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Four-Coordinate Titanium Alkylidene Complexes: Synthesis, Reactivity, and Kinetic Studies Involving the Terminal Neopentylidene Functionality

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A series of titanium complexes containing a terminal neopentylidene functionality have been prepared by a one electron oxidatively induced α-hydrogen abstraction from the corresponding bis-neopentyl precursor (Nacnac)Ti(CH$_2{}^t$Bu)$_2$ (Nacnac$^-$ = [Ar]NC(CH$_3$)CHC(CH$_3$)N[Ar], Ar = 2,6-(CHMe$_2$)$_2$C$_6$H$_3$), among them (Nacnac)Ti=CH^{t}Bu(OTf) and (Nacnac)Ti=CH^{t}Bu(I). It was determined that bulky alkyl groups bound to titanium as well as a bulky coordinating anion from the oxidant are needed to promote α-hydrogen abstraction. Complex (Nacnac)Ti=CH^{t}Bu(OTf) serves as a template for other four-coordinate titanium neopentylidene complexes such as (Nacnac)Ti=CH^{t}Bu(X) (X$^-$ = Cl, Br, and BH$_4$). Complexes (Nacnac)Ti=CH^{t}Bu(X) undergo cross-metathesis reactivity with the imine functionality of the Nacnac$^-$ ligand forming the imido complexes (H^{t}BuC=C(Me)CHC(Me)N[Ar])Ti=NAr(X) (X$^-$ = OTf, Cl, Br, I, BH$_4$). In addition, C−H activation of two tertiary carbons also takes place to afford the titanacycles Ti[2,6-(CMe$_2$)(CHMe$_2$)C$_6$H$_3$]NC(Me)CHC(Me)N[2,6-(CMe$_2$)(CHMe$_2$)C$_6$H$_3$](X) (X$^-$ = OTf, Cl, Br and η^2-BH$_4$). Kinetic studies in C$_6$D$_6$ reveal the formation of (H^{t}BuC=C(Me)CHC(Me)N[Ar])Ti=NAr(I) from (Nacnac)Ti=CH^{t}Bu(I) to be independent of solvent (C$_6$D$_6$, Et$_2$O−d$_{10}$, THF-d$_8$) and the reaction to be first order in titanium ($k = 8.06 \times 10^{-4}$ s^{-1} at 57 °C, with activation parameters $\Delta H^\ddagger = 21.3(2)$ kcal/mol, $\Delta S^\ddagger = -8(3)$ cal/mol K). Compound (Nacnac)Ti=CH^{t}Bu(OTf) reacts with various substrates to afford products in which the alkylidene functionality has been significantly transformed. When the alkylidene derivatives (Nacnac$_{\text{tBu}}$)Ti=CH^{t}Bu(X) (X$^-$ = OTf, I; Nacnac$_{\text{tBu}}{}^-$ = [Ar]NC(^{t}Bu)CHC(^{t}Bu)N[Ar]) were prepared, the intramolecular cross-metathesis transformation observed with (Nacnac)Ti=CH^{t}Bu(X) was inhibited completely.

Introduction

High-oxidation-state transition-metal alkylidenes play an important role in industrial processes such as cross-metathesis, ring-closing metathesis, ring-opening metathesis, ring-opening metathesis polymerization, acyclic diene metathesis polymerization, acetylene polymerization, and Wittig-type or group-transfer reactions. The increasing importance and need for metal alkylidene complexes has been manifested in several reviews[1] and highlights.[2] To prepare high-oxidation-state metal alkylidenes, one must promote α-abstraction or α-deprotonation reactions from metal alkyl complexes lacking β-hydogens.[1,3] Promoting α-hydrogen abstraction to yield high-oxidation-state metal alkylidenes is typically induced thermally, photochemically, or with the aid of Lewis bases.[1,3−5] Hence the entry into d^0-metal alkylidenes is often restricted to this methodology, and access to low-coordinate and redox-active systems possessing this functionality can be difficult or limited since formation of the metal carbon double bond stems typically from a high-oxidation-state (or alternatively a singlet ground state) and often coordinatively saturated precursors. For this reason an attractive entry to the assembly of metal−ligand multiple bonds could derive from a redox reaction. Only a handful of examples of a one-electron oxidation leading to M=C bond formation have been reported.[6]

