(5); C(4)–C(5)–N(6), 118.8(5); N(6)–C(27)–C(32), 117.3(5); C(27)–C(32)–C(33), 118.8(5); C(32)–C(33)–C(34), 109.0(5).

Scheme 7



(65%), inasmuch as t BuH, isobutene, and hexamethyl-ethane are generated as organic side products from the one-electron reduction reaction (confirmed by ^1H NMR spectra of the volatiles).²⁷ Solution magnetic measurements by the method of Evans, solution X-band EPR spectra, and single-crystal X-ray diffraction studies (Figure 6) are all consistent with the proposed connectivity in **10**. At room temperature, complex **10** exhibits a solution magnetic moment of $1.83 \mu_{\text{B}}$, which is in close agreement with the calculated value obtained by applying the g_{iso} value from the EPR spectrum.

However, room-temperature manipulation of the product leads to gradual decomposition.

In the molecular structure of **10**, the Ti(III) center resides in a highly distorted tetrahedral environment (Figure 6) and resembles closely the gross structural features of complex **9**. 1,2-Addition of the nearby methyl across the $\text{Ti}=\text{CH}^t\text{Bu}$ bond gives rise to two Ti–alkyl ligands, which are manifested by the Ti–C bond lengths of 2.143(2) and 2.173(2) Å. These values compare well with typical Ti(III) bis-alkyl distances reported in the literature.²⁸ As in complex **9**, there appears to be significant ring strain resulting from the cyclometalation, which is manifested by the dihedral angle (4.6–

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(2°) defined by the atoms N(6)–C(27)–C(32)–C(33) and angles constructing the metallacycle (Figure 6 gives selected bond lengths and angles for **10**, and Table 3 lists crystallographic and refinement data). Such a claim is speculative, since there is a disorder present with the titanium atom, which appears to shift to the other side of the plane defined by the atoms N(2), N(6), and C(39).

Most notably, it was found that one-electron oxidation of **10** with AgOTf generates back the alkylidene precursor (L_3)Ti=CH^tBu(OTf) quantitatively, as suggested by both ¹H and ¹³C NMR spectra (Scheme 7). Oxidation of **10** likely results from formation of the putative five-coordinate species **10-OTf** (Scheme 7),²⁹ which rapidly undergoes α -hydrogen abstraction to generate (L_3)Ti=CH^tBu(OTf). Similarly, when the isotopomer **10-d**₁³⁰ is oxidized with AgOTf, the complex (L_3)Ti=CH(D)^tBu(OTf)-d₁ is generated back and deuterium scrambling is observed in all isopropyl methyl groups, as evidenced by ¹H and ²H NMR spectra. Hence, the one-electron reduction of (L_3)Ti=CH^tBu(OTf) to **10** and its one-electron oxidation back to the alkylidene is best described as a *redox-controlled 1,2-addition and α -hydrogen abstraction reaction*. This type of reaction parallels Cummins' reversible β -hydride elimination reactions of Nb and Mo metallaaziridine systems.³¹

Despite complex **10** having a β -hydrogen, this system appears to be relatively stable under low-temperature conditions. Similar stability has been observed in analogous Ti(III) bis-alkyl species studied by Budzelaar and co-workers.²⁸ We speculate that the unusual stability observed in **10** arises likely from the rigidity of the metal-based ring. Hence, the orientation of the methine carbon places the β -hydrogen on C(33) away from the metal center and less susceptible to elimination or abstraction processes. However, the possibility remains that β -hydride elimination and reinsertion of the putative titanium–hydride into the pendant olefin exists in solution. This process has been observed in Pt systems studied by Goldberg and co-workers¹² and could give rise to two isomers resulting from hydride insertion into the terminal or proximal sites of the pendant olefinic arm of the Nacnac^tBu[−] ligand.

Conclusions

Alkylation of a series of the four-coordinate titanium alkylidene complexes was found to generate alkylidene–alkyl species of the type (Nacnac)Ti=CH^tBu(alkyl) (Nacnac[−] = [Ar]NC(R)CHC(R)N[Ar], Ar = 2,6-(CHMe₂)₂-C₆H₃), R = CH₃, ^tBu). Depending on the nature of the Nacnac[−] ligand and alkyl group, deprotonation of the methyl group attached to the β -carbon can occur to yield a four-coordinate titanium alkylidene species supported by a dianionic chelating bis-anilide ligand. When the

more sterically hindered Nacnac^tBu[−] derivative was used, the alkylidene–alkyl systems were found to be more kinetically stable by blocking C–H activation and intramolecular Wittig reactions observed with the conventional [Ar]NC(Me)CHC(Me)N[Ar] (Ar = 2,6-(CHMe₂)₂-C₆H₃) ligand. It was found that reduction of the complex (L_3)Ti=CH^tBu(OTf) to **10** and one-electron oxidation of the product back to the alkylidene provide a reversible and intramolecular 1,2-addition and α -abstraction reaction which is controlled by a one-electron redox switch. 1,2-CH addition across the titanium–alkylidene is likely mitigated by the radical nature of the Ti=C bond, while α -hydrogen abstraction takes place exclusively at the Ti–CH₂^tBu ligand. In addition, the redox-controlled 1,2-addition and α -abstraction reactions are specific only to the isopropyl methyl attached to the aryl group of the β -diketiminato ligand. We are currently exploring what factors govern the preference of 1° vs 3° C–H bonds when activated by low-coordinate titanium–alkylidenes as well as exploring alternate surrogates for the present ligand in order to stabilize the elusive titanium alkylidyne functionality.