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Despite rapid growth of research in this area, far less attention has been applied to the synthesis and reactivity of terminal alkylidene complexes of titanium. Titanium alkylidenes generated in situ are utilized commonly as stoichiometric reagents in organic synthesis.[7] Their reactivity is typically manifested by the oxophilicity of the metal, thus leading to cross-metathesis transformations (also referred to as Wittig-like). The $Ti{=}C$ bond is expected to be highly nucleophilic or "Schrock-like", as the ligand is bound to a very electropositive metal. Hence, complexes of this type are often represented as $M^+{-}CR_2^- \approx M{=}CR_2$ much like ylides would resonate.[8] Prototypical among nucleophilic alkylidenes are those that can readily react with Lewis acids to make zwitterionic-like complexes.[7n] Using such a characteristic as a basis, group 4 alkylidenes are expected to be more reactive yet less tolerant to organic group functionalities. However, a clear contradiction to this dichotomy is Tebbe's reagent.[9] Such a system has been reported to tolerate a high degree of organic group functionality, disfavor epimerization of optically active substrates, and yet possess a very reactive alkylidene functionality.[7]

Unlike groups 5 and 6, isolable and terminal alkylidene complexes of the group 4 metals remain very elusive.[10] This fact likely arises from the lack of suitable synthetic entries to the reactive alkylidene functionality. Only a handful of group 4 complexes having a terminal alkylidene are known, and the vast majority are titanium based with coordination numbers ≥ 5.[1c,4,5,11] Therefore one would argue that the quest for reactive group 4 alkylidenes is most desirable for systems having low coordination numbers since reported d^0 metal alkylidene complexes with high catalytic activity (e.g., group 5 and 6 transition metals) are four-coordinate. In fact, even the late transition-metal complexes such as the ruthenium-based carbene catalyst precursors studied by Grubbs and co-workers have been described as "active" when the system dissociates a labile ligand to become four-coordinate.[12] The latter characteristic is especially important since organotransition metal complexes with low coordination numbers are inherently reactive and consequently provide useful templates to study processes such as small molecule activation and catalysis.

In contrast to Schrock's work on α-hydrogen elimination reactions to prepare $Ta{=}C$ linkages, which involve one-electron reduction of the corresponding alkyl halide (referred to as α-H elimination, 1,2-H migration),[13] we report the opposite, an oxidation reaction resulting in α-hydrogen abstraction concomitant with formation of a low-coordinate complex having a metal carbon double bond.[14] Of particular interest was the seminal work reported by Budzelaar[15a] and Theopold[15f] on redox-active and stable early-transition-metal d^x ($x = 1-3$) complexes having metal alkyl ligands.

Herein we describe a synthetic strategy leading to a family of four-coordinate, terminal titanium(IV) alkylidenes and subsequent transformations of the corresponding terminal $Ti{=}CH^tBu$ functionality. The choice of oxidant, alkyl group on the metal, and supporting chelate ligand all have a profound effect in the formation, kinetic stability, and reactivity of the alkylidene group.

Results and Discussion

Synthesis of Terminal and Four-Coordinate Titanium Neopentylidene Complexes. Our approach for preparing low-coordinate and terminal titanium alkylidene complexes involves an adaptation for the synthesis of the precursor (Nacnac)$TiCl_2$ ($Nacnac^-$ = [Ar]NC(Me)CHC(Me)N[Ar], Ar = 2,6-$(CHMe_2)_2C_6H_3$) complex reported previously by Budzelaar and co-workers.[15a] Following Budzelaar's procedure we recrystallized the THF base adduct (Nacnac)$TiCl_2$(THF) (**1**) from toluene in 70% yield as dark green blocks.[14,15a] Isolation of **1** avoids lower yields as well as additional steps in forming the THF-free complex (Nacnac)$TiCl_2$.

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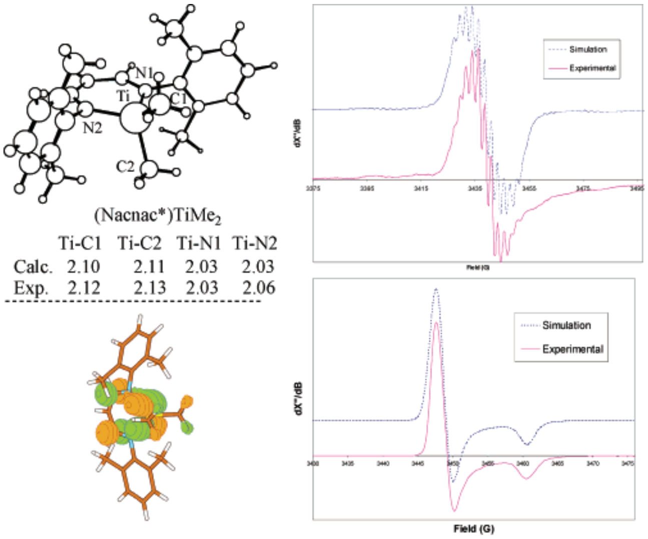


(Nacnac*)TiMe$_2$

	Ti-C1	Ti-C2	Ti-N1	Ti-N2
Calc.	2.10	2.11	2.03	2.03
Exp.	2.12	2.13	2.03	2.06

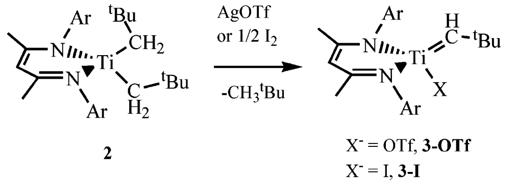
Figure 1. DFT calculations on the model complex (Nacnac*)TiMe$_2$ and structural comparisons with **2**. The SOMO is also depicted along with the room-temperature (298 K, top) and low-temperature EPR spectra (4.7 K, bottom, $g_\perp$ =1.963 and $g_\parallel$ = 1.955).

Complex **1** was characterized by a combination of ^{1}H NMR spectroscopic methods, elemental analysis, and single-crystal X-ray diffraction.[14] Ethereal solutions of **1** react rapidly with 2 equiv of LiCH$_2$^{t}Bu[3b] to afford emerald green solutions of (Nacnac)Ti(CH$_2$^{t}Bu)$_2$ (**2**), which was isolated as dark green blocks in 75% yield. Complex **2** was fully characterized,[14] and the molecular structure indicates no α-agostic interactions or remarkable features different from that of the reported dimethyl derivative.[15a] Complex **2** is amazingly stable unlike most low-coordinate bis-alkyl species of Ti(IV), and no elimination or abstraction reactions are observed under forcing conditions. In addition, complex **2** does not bind Lewis bases such as THF or PMe$_3$.

EPR spectra of **2** are consistent with a d^1 paramagnetic complex. Room-temperature EPR spectra reflect hyperfine coupling of the unpaired electron to titanium (^{47}Ti, I = 5/2, 7.4%; ^{49}Ti, I = 7/2, 5.4%, 14.9 G), as well as superhyperfine coupling to the two α-nitrogens (^{14}N, I = 1, 96.63%, 4.6 G) and super superhyperfine couling to four α-hydrogens (^{1}H, I = 1/2, 99.99%, 2.4 G). Low-temperature EPR spectra (77 K) display axial symmetry, suggesting that the orbital housing the unpaired electron lies in a plane perpendicular to the z-axis (z-axis is along the Ti−C$_\gamma$ of the NCC$_\gamma$CN−Nacnac$^-$ ring, Figure 1).[14] In fact, DFT calculations on the model complex (Nacnac*)TiMe$_2$ (Nacnac*$^-$ = [Ar]NCHCHCH-N[Ar], Ar = 2,6-Me$_2$C$_6$H$_3$) reproduced the key geometrical features of the solid-state structure of **2**. The calculated SOMO (singly occupied molecular orbital) has mostly d$_{xy}$ metal character, hence is perpendicular to the z-axis, which is clearly consistent with the anisotropic EPR spectra for **2** (Figure 1).

Seminal work by Budzelaar and co-workers has reported that titanium(III) bis-alkyl complexes react with electrophiles (e.g., [CPh$_3$][B(C$_6$F$_5$)$_4$][16]) to form highly reactive zwitterion Ti(III) species.[15a] Although these species polymerize ethylene, the characterization of the active product was hampered by its rapid decomposition. Suspecting that electrophiles such as [CPh$_3$]$^+$ might be good oxidants (E_{red} = −0.11 V vs FeCp$_2$/FeCp$_2$$^+$)[17] and that Ti(III) are good reductants we reasoned that oxidation of the metal was taking place instead of abstraction of the alkyl group. In fact, a cyclic voltammogram of a solution of **2** (THF/TBAH, TBAH = n-tetrabutylammonium hexafluorophosphate) showed one irreversible oxidation wave at −0.90 V (referenced vs FeCp$_2$/FeCp$_2$$^+$) for the Ti(III)/Ti(IV) couple, thus suggesting that [CPh$_3$]$^+$ could be oxidizing the Ti(III) center.[14]

Scheme 1. Synthesis of Four-Coordinate Titanium Alkylidenes by a One-Electron Oxidation Reaction