Experimental Section

General Considerations. Unless otherwise stated, all operations were performed in a M. Braun Lab Master double-dry box under an atmosphere of purified nitrogen or using high-vacuum standard Schlenk techniques under an argon atmosphere.³² Anhydrous *n*-hexane, pentane, toluene, and benzene were purchased from Aldrich in Sure-Seal reservoirs (18 L) and dried by passage through one column of activated alumina and one of Q-5.³² Diethyl ether and CH₂Cl₂ were dried by passage through two columns of activated alumina.³³ THF was distilled, under nitrogen, from purple sodium benzophenone ketyl and stored over sodium metal. Distilled THF was transferred under vacuum into bombs before being pumped into a drybox. C₆D₆ and CD₂Cl₂ were purchased from Cambridge Isotope Laboratory (CIL), degassed, and dried over 4 Å molecular sieves and CaH₂, respectively. CD₂Cl₂ was vacuum-transferred from the CaF₂ mixture and stored in a reaction vessel under N₂. Et₂O-d₁₀ and THF-d₈ were purchased from CIL and stored over Na film. Celite, alumina, and 4 Å molecular sieves were activated under vacuum overnight at 200 °C. Li(L₁)³⁴ (L₁[−] = [Ar]NC(Me)CHC(Me)N[Ar], Ar = 2,6-(CHMe₂)₂-C₆H₃), (Nacnac)TiCl₂(THF)^{9a,28} LiCH₂^tBu,³⁵ KC₈,³⁶ KCH₂Ph,³⁷ Li(L₃)²⁸ (L₃[−] = [Ar]NC(^tBu)CHC(^tBu)N[Ar]), (L₁)Ti=CH^tBu(OTf),^{9a} (η^2 -H^tBuC=C(Me)CHC(Me)N[Ar])Ti=NAr(OTf),^{9a} Ti[2,6-(CMe₂)(CHMe₂)C₆H₃]NC(Me)CHC(Me)N[2,6-(CMe₂)(CHMe₂)C₆H₃](OTf),¹⁴ and (L₃)Ti=CH^tBu(OTf)¹⁴ were prepared according to the literature. Solid Li^tBu was collected by cooling a saturated pentane solution to −78 °C followed by rapid filtration. Crystals of LiCH₂Si(CH₃)₃ were collected by cooling of a saturated pentane solution to −35 °C. All other chemicals were used as received. CHN analysis was performed by Desert Analytics, Tucson, AZ. ¹H, ²H, ¹³C, and ¹⁹F NMR

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(30) The complex **10-d** was prepared from (L₃)Ti=CD^tBu(OTf) and Li^tBu in Et₂O at −35 °C. Preparation of the precursor (L₃)Ti=CD^tBu(OTf) was analogous to that of the protio derivative, but instead, LiCD₂^tBu^{6e} was used as the alkylating reagent.

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spectra were recorded on Varian 400 and 300 MHz NMR spectrometers. ^1H and ^{13}C NMR are reported with reference to solvent resonances (residual $\text{C}_6\text{D}_6\text{H}$ in C_6D_6 , 7.16 and 128.0 ppm; residual CH_2Cl_2 in CD_2Cl_2 , 5.32 and 53.8 ppm). ^{19}F NMR chemical shifts are reported with respect to external HOCOCF_3 (-78.5 ppm). Magnetic moments were obtained by the method of Evans.³⁸ Room-temperature and solution X-band EPR spectra were recorded on a Bruker EMX spectrometer. Acquisition and simulation were performed using an integrated WIN-EPR software package (Bruker).³⁹ LDI MS was collected using a Bruker Biflex III time-of-flight mass spectrometer. The mass spectrum was recorded by irradiating the sample spot with 337 nm light from a nitrogen laser. X-ray diffraction data were collected on a SMART6000 (Bruker) system under a stream of $\text{N}_2(\text{g})$ at low temperatures.

Synthesis of 1. In a vial containing 10 mL of pentane was dissolved $(\text{L}_1)\text{Ti}=\text{CH}^t\text{Bu}(\text{OTf})$ (411 mg, 0.60 mmol), and the solution was cooled to -35°C . To the cold solution was added a cold pentane solution (~ 5 mL) of $\text{LiCH}_2\text{SiMe}_3$ (56.50 mg, 0.60 mmol), and the reaction mixture was warmed to room temperature and stirred for an additional 45 min. The solution was filtered and the filtrate concentrated and cooled overnight at -35°C to afford in two crops dark large blocks of $(\text{L}_1)\text{Ti}=\text{CH}^t\text{Bu}(\text{CH}_2\text{SiMe}_3)$ (**1**; 305 mg, 0.49 mmol, 82% yield).

Data for **1** are as follows. ^1H NMR (23 $^\circ\text{C}$, 399.8 MHz, C_6D_6): δ 7.21–7.02 (m, C_6H_3 , 6H), 5.69 (s, $\text{Ti}=\text{CH}^t\text{Bu}$, 1H), 4.82 (s, $\text{C}(\text{Me})\text{CHC}(\text{Me})$, 1H), 3.72 (septet, $\text{CH}(\text{Me})_2$, 2H), 3.07 (septet, $\text{CH}(\text{Me})_2$, 2H), 2.37 (s, $\text{Ti}-\text{CH}_2\text{SiMe}_3$, 2H), 1.64 (d, CHMe_2 , 6H), 1.57 (s, $\text{C}(\text{Me})\text{CHC}(\text{Me})$, 6H), 1.45 (d, CHMe_2 , 6H), 1.26 (d, CHMe_2 , 6H), 1.21 (d, CHMe_2 , 6H), 0.74 (s, $\text{Ti}=\text{CH}^t\text{Bu}$, 9H), 0.15 (s, $\text{Ti}-\text{CH}_2\text{SiMe}_3$, 9H). ^{13}C NMR (25 $^\circ\text{C}$, 100.6 MHz, C_6D_6): δ 270.7 ($\text{Ti}=\text{CH}^t\text{Bu}$, $J_{\text{C-H}} = 99$ Hz), 167.3 ($\text{C}(\text{Me})\text{CHC}(\text{Me})$), 145.6 (*ipso*- C_6H_3), 142.6 (*o*- C_6H_3), 140.8 (*o*- C_6H_3), 126.6 (*p*- C_6H_3), 124.4 (*m*- C_6H_3), 124.3 (*m*- C_6H_3), 96.35 ($\text{C}(\text{Me})\text{CHC}(\text{Me})$, $J_{\text{C-H}} = 159$ Hz), 57.79 ($\text{Ti}-\text{CH}_2\text{SiMe}_3$, $J_{\text{C-H}} = 103$ Hz), 47.03 ($\text{Ti}=\text{CHCMe}_3$), 31.80 ($\text{Ti}=\text{CH}^t\text{Bu}$), 28.86 (CHMe_2), 28.45 (CHMe_2), 26.55 (*Me*), 24.99 (*Me*), 24.81 (*Me*), 24.16 (*Me*), 3.48 ($\text{Ti}-\text{CH}_2\text{SiMe}_3$). Anal. Calcd for $\text{C}_{38}\text{H}_{62}\text{N}_2\text{SiTi}$: C, 73.27; H, 10.03; N, 4.50. Found: C, 72.70; H, 10.10; N, 4.99.