2

X$^-$ = OTf, **3-OTf**
X$^-$ = I, **3-I**

Chemically, it was found that treatment of **2** with AgOTf or 0.5 equiv of I$_2$ caused a rapid color change from green to red-brown, concomitant with formation of the alkylidene complexes (Nacnac)Ti=CH^{t}Bu(X) (X$^-$ = OTf, **3-OTf**, 89%; X$^-$ = I, **3-I**, 61%), as evaluated by ^{1}H and ^{13}C NMR spectroscopic methods (Scheme 1).[14] The moderate yield observed in the isolation of **3-I** reflects its thermal decomposition both in solution and in the solid state (vide infra). On the NMR time scale compounds **3-OTf** and **3-I** display spectroscopic features consistent with the molecule retaining C_s symmetry in solution. A C$_\alpha$ resonance centered at δ ~271−272 with a J_{CH} coupling constant of 90−85 Hz is diagnostic of both complexes having a terminal alkylidene functionality.[4,5] The J_{CH} coupling from the ^{13}C NMR spectral data suggests significant α-hydrogen agostic interaction with the electron-deficient metal center, especially for complex **3-I**.[1c] In compounds **3-OTf** and **3-I**, the ^{1}H NMR CH$_\alpha$ resonance was located and differentiated unambiguously from the CH$_\gamma$ resonance for the Nacnac$^-$ backbone using HMQC NMR methods.[18] Complexes **3-OTf** and **3-I** are likely formed from the putative five-coordinate and d^0 intermediate (Nacnac)Ti(CH$_2$^{t}Bu)$_2$-(X)[19] (X$^-$ = OTf, I), which then undergoes smooth α-hydrogen abstraction to form the Ti=C linkage.

Formation of complexes **3-OTf** and **3-I** raised two interesting questions in the α-hydrogen abstraction process: the role of the anion present in the oxidant, and the role of the alkyl group on titanium. Having considered these, it was determined that OTf$^-$ does in fact promote α-hydrogen abstraction since oxidation of **2** with [FeCp*$_2$][B(C$_6$F$_5$)$_4$][20−22] affords a relatively stable

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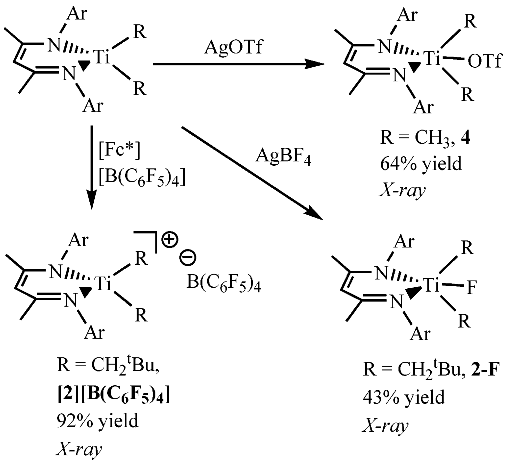
Scheme 2. Oxidation of 2 with $[FeCp^*_2][B(C_6F_5)_4]$ and $AgBF_4$, and Oxidation of Budzelaar's (Nacnac)$Ti(CH_3)_2$ with AgOTf



bis-alkyl cation, $[(Nacnac)Ti(CH_2{}^tBu)_2][B(C_6F_5)_4]$ (**[2][B(C$_6$F$_5$)$_4$]**), which gradually decomposes in solution at room temperature (Scheme 2). Lewis bases such as THF or PMe_3 appear to rapidly catalyze the decomposition of **[2][B(C$_6$F$_5$)$_4$]**. ^{1}H and ^{13}C NMR spectra (CD_2Cl_2, ranging from −60 to 25 °C) do not suggest the presence of α-agostic interactions in solution under these conditions and are consistent with two inequivalent neopentyl groups. The molecular structure and elemental analysis of **[2][B(C$_6$F$_5$)$_4$]** are also consistent with the proposed connectivity (Figure 2). To the best of our knowledge, four-coordinate and monomeric Ti(IV) bis-alkyl cations have not been reported, which is in sharp contrast to four-coordinate ion-paired or neutral species described in the literature.[23] The average Ti−C bond distance for **[2][B(C$_6$F$_5$)$_4$]** (∼2.03 Å) compares well with the M−C bond length of electron-deficient titanium zwitterions (2.081(5) Å).[23] In the solid-state structure of **[2][B(C$_6$F$_5$)$_4$]** it is difficult to ascertain whether α-H agostic interactions with the titanium center are taking place, but the discrepancy between $Ti-C_\alpha-C_\beta$ angles (Ti1−C33−C34 = 130.2(3)° vs Ti1−C38−C39 = 145.6(3)°) suggests that such an interaction might be playing a role (Figure 2). Due to the limited quality of the X-ray data for **[2][B(C$_6$F$_5$)$_4$]**, we are being conservative about the discussion of structural details. Based on preliminary data reported by Budzelaar and co-workers complex **[2][B(C$_6$F$_5$)$_4$]** could be in principle the olefin polymerization catalyst generated upon addition of the electrophile to the Ti(III) precursor,[15a] and we are currently examining this possibility.

The anion present in the oxidant must be sterically encumbering since oxidation of **2** with $AgBF_4$ leads only to oxidation and formation of $(Nacnac)Ti(CH_2{}^tBu)_2(F)$, **(2)-F** (Scheme 2). The connectivity of **2-F** has also been confirmed by a combination of NMR spectra and single-crystal X-ray diffraction studies (see Experimental Section and Supporting Information). It was determined that bulky alkyl groups are also needed to promote steric crowding and subsequent α-hydrogen abstraction. Accordingly, oxidation of Budzelaar's dimethyl complex $(Nacnac)Ti(CH_3)_2$[15a] with AgOTf does not lead to formation of the parent methylidene but instead affords the five-coordinate Ti(IV) dimethyl triflato complex $(Nacnac)Ti(CH_3)_2(OTf)$ (**4**) in moderate yield (Scheme 2). Thermolysis of **4** does not induce α-hydrogen abstraction, but instead gives rise to a myriad of products, several of which include Ti(III) compounds. Figure 2 displays the molecular structure for **4** along with selected metrical parameters.

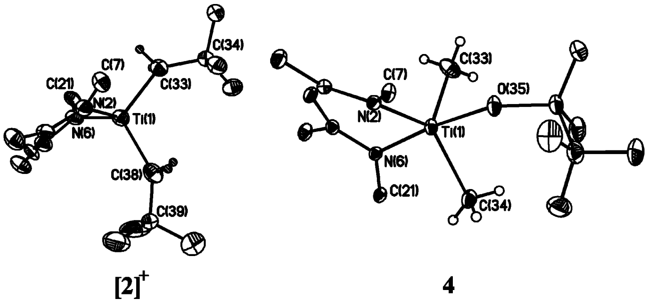


Figure 2. Molecular structures of **[2]**$^+$ and **4** showing the atom-labeling scheme with thermal ellipsoids at the 50% probability level. H atoms with the exception of the α-H and aryl groups with the exception of the ipso-carbon on the Nacnac$^-$ ligand have been excluded for clarity. Crystallographic data are reported in Table 3. Selected metrical parameters: For **[2]**$^+$: Ti1−N6, 1.934(3); Ti1−N2, 2.006(3); Ti1−C38, 2.009(5); Ti1−C33, 2.062(4) Å; N6−Ti1−N2, 95.2(4); N6−Ti1−C38, 115.5(7); N6−Ti1−C33, 109.3(7); N2−Ti1−C33, 112.4(7); C38−Ti1−C33, 112.6(9); Ti1−C33−C(34), 130.2(3); Ti(1)−C(38)−C(39), 145.6(3)°. For **4**: Ti1−N6, 2.039(3); Ti1−N2, 2.0409(13); Ti1−O35, 2.044(1); Ti1−C33, 2.079(9); Ti1−C34, 2.097(7) Å; N6−Ti1−N2, 90.79(5); N6−Ti1−O35, 174.16(5); N2−Ti1−O35, 90.70(5); N6−Ti1−C33, 94.66(7); O35−Ti1−C33, 90.09(7); N6−Ti1−C34, 89.48(6); N2−Ti1−C34, 127.67(7); O35−Ti1−C34, 85.14(6); C33−Ti1−C34, 121.17(8)°.

The derivatives $(Nacnac)Ti{=}CH^tBu(X)$ (X^- = Cl, **3-Cl**; Br, **3-Br**; BH_4, **3-BH$_4$**) can be readily prepared by the corresponding salt metathesis with **3-OTf** as depicted in Scheme 3. Although the preparation of **3-Cl** and **3-BH$_4$** is straightforward and involves simple anion exchange using $MgCl_2$[24] and $LiBH_4$, the synthesis of **3-Br** was somewhat less obvious. Greater yields of **3-Br** were obtained when the LiBr-ylide adduct $Ph_3P{=}CH_2\cdot LiBr$[25] was used in place of $MgBr_2$. The ylide salt adduct is apparently a much more soluble Br^- source than $MgBr_2$, and rapid Br^- exchange reduces the decomposition of thermally unstable **3-Br** (vide infra). Table 1 lists all the relevant spectroscopic features for **3-OTf**, **3-I**, **3-Cl**, **3-Br**, and **3-BH$_4$**. Judging from the ^{1}H and ^{13}C NMR spectra, as well as J_{C-H} coupling constants of the α-alkylidene C−H group, it is evident that electrophilicity of the metal center increases in the order **3-BH$_4$** < **3-Cl** < **3-OTf** < **3-Br** < **3-I**. The order of electrophilicity is reflective of the X^- ligand being a weaker π-donor (excluding **3-BH$_4$**); thus the metal participates

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[22] Basuli, F.; Bailey, B. C.; Huffman, J. C.; Mindiola, D. J. *Chem. Commun.* **2003**, 1554−1555.