Synthesis of 2. In a vial containing 10 mL of THF was dissolved $(\text{L}_1)\text{Ti}=\text{CH}^t\text{Bu}(\text{OTf})$ (150 mg, 0.22 mmol) and the solution cooled to -35°C . To the cold solution was added a cold THF solution (~ 5 mL) containing KCH_2Ph (29.9 mg, 0.23 mmol). After it was warmed to room temperature, the mixture was stirred for an additional 25 min and solvent was evaporated under reduced pressure. The solid was extracted with hexane, the extract filtered, and the filtrate concentrated and stored at -35°C for 24 h to afford dark red crystals of $(\text{L}_2)\text{Ti}=\text{CH}^t\text{Bu}(\text{THF})$ (**2**; 84 mg, 0.14 mmol, 64% yield, two crops).

Data for **2** are as follows. ^1H NMR (23 $^\circ\text{C}$, 399.8 MHz, C_6D_6): δ 7.48–7.18 (m, C_6H_3 , 6H), 5.05 (s, $\text{Ti}=\text{CH}^t\text{Bu}$, 1H, based on HMQC), 4.92 (s, $\text{C}(\text{Me})\text{CHC}(\text{CH}_2)$, 1H), 4.16 (septet, CHMe_2 , 1H), 4.03 (septet, CHMe_2 , 1H), 4.02 (m, *THF*, 2H), 3.87 (m, *THF*, 2H), 3.64 (s, $\text{C}(\text{Me})\text{CHC}(\text{CH}_2)$, 1H), 3.51 (septet, CHMe_2 , 1H), 3.31 (septet, CHMe_2 , 1H), 3.25 (s, $\text{C}(\text{Me})\text{CHC}(\text{CH}_2)$, 1H), 1.78 (d, CHMe_2 , 3H), 1.76 (d, CHMe_2 , 3H), 1.70 (d, CHMe_2 , 3H), 1.67 (d, CHMe_2 , 3H), 1.65 (s, $\text{C}(\text{Me})\text{CHC}(\text{CH}_2)$, 3H), 1.63 (d, CHMe_2 , 3H), 1.62 (d, CHMe_2 , 3H), 1.55 (d, CHMe_2 , 3H), 1.45–1.41 (m, *THF* and CHMe_2 , 7H), 0.83 (s, $\text{Ti}=\text{CH}^t\text{Bu}$, 9H). ^{13}C NMR (25 $^\circ\text{C}$, 100.6 MHz, C_6D_6): δ 254 ($\text{Ti}=\text{CH}^t\text{Bu}$, $J_{\text{C-H}} = 93$ Hz), 153.2 ($\text{C}(\text{Me})\text{CHC}(\text{CH}_2)$), 148.7 (*ipso*- C_6H_3), 147.0 (*ipso*- C_6H_3), 145.2 (*o*- C_6H_3), 145.0 (*o*- C_6H_3), 142.7 (*o*- C_6H_3), 142.6 (*o*- C_6H_3), 141.9 ($\text{C}(\text{Me})\text{CHC}(\text{CH}_2)$), 125.6 (*p*- C_6H_3), 125.5 (*p*- C_6H_3), 124.7 (*m*- C_6H_3), 124.0 (*m*- C_6H_3), 123.1 (*m*- C_6H_3), 122.9 (*m*- C_6H_3), 99.21 ($\text{C}(\text{Me})\text{CHC}(\text{CH}_2)$, $J_{\text{C-H}} = 154$ Hz), 82.99 (based on HMQC, $\text{C}(\text{Me})\text{CHC}(\text{CH}_2)$, $J_{\text{C-H}} = 162$ Hz),

77.41 (*THF*), 47.85 ($\text{Ti}=\text{CHCMe}_3$), 32.09 ($\text{Ti}=\text{CHCMe}_3$), 28.89 (CHMe_2), 28.81 (CHMe_2), 28.72 (CHMe_2), 28.54 (CHMe_2), 26.42 (*Me*), 26.30 (*Me*), 25.93 (*Me*), 25.87 (*Me*), 25.89 (*Me*), 25.16 (*Me*), 25.02 (*THF*), 24.66 (*Me*), 24.21 (*Me*), 23.85 (*Me*). Anal. Calcd for $\text{C}_{38}\text{H}_{58}\text{N}_2\text{OTi}$: C, 75.22; H, 9.63; N, 4.62. Found: C, 74.00; H, 9.50; N, 4.72.

Synthesis of 3. In a vial was dissolved $(\text{L}_3)\text{Ti}=\text{CH}^t\text{Bu}(\text{OTf})$ (116 mg, 0.15 mmol) in 10 mL of pentane, and the solution was cooled to -35°C . To the cold solution was added a cold pentane solution (~ 5 mL) containing $\text{LiCH}_2\text{SiMe}_3$ (14.42 mg, 0.15 mmol). After it was warmed, the mixture was stirred for an additional 20 min. The solution was filtered and the filtrate concentrated and stored at -35°C for 24 h to afford dark blocks of $(\text{L}_3)\text{Ti}=\text{CH}^t\text{Bu}(\text{CH}_2\text{SiMe}_3)$ (**3**; 96 mg, 0.13 mmol, 89% yield, two crops).