[23] For a comprehensive review on activated and low-coordinate catalysts see: Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391−1434. A three-coordinate titanium alkyl cation has been proposed, but the geometry remains uncertain. Shafir, A.; Arnold, J. *J. Am. Chem. Soc.* **2001**, *123*, 9212−9213.

[24] For a similar preparation concerning halide metathesis in low-coordinate titanium complexes see: Cummins, C. C.; Schaller, C. P.; Van Duyne, G. D.; Wolczanski, P. T.; Chan, A. W. E.; Hoffmann, R. *J. Am. Chem. Soc.* **1991**, *113*, 2985−2994.

[25] (a) Schmidbaur, H.; Stühler, H.; Vornberger, W. *Chem. Ber.* **1972**, *105*, 1084−1086. (b) Reger, D. L.; Culbertson, E. C. *J. Organomet. Chem.* **1977**, *131*, 297−300.

Scheme 3. Synthesis of Terminal Titanium Alkylidene Complexes (Nacnac)Ti=CH^{t}Bu(X) (X$^-$ = Cl, Br, BH$_4$) by Salt Metathesis

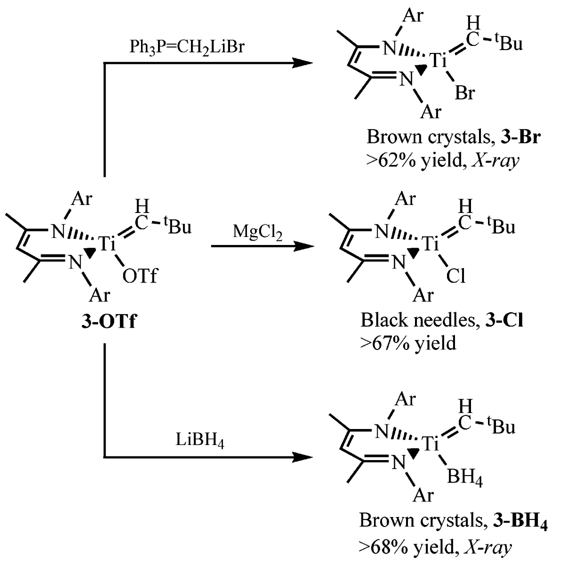

Table 1. Spectroscopic Data for the Alkylidene Complexes 3-X (X$^-$ = I, Br, OTf, Cl, BH$_4$)

	3-I	3-Br	3-OTf	3-Cl	3-BH$_4$
^{1}H NMR (δ) of Ti = C*H*	3.3	4.5	5.2	5.5	5.32
^{13}C NMR (δ) of Ti = *C*H	272	274	271	276	267
J_{C-H} (Hz)	85	88	90	93	95

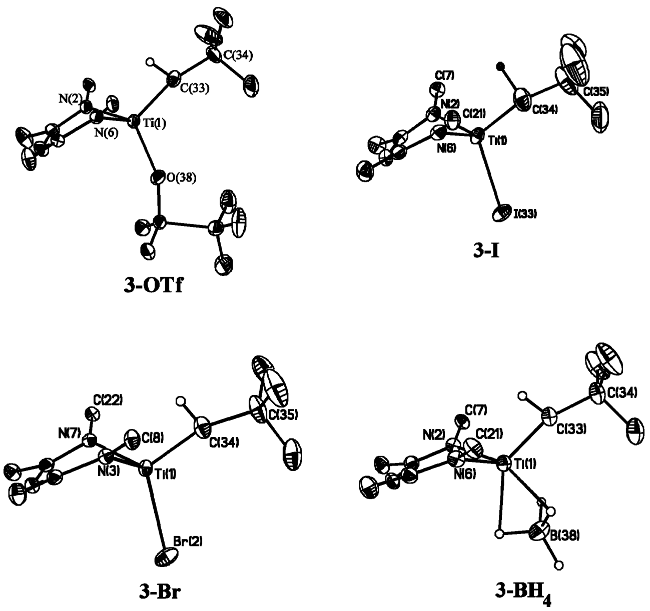

Figure 3. Molecular structures of **3-X** (X$^-$ = OTf, I, Br, BH$_4$) showing the atom-labeling scheme with thermal ellipsoids at the 50% probability level. H atoms with the exception of the α-hydrogens have been omitted for clarity. Aryl groups with the exception of the ipso-carbon on the Nacnac$^-$ ligand have been also excluded. Table 2 lists selected metrical parameters, and crystallographic data are reported in Table 3.

more in α-agostic interaction with the alkylidene hydrogen. In the case of **3-BH$_4$**, the hapticity of the BH$_4^-$ ligand remains uncertain. Although the borohydride resonance was not located in the ^{1}H NMR, the ^{11}B NMR spectrum displayed a quintet with J_{B-H} = 89 Hz, consistent with a fluxional BH$_4^-$ ligand.