Data for **3** are as follows. ^1H NMR (23 $^\circ\text{C}$, 399.8 MHz, C_6D_6): δ 7.13–7.05 (m, C_6H_3 , 6H), 5.47 (s, (^tBu) CCHC^tBu), 1H, based on HMQC), 4.54 (s, $\text{Ti}=\text{CH}^t\text{Bu}$, 1H), 3.49 (septet, CHMe_2 , 2H), 3.37 (septet, CHMe_2 , 2H), 1.77 (d, CHMe_2 , 6H), 1.75 (s, $\text{Ti}-\text{CH}_2\text{SiMe}_3$, 2H), 1.42 (d, CHMe_2 , 12H), 1.33 (d, CHMe_2 , 6H), 1.05 (s, (^tBu) CCHC^tBu), 18H), 0.68 (s, $\text{Ti}=\text{CH}^t\text{Bu}$, 9H), 0.39 (s, $\text{Ti}-\text{CH}_2\text{SiMe}_3$, 9H). ^{13}C NMR (25 $^\circ\text{C}$, 100.6 MHz, C_6D_6): δ 260.8 ($\text{Ti}=\text{CH}^t\text{Bu}$, $J_{\text{C-H}} = 88$ Hz), 174.5 ((^tBu) CCHC^tBu), 147.8 (*ipso*- C_6H_3), 142.6 (*o*- C_6H_3), 139.9 (*o*- C_6H_3), 126.0 (*p*- C_6H_3), 124.3 (*m*- C_6H_3), 124.1 (*m*- C_6H_3), 93.58 ((^tBu) CCHC^tBu , $J_{\text{C-H}} = 152$ Hz), 56.00 ($\text{Ti}-\text{CH}_2\text{SiMe}_3$, $J_{\text{C-H}} = 98$ Hz), 47.49 ($\text{Ti}=\text{CHCMe}_3$), 44.49 ((CMe_3) $\text{CCHC}(\text{CMe}_3)$), 32.35 ((CMe_3) $\text{CCHC}(\text{CMe}_3)$), 31.60 ($\text{Ti}=\text{CHCMe}_3$), 29.06 (CHMe_2), 28.75 (CHMe_2), 27.94 (*Me*), 26.63 (*Me*), 24.92 (*Me*), 24.86 (*Me*), 4.25 ($\text{TiCH}_2\text{SiMe}_3$). Anal. Calcd for $\text{C}_{44}\text{H}_{74}\text{N}_2\text{SiTi}$: C, 74.74; H, 10.55; N, 3.96. Found: C, 74.05; H, 10.81; N, 4.12.

Synthesis of 4. In a vial was dissolved $(\text{L}_3)\text{Ti}=\text{CH}^t\text{Bu}(\text{OTf})$ (108 mg, 0.14 mmol) in 10 mL of THF and the solution cooled to -35°C . To the cold solution was added a cold THF solution (~ 5 mL) containing KCH_2Ph (18.78 mg, 0.14 mmol). After it was warmed, the mixture was stirred for an additional 20 min. Solvent was then removed under reduced pressure, the solid extracted with hexane, the extract filtered, and the filtrate concentrated and stored at -35°C for 24 h to afford dark blocks of $(\text{L}_3)\text{Ti}=\text{CH}^t\text{Bu}(\text{CH}_2\text{Ph})$ (**4**; 74 mg, 0.10 mmol, 72% yield, two crops).

Data for **4** are as follows. ^1H NMR (23 $^\circ\text{C}$, 399.8 MHz, C_6D_6): δ 7.32–6.91 (m, aryl, 11H), 5.31 (s, (^tBu) CCHC^tBu), 1H), 3.70 (s, $\text{Ti}=\text{CH}^t\text{Bu}$, 1H), 3.35 (septets, CHMe_2 , 4H), 3.29 (s, $\text{Ti}-\text{CH}_2\text{Ph}$, 2H), 1.67 (d, CHMe_2 , 6H), 1.40 (d, CHMe_2 , 6H), 1.36 (d, CHMe_2 , 6H), 1.30 (d, CHMe_2 , 6H), 0.99 (s, (^tBu) CCHC^tBu), 18H), 0.65 (s, $\text{Ti}=\text{CH}^t\text{Bu}$, 9H). ^{13}C NMR (25 $^\circ\text{C}$, 100.6 MHz, C_6D_6): δ 253.9 ($\text{Ti}=\text{CH}^t\text{Bu}$, $J_{\text{C-H}} = 88$ Hz), 174.1 ((^tBu) CCHC^tBu), 152.0 (*ipso*-aryl), 148.0 (*ipso*-aryl), 142.7 (*o*-aryl), 139.5 (*o*-aryl), 127.9 (*o*-aryl), 126.6 (*p*-aryl), 126.1 (*p*-aryl), 124.3 (*m*-aryl), 123.8 (*m*-aryl), 120.6 (*m*-aryl), 90.74 ((^tBu) CCHC^tBu , $J_{\text{C-H}} = 152$ Hz), 67.13 ($\text{Ti}-\text{CH}_2\text{Ph}$, $J_{\text{C-H}} = 114$ Hz), 48.42 ($\text{Ti}=\text{CHCMe}_3$), 44.67 ((CMe_3) $\text{CCHC}(\text{CMe}_3)$), 32.14 ((CMe_3) $\text{CCHC}(\text{CMe}_3)$), 31.41 ($\text{Ti}=\text{CHCMe}_3$), 29.60 (CHMe_2), 28.80 (CHMe_2), 27.44 (*Me*), 26.29 (*Me*), 24.73 (*Me*), 24.60 (*Me*). Anal. Calcd for $\text{C}_{47}\text{H}_{70}\text{N}_2\text{Ti}$: C, 79.40; H, 9.92; N, 3.94. Found: C, 78.98; H, 9.36; N, 3.61.