Structural Comparisons of (Nacnac)Ti=CH^{t}Bu(X) (X$^-$ = OTf, Br, I, and η^3-BH$_4$). The molecular structures for complexes **3-X** (X$^-$ = OTf, Br, I, and BH$_4$) are isostructural and are shown in Figure 3. These systems are rare examples of terminal and low-coordinate titanium alkylidene complexes that contain very short Ti=C bonds (~1.830 Å).[5,14,26,27] Selected metrical parameters are displayed in Table 2. The molecular structures for **3-X** (X$^-$ = OTf, I, and Br) reveal a four-coordinate titanium complex having C_s symmetry, and in all systems the *tert*-butyl group is along the σ-plane bisecting the N−Ti−N angle and is oriented *syn* with respect to the X$^-$ ligand. The Ti=C$_\alpha$H$_\alpha$ hydrogen was located in the Fourier electron map for all **3-X** (excluding **3-I** and **3-BH$_4$**) systems and was refined isotropically (Ti−H$_\alpha$ distances are reported in Table 2). Even though there is a systematic error in detection of hydrogens by X-ray diffraction[28] the location of the hydrogens in the Fourier map leaves little uncertainty about their presence in each structure. However, stronger evidence suggesting an α-H agostic interaction occurring in complexes **3-X** arises from the low J_{C-H} coupling (85−95 Hz, Table 1). Judging from the J_{C-H} and the ^{1}H NMR resonance for α-H, complex **3-I** appears to have the greatest Lewis acidic character (Table 1). The α-H agostic interaction observed in all complexes (structurally or spectrocopically) is also substantiated by the large Ti(1)=C(33)−C(34) angle of 160−164°. The structure of **3-BH$_4$** is nearly identical to that of the halide and pseudohalide derivatives. Although the BH$_4^-$ protons were not observed by ^{1}H NMR spectroscopy,[29] location and refinement of the hydrogens in the X-ray structure suggest this ligand to be η^3.[30] We are however doubtful of how accurate the hapticity of the BH$_4$ ligand really is in **3-BH$_4$**. Solution IR and ^{11}B NMR spectroscopy are also consistent with a tetrahydroborate ligand being present.

Thermal Transformation of the Titanium Neopentylidene Complexes 3-X. Although stable as solid complexes, **3-X** (X$^-$ = OTf, Cl, Br, I, and BH$_4$) are all kinetic products since these systems transform gradually in solution in the order **3-OTf** < **3-Cl** < **3-Br** < **3-I** < **3-BH$_4$**, as evidenced by ^{1}H and ^{13}C NMR spectroscopy. Heating benzene solutions of **3-OTf**, **3-Cl**, and **3-Br** to 60 °C for several hours affords the titanium imido triflato complex supported by the chelating anilide diene ligand, (H^{t}BuC=C(Me)CHC(Me)N[Ar])Ti=NAr(X), **5-X**

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(26) A search of the Cambridge Crystallographic Database for titanium−alkylidene bond lengths indicate values to be ≥ 1.884(4) Å, see ref 5.

(27) A four-coordinate titanium complex having a bridging alkylidene functionality has been reported: (a) Riley, P. N.; Fanwick, P. E.; Rothwell, I. P. *J. Chem. Soc., Dalton Trans.* **2001**, 181−186. A transient three-coordinate titanium methylidene has been proposed in a decomposition reaction: (b) Scollard, J. D.; McConville, D. H.; Rettig, S. J. *Organometallics* **1997**, *16*, 1810−1812.

(28) Bau, R.; Drabnis, M. H. *Inorg. Chim. Acta* **1997**, *259*, 27−50.

(29) We have not been able to locate the hydride resonance in the ^{1}H NMR spectrum, presumably due to broadening of the signal by coupling of the hydride to the ^{11}B (I = 3/2, 80%) quadrupolar nuclei. (a) Harris, R. K., Mann, B. E., Eds. *NMR and the Periodic Table*; Academic Press: London, 1978. (b) Akitt, J. W. *NMR and Chemistry, An Introduction to the Fourier Transform-Multinuclear Era*; Chapman Hall: New York, 1983; Chapter 4.

(30) For some examples of tridentate borohydride complexes of titanium(IV) see: (a) Nöth, H.; Schmidt, M. *Organometallics* **1995**, *14*, 4601−4610. (b) Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1991**, *30*, 145−148. (c) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263−293.