Synthesis of 5 and 6 from Thermolysis of 1. In a vial was dissolved $(\text{L}_1)\text{Ti}=\text{CH}^t\text{Bu}(\text{CH}_2\text{SiMe}_3)$ (**1**; 175 mg, 0.28 mmol) in 10 mL of hexane. After 10 days at 25 $^\circ\text{C}$ red crystals of $\text{Ti}[2,6-(\text{CMe}_2)(\text{CHMe}_2)\text{C}_6\text{H}_3]\text{NC}(\text{Me})\text{CHC}(\text{Me})\text{N}[2,6-(\text{CMe}_2)(\text{CHMe}_2)\text{C}_6\text{H}_3](\text{CH}_2\text{SiMe}_3)$ (**5**; 22 mg, 0.04 mmol, 14% yield) slowly precipitated. The crystals were separated, and the filtrate was cooled to -35°C for 15 days to afford orange-yellow crystals of $[\text{Ti}=\text{NAr}(\text{Ar})\text{NC}(\text{Me})\text{CHC}(\mu\text{-CH}_2)=\text{CH}^t\text{Bu})]_2$ (**6**; 57 mg, 0.05 mmol). After separation of **5** and **6**, examination of the filtrate revealed a myriad of products present, including complex **6**. Crystals of **6** are sparingly soluble in most common organic solvents, as well as in CH_2Cl_2 . Complex **6** does dissolve slowly in THF, but upon solvation it gradually transforms over several minutes to complex **8**.

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Data for **5** are as follows. ^1H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.54–7.08 (m, C_6H_3 , 6H), 5.45 (s, $\text{C}(\text{Me})\text{CHC}(\text{Me})$, 1H), 2.82 (septet, CHMe_2 , 2H), 2.28 (s, CMe_2 , 6H), 2.06 (s, CHMe_2 , 6H), 1.22 (d, CHMe_2 , 6H), 0.77 (s, $\text{C}(\text{Me})\text{CHC}(\text{Me})$, 6H), 0.61 (d, CHMe_2 , 6H), 0.05 (s, $\text{Ti}-\text{CH}_2\text{SiMe}_3$, 9H), -1.38 (s, $\text{CH}_2\text{-SiMe}_3$, 2H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 160.6 ($\text{C}(\text{Me})\text{CHC}(\text{Me})$), 142.8 (*ipso*- C_6H_5), 141.5 (*o*- C_6H_3), 136.0 (*o*- C_6H_3), 130.9 (*p*- C_6H_3), 127.9 (*m*- C_6H_3), 124.6 (*m*- C_6H_3), 104.5 ($\text{C}(\text{Me})\text{CHC}(\text{Me})$), 80.06 (CMe_2), 63.13 ($\text{Ti}-\text{CH}_2\text{SiMe}_3$), 27.93 (CMe_2), 27.75 (CHMe_2), 25.20 (Me), 24.38 (Me), 22.09 (Me), 21.65 (Me), 2.89 ($\text{TiCH}_2\text{SiMe}_3$). Anal. Calcd for $\text{C}_{33}\text{H}_{50}\text{N}_2\text{SiTi}$: C, 71.97; H, 9.15; N, 5.09. Found: C, 71.82; H, 9.25; N, 5.32.

Data for **6** are as follows. ^1H NMR (23 °C, 399.8 MHz, $\text{THF}-d_8$): δ 7.20–7.10 (m, C_6H_3 , 3H), 6.84 (d, C_6H_3 , 2H), 6.62 (t, C_6H_3 , 1H), 5.51 (br, $^t\text{BuHCC}(\text{CH}_2)\text{CHC}(\text{Me})$, based on HMQC, 1H), 5.07 (br, $^t\text{BuHCC}(\text{CH}_2)\text{CHC}(\text{Me})$, based on HMQC, 1H), 3.97 (br, CHMe_2 , 2H), 3.74 (br, CHMe_2 , 2H), 3.01 (br, $^t\text{BuHCC}(\text{CH}_2)\text{CHC}(\text{Me})$, 1H), 2.30 (br, $^t\text{BuHCC}(\text{CH}_2)\text{CHC}(\text{Me})$, 1H), 1.80 (s, $^t\text{BuHCC}(\text{CH}_2)\text{CHC}(\text{Me})$, 3H), 1.38 (s, ($\text{Me}_3\text{C})\text{HCC}(\text{CH}_2)\text{-CHC}(\text{Me})$, 9H), 1.33 (overlapping doublets, CHMe_2 , 12H), 1.16 (d, CHMe_2 , 6H), 1.09 (d, CHMe_2 , 6H). ^{13}C NMR (25 °C, 100.6 MHz, $\text{THF}-d_8$): δ 157.8 ($^t\text{BuHCC}(\text{CH}_2)\text{CHC}(\text{Me})$), 150.1 (br, $^t\text{BuHCC}(\text{CH}_2)\text{CHC}(\text{Me})$), 143.8 (C_6H_3), 142.9 (C_6H_3), 140.4 (C_6H_3), 131.3 (br, $^t\text{BuHCC}(\text{CH}_2)\text{CHC}(\text{Me})$), 124.4 (C_6H_6), 123.7 (C_6H_3), 122.3 (C_6H_3), 119.5 (C_6H_3), 103.1 (br, $^t\text{BuHCC}(\text{CH}_2)\text{-CHC}(\text{Me})$), 69.23 (br, $^t\text{BuHCC}(\text{CH}_2)\text{CHC}(\text{Me})$), 33.47 ($\text{Me}_3\text{-CHCC}(\text{Me})\text{CHC}(\text{Me})$), 32.60 (br, 28.82 (br), 27.9 (br), 25.9 (br), 24.40 (br). Anal. Calcd for $\text{C}_{68}\text{H}_{100}\text{N}_4\text{Ti}_2$: C, 76.38; H, 9.43; N, 4.24. Found: C, 76.04; H, 9.25; N, 5.14. LDI MS for $\text{C}_{63}\text{H}_{88}\text{N}_4\text{-Ti}_2$: calcd m/z , 1069 (M^+); found m/z , 1068.

Independent Synthesis of Complex 5. In a vial was loaded $\text{Ti}[2,6-(\text{CMe}_2)(\text{CHMe}_2)\text{C}_6\text{H}_3]\text{NC}(\text{Me})\text{CHC}(\text{Me})\text{N}[2,6-(\text{CMe}_2)(\text{CHMe}_2)\text{C}_6\text{H}_3](\text{OTf})$ (75 mg, 0.12 mmol), the solid dissolved in 10 mL of Et_2O , and the solution cooled to -35 °C. To the cold solution was added a cold Et_2O solution (~ 5 mL) containing $\text{LiCH}_2\text{SiMe}_3$ (12.1 mg, 0.13 mmol). After the reaction mixture was warmed to room temperature it was stirred for an additional 1 h. Solvent was then evaporated under reduced pressure, the solid extracted with benzene, the extract filtered, and solvent again evaporated under reduced pressure. The solid was then dissolved in Et_2O , the solution filtered, and the filtrate concentrated and stored at -35 °C for 24 h to afford dark red crystals of $\text{Ti}[2,6-(\text{CMe}_2)(\text{CHMe}_2)\text{C}_6\text{H}_3]\text{NC}(\text{Me})\text{CHC}(\text{Me})\text{N}[2,6-(\text{CMe}_2)(\text{CHMe}_2)\text{C}_6\text{H}_3](\text{CH}_2\text{SiMe}_3)$ (**5**; 59 mg, 0.11 mmol, 87% yield, two crops). ^1H and ^{13}C NMR spectra were identical with independent samples of **5** prepared via thermolysis of **1**.

Synthesis of Complex 7. In a reaction vessel was dissolved ($^t\text{BuC}=\text{C}(\text{Me})\text{CHC}(\text{Me})\text{N}[\text{Ar}])\text{Ti}=\text{NAr}(\text{OTf})$ (200 mg, 0.29 mmol) in pentane (10 mL), and the solution was cooled to -35 °C. To the cold solution was added a cold pentane solution (~ 5 mL) containing $\text{LiCH}_2\text{SiMe}_3$ (27.5 mg, 0.29 mmol). After the mixture was stirred for 30 min, the solution was filtered and the filtrate concentrated and stored at -35 °C for 24 h to afford red blocks of ($^t\text{BuC}=\text{C}(\text{Me})\text{CHC}(\text{Me})\text{N}[\text{Ar}])\text{Ti}=\text{NAr}(\text{CH}_2\text{-SiMe}_3)$ (**7**; 151 mg, 0.24 mmol, 83% yield, two crops).

Data for **7** are as follows. ^1H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.07–6.84 (m, C_6H_3 , 6H), 5.00 (s, $^t\text{BuHCC}(\text{Me})\text{CHC}(\text{Me})$, 1H), 3.53 (septet, CHMe_2 , 2H), 2.43 (s, $^t\text{BuHCC}(\text{Me})\text{CHC}(\text{Me})$, 1H), 2.23 (septet, $\text{CH}(\text{Me})_2$, 2H), 1.97 (s, $^t\text{BuHCC}(\text{Me})\text{-CHC}(\text{Me})$, 3H), 1.92 (d, $\text{TiCH}_2\text{SiMe}_3$, 1H, $J_{\text{H-H}} = 10$ Hz), 1.74 (s, $^t\text{BuHCC}(\text{Me})\text{CHC}(\text{Me})$, 3H), 1.39 (d, CHMe_2 , 6H), 1.23 (s, $^t\text{BuHCC}(\text{Me})\text{CHC}(\text{Me})$, 9H), 1.14 (d, CHMe_2 , 6H), 1.08 (d, CHMe_2 , 6H), 1.04 (d, CHMe_2 , 6H), 0.25 (d, $\text{TiCH}_2\text{SiMe}_3$, 1H, $J_{\text{H-H}} = 10$ Hz), 0.22 (s, $\text{TiCH}_2\text{SiMe}_3$, 9H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 160.9 ($^t\text{BuHCC}(\text{Me})\text{CHC}(\text{Me})$), 157.6 ($^t\text{BuHCC}(\text{Me})\text{CHC}(\text{Me})$), 155.2 (C_6H_3), 145.7 (C_6H_3), 142.8 (C_6H_3), 139.8 (C_6H_3), 131.6 ($^t\text{BuHCC}(\text{Me})\text{CHC}(\text{Me})$, based on HMQC, $J_{\text{C-H}} = 123$ Hz), 127.9 (C_6H_6), 126.7 (C_6H_3), 125.2 (C_6H_3), 123.5 (C_6H_3), 122.6 (C_6H_3), 121.8 (C_6H_6), 97.71 ($^t\text{BuHCC}(\text{Me})\text{CHC}(\text{Me})$, $J_{\text{C-H}} = 163$ Hz), 54.23 ($\text{TiCH}_2\text{SiMe}_3$, $J_{\text{C-H}}$

$= 107$ Hz), 35.23 ($\text{Me}_3\text{CHCC}(\text{Me})\text{CHC}(\text{Me})$), 32.51 ($\text{Me}_3\text{CHCC}(\text{Me})\text{CHC}(\text{Me})$), 29.65 (CHMe_2), 28.21 (CHMe_2), 25.52 (Me), 25.28 (Me), 25.13 (Me), 24.72 (Me), 24.28 (Me), 24.14 (Me), 23.34 (Me), 22.85 (Me), 3.33 ($(\text{TiCH}_2\text{SiMe}_3)$). Anal. Calcd for $\text{C}_{38}\text{H}_{62}\text{N}_2\text{SiTi}$: C, 73.28; H, 10.03; N, 4.50. Found: C, 73.11; H, 9.95; N, 4.60.

Synthesis of ($\text{H}_2\text{C}=\text{C}(\text{CH}^t\text{Bu})\text{CHC}(\text{Me})\text{N}[\text{Ar}])\text{Ti}=\text{NAr}(\text{THF})$ (8**).** In a vial was dissolved complex **6** in 10 mL of THF (75 mg, 0.75 mmol), and after a few minutes the solvent was evaporated under reduced pressure to afford ($\text{H}_2\text{C}=\text{C}(\text{CH}^t\text{Bu})\text{-CHC}(\text{Me})\text{N}[\text{Ar}])\text{Ti}=\text{NAr}(\text{THF})$ (**8**) quantitatively. Single crystals can be readily obtained from Et_2O at -35 °C.

Data for **8** are as follows. ^1H NMR (23 °C, 399.8 MHz, $\text{THF}-d_8$): δ 7.16–6.89 (m, C_6H_3 , 6H), 5.29 (s, $^t\text{BuHCC}(\text{CH}_2)\text{CHC}(\text{Me})$ and $^t\text{BuHCC}(\text{CH}_2)\text{CHC}(\text{Me})$, 2H, based on HMQC), 3.86 (br, THF , 4H), 3.79 (septet, $\text{CH}(\text{Me})_2$, 2H), 3.67 (d, $^t\text{BuHCC}(\text{CH}_2)\text{-CHC}(\text{Me})$, 1H, $J_{\text{H-H}} = 9$ Hz), 3.46 (septet, CHMe_2 , 1H), 3.05 (septet, CHMe_2 , 1H), 2.78 (d, $^t\text{BuHCC}(\text{CH}_2)\text{CHC}(\text{Me})$, 1H, $J_{\text{H-H}} = 9$ Hz), 1.59 (s, $^t\text{BuHCC}(\text{CH}_2)\text{CHC}(\text{Me})$, 3H), 1.36 (d, CHMe_2 , 3H), 1.32 (s, ($\text{Me}_3\text{C})\text{HCC}(\text{CH}_2)\text{CHC}(\text{Me})$, 9H), 1.30 (br, THF , 4H), 1.27 (d, CHMe_2 , 3H), 1.22 (mixture of two doublet CHMe_2 , 6H), 1.34 (d, CHMe_2 , 9H), 0.88 (d, CHMe_2 , 3H). ^{13}C NMR (25 °C, 100.6 MHz, $\text{THF}-d_8$): δ 157.9 ($^t\text{BuHCC}(\text{CH}_2)\text{CHC}(\text{Me})$), 147.9 ($^t\text{BuHCC}(\text{CH}_2)\text{CHC}(\text{Me})$), 144.0 (C_6H_3), 143.3 (C_6H_3), 142.8 (C_6H_3), 138.3 (C_6H_6), 136.2 (C_6H_6), 136.2 ($^t\text{BuHCC}(\text{CH}_2)\text{-CHC}(\text{Me})$, based on HMQC, $J_{\text{C-H}} = 146$ Hz), 125.4 (C_6H_6), 124.1 (C_6H_3), 123.0 (C_6H_3), 122.4 (C_6H_6), 119.7 (C_6H_3), 103.7 ($^t\text{BuHCC}(\text{CH}_2)\text{CHC}(\text{Me})$, $J_{\text{C-H}} = 159$ Hz), 74.92 (br, $^t\text{BuHCC}(\text{CH}_2)\text{CHC}(\text{Me})$, based on HMQC), 71.04 (THF), 33.00 ($\text{Me}_3\text{-CHCC}(\text{CH}_2)\text{CHC}(\text{Me})$), 31.47 ($\text{Me}_3\text{CHCC}(\text{Me})\text{CHC}(\text{Me})$), 28.89 (CHMe_2), 28.28 (CHMe_2), 25.44 (THF), 25.22 (Me), 25.09 (Me), 24.61 (Me), 24.40 (Me), 24.20 (Me), 23.36 (Me), 22.94 (Me). Complex **8** is thermally unstable, and multiple attempts to obtain satisfactory elemental analysis were unsuccessful.

Synthesis of 9. In a vial was dissolved (L_1) $\text{Ti}=\text{CH}^t\text{Bu}(\text{CH}_2\text{-SiMe}_3)$ in 3 mL of toluene (175 mg, 0.256 mmol) and the brown solution cooled to -35 °C. To the cold solution was added dropwise a cooled (-35 °C) suspension of KC_8 (38 mg, 281 mmol) in THF (~ 3 mL). The solution quickly changes to a dark green-brown and was stirred for 1 h. The solution was dried in vacuo, and the residue was extracted with pentane. The green-brown solution was filtered and then pumped dry to give crude $\text{Ti}([\text{Ar}])\text{NC}(\text{Me})\text{CHC}(\text{Me})\text{N}[2,6-(\text{CHMe}_2)(\text{CH}(\text{CH}_2)(\text{Me})\text{-C}_6\text{H}_3)](\text{CH}_2^t\text{Bu})$ (**9**; 135 mg). Examination of the product by ^1H NMR spectra reveals a myriad of products including starting material. Attempts to recrystallize the crude material led to formation of a few single crystals of **9** along with significant decomposition. The crude product gave $\mu_{\text{eff}} = 1.756 \mu_{\text{B}}$ (C_6D_6 , 298 K, Evans' method). X-band EPR of the crude product gives $g_{\text{iso}} = 1.957$ G (in an 1/1 Et_2O /pentane mixture). EPR spectra also display signals consistent with other paramagnetic Ti species present in solution. Coupling is observed but not adequately simulated. Attempts to obtain satisfactory elemental analysis were unsuccessful.

Synthesis of 10. In a vial was dissolved (L_3) $\text{Ti}=\text{CH}^t\text{Bu}(\text{OTf})$ (108 mg, 0.14 mmol) in 10 mL of Et_2O , and the solution was cooled to -35 °C. To the cold solution was added a cold Et_2O solution (5 mL) containing Li^tBu (10.18 mg, 0.16 mmol). After it was warmed, the mixture was stirred for an additional 5 min and solvent was evaporated under reduced pressure. The solid was extracted with pentane, the extract filtered, and the filtrate concentrated and stored at -35 °C for 24 h to afford dark green crystals of $\text{Ti}([\text{Ar}])\text{NC}(\text{Me})\text{CHC}(\text{Me})\text{N}[2,6-(\text{CHMe}_2)(\text{CH}(\text{CH}_2)(\text{Me})\text{-C}_6\text{H}_3)](\text{CH}_2^t\text{Bu})$ (**10**; 58 mg, 0.09 mmol, 65% yield, three crops). The compound (L_3) $\text{Ti}=\text{CH}^t\text{Bu}(\text{OTf})$ can also be reduced with 1.2 equiv of KC_8 (0.5 h) in THF/toluene and worked up analogously to afford **10** in low yield.

Data for **10** are as follows. ^1H NMR (23 °C, 399.8 MHz, C_6D_6): δ 8.22 ($\Delta\nu_{1/2} = 957$ Hz), 7.86 ($\Delta\nu_{1/2} = 257$ Hz), 5.78 ($\Delta\nu_{1/2} = 153$ Hz), 2.65 ($\Delta\nu_{1/2} = 1210$ Hz), 2.05 ($\Delta\nu_{1/2} = 116$ Hz), 0.29 ($\Delta\nu_{1/2} = 203$ Hz), -0.92 ($\Delta\nu_{1/2} = 2085$ Hz). $\mu_{\text{eff}} = 1.83 \mu_{\text{B}}$ (C_6D_6 ,

298 K, Evans' method). Complex **10** is thermally unstable, and multiple attempts to obtain satisfactory elemental analysis were unsuccessful.

Oxidation of **10 to $(L_3)Ti=CH^tBu(OTf)$.** In a reaction vessel was dissolved **10** (103 mg, 0.17 mmol) in 10 mL of THF, and the solution was cooled to $-35\text{ }^\circ\text{C}$. To the cold solution was added a cold THF solution ($\sim 5\text{ mL}$) containing $AgOTf$ (44.8 mg, 0.17 mmol), causing an immediate color change from green to brown. After the mixture was stirred for 15 min, the solution was filtered, and the filtrate was evaporated under reduced pressure. The solid was dissolved in pentane, the solution filtered, and the filtrate concentrated and stored at $-35\text{ }^\circ\text{C}$ for 24 h to afford dark crystals of $(L_3)Ti=CH^tBu(OTf)$ (120 mg, 0.16 mmol, 94% yield, two crops). 1H and ^{13}C NMR spectra of the product were compared to samples prepared independently.

Structure Solution and Refinement. A summary of crystal data and refinement details for all structures are given in Tables 2 and 3.

General Parameters for Data Collection and Refinement. Single crystals of **1** (pentane), **2** (hexane), **4** (hexane), **6**- C_5H_{12} (pentane), **7** (hexane), **8** (Et_2O), **9** (hexane), and **10** (pentane) were grown at $-35\text{ }^\circ\text{C}$. Inert-atmosphere techniques were used to place the crystal onto the tip of a glass capillary (0.06–0.20 mm), which was mounted on a SMART6000 diffractometer (Bruker) at 127–140(2) K. A preliminary set of cell constants was calculated from reflections obtained from three nearly orthogonal sets of 20–30 frames. The data collection was carried out using graphite-monochromated $Mo\ K\alpha$ radiation with a frame time of 3 s and a detector distance of 5.0 cm. A randomly oriented region of a sphere in reciprocal space was surveyed. Three sections of 606 frames were collected with 0.30° steps in ω at different ϕ settings with the detector set at -43° in 2θ . Final cell constants were calculated from the xyz centroids of strong reflections from the actual data collection after integration (SAINT).⁴⁰ The structure was solved using SHELXS-97 and refined with SHELXL-97.⁴¹ A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least-squares/difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters (unless otherwise mentioned). All hydrogen atoms were refined with isotropic displacement parameters (unless otherwise mentioned).

For **2**, intensity statistics and systematic absences suggested the noncentrosymmetric trigonal space group $P3_1$, and subsequent solution and refinement confirmed this choice. Several different crystals were examined, and all were badly split with large mosaic character. Three crystallographically independent but chemically equivalent molecules were confined in the cell.

For **6**- C_5H_{12} , intensity statistics and systematic absences suggested the centrosymmetric triclinic space group $P\bar{1}$, and subsequent solution and refinement confirmed this choice. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least-squares/difference Fourier cycles were performed which located the remaining non-hydrogen atoms, including a disordered pentane solvent. All non-hydrogen atoms were refined with anisotropic displacement parameters. With the exception of those associated with the solvent molecule, all hydrogen atoms were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement.

For **8**, intensity statistics and systematic absences suggested

the centrosymmetric space group $P2_1/n$, and subsequent solution and refinement confirmed this choice. All non-hydrogen atoms were refined with anisotropic displacement parameters. A disorder involving a diethyl ether is present at the THF site but was easily modeled. All hydrogen atoms except those associated with the partial occupancy diethyl ether were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement. The hydrogen atoms associated with the ether were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The remaining electron density was located in bonds.

For **9**, the crystals occur as dark green clusters of crystals with few well-defined faces. Several crystals were examined and found to be badly split and twinned. It was finally possible to locate a fragment which had only three components, with one that was clearly dominant. Intensity statistics and systematic absences suggested the centrosymmetric space group $P2_1/c$, and subsequent solution and refinement confirmed this choice. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least-squares/difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. There is a slight disorder, with 7.3% of the sites having an alternate Ti position. All hydrogen atoms were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement.

For **10**, intensity statistics and systematic absences suggested the centrosymmetric space group $P2_1/n$, and subsequent solution and refinement confirmed this choice. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least-squares/difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. There is a disorder present with the titanium atom shifted to the other side of the plane defined by N(2), N(6), and C(39). All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement. The final full-matrix least-squares refinement converged to $R1 = 0.0441$ and $wR2 = 0.1134$ (F^2 , all data). The remaining electron density is located on bonds.

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Supporting Information Available: CIF files giving complete details for data sets, including tables with atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and structural diagrams for complexes **1**, **2**, **4**, **6**- C_5H_{12} , and **7**–**10**, and figures giving additional NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(40) SAINT 6.1; Bruker Analytical X-ray Systems, Madison, WI.

(41) SHELXTL-Plus V5.10; Bruker Analytical X-ray Systems, Madison, WI.