Table 2. Selected Structural Parameters for the Alkylidene Complexes 3-X (X^- = I, Br, OTf, BH_4)[a]

	3-I[b]	3-Br	3-OTf	3-BH_4
Ti=C_α	Ti1−C34, 1.829(4)	Ti1−C34, 1.826(2)	Ti1−C33, 1.830(3)	Ti1−C33,1.840(8)
Ti−N_{Nacnac}	Ti1−N2, 2.008(3)	Ti1−N3, 2.032(5)	Ti1−N2, 2.012(3)	Ti1−N2, 2.039(3)
Ti−N_{Nacnac}	Ti1−N6, 2.029(3)	Ti1−N7, 2.013(6)	Ti1−N6, 2.025(3)	Ti1−N6, 2.069(4)
Ti−X	Ti1−I33, 2.6616(8)	Ti1−Br2, 2.4452(4)	Ti1−O38, 1.957(2)	Ti1−B38, 2.200(2)
Ti−H (agostic)	n/a	Ti1−H81, 1.99(2)	Ti1−H87, 1.92(3)	n/a
C_α−H	n/a	C34−H81, 0.92(3)	C33−H87, 0.91(4)	n/a
Ti−C−C	Ti1−C35−C36, 163.8(4)	Ti1−C34−C35, 162.1(2)	Ti1−C33−C34, 163.9(3)	Ti1−C34−C33, 160.3(5)
C_α−Ti−X	C34−Ti1−I33, 112.3(3)	C34−Ti1−Br2 112.43(8)	C33−Ti1−O38, 112.5(3)	C33−Ti1−B38, 108.23(9)
N_{Nacnac}−Ti−N_{Nacnac}	N2−Ti1−N6, 93.6(1)	N3−Ti1−N7, 92.95(6)	N2−Ti1−N6, 94.2(1)	N2−Ti1−N6, 91.87(5)
C_α−Ti−N_{Nacnac}	C34−Ti1−N2, 115.2(5)	C34−Ti1−N3, 105.90(8)	C33−Ti1−N2, 109.8(3)	C33−Ti1−N2, 110.39(7)
C_α−Ti−N_{Nacnac}	C34−Ti1−N6, 105.7(5)	C34−Ti1−N7, 114.45(9)	C33−Ti1−N6, 111.2(3)	C33−Ti1−N6, 111.03(7)
X−Ti−N_{Nacnac}	I33−Ti1−N2, 116.32(8)	Br2−Ti1−N3, 111.59(5)	O38−Ti1−N2, 115.6(1)	B38−Ti1−N2, 119.50(7)
X−Ti−N_{Nacnac}	I33−Ti1−N6, 111.46(7)	Br2−Ti1−N7, 117.25(5)	O38−Ti1−N6, 112.7(1)	B38−Ti1−N6, 115.01(8)

[a] Bond lengths are reported in Å and bond angles in deg. [b] Complex **3-I** suffers from disorder resulting from alternate positions of the Ti and I atoms; hence bond lengths and angles may not be highly accurate.

Table 3. Crystallographic Data for Complexes [2][B(C_6F_5)$_4$], 3-X (X^- = Br, I, BH_4), and 4

	[2][B(C_6F_5)$_4$]	**3-Br**	**3-I**	**3-BH_4**	**4**
empirical formula	$C_{63}H_{63}BF_{20}N_2Ti$	$C_{34}H_{51}BrN_2Ti$	$C_{34}H_{51}IN_2Ti$	$C_{34}H_{55}BN_2Ti$	$C_{32}H_{47}F_3N_2O_3STi$
fw	1286.86	615.58	662.57	550.51	644.68
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	triclinic
space group	*Pbca*	*P*2(1)/*n*	*P*2(1)/*n*	*P*2(1)/*n*	$P\bar{1}$
a (Å)	21.529(3)	10.2863(4)	10.4564(8)	10.522(2)	9.1297(11)
b (Å)	22.213(3)	27.5797(11)	27.710(2)	19.451(4)	10.3411(12)
c (Å)	25.426(4)	12.3294(5)	12.3526(9)	17.009(3)	19.701(2)
α (deg)	90				78.359(3)
β (deg)	90	106.6320(10)	107.242(2)	102.739(6)	87.518(3)
γ (deg)	90				64.550(3)
V (Å^3)	12159(3)	3351.4(2)	3418.3(4)	3395.4(12)	1643.0(3)
Z	8	4	4	4	2
D_c (g·cm^{-3})	1.406	1.220	1.287	1.077	1.303
T (K)	118(2)	132(2)	113(2)	132(2)	135(2)
cryst size (mm)	0.30 × 0.25 × 0.15	0.30 × 0.10 × 0.10	0.15 × 0.15 × 0.14	0.25 × 0.25 × 0.20	0.30 × 0.25 × 0.25
solvent, color	Et_2O/TMS_2O, orange	Et_2O, brown	pentane, dark brown	hexane, brown	THF/pentane, orange
(*h*, *k*, *l*)	$-23 \le h \le 23$ $-24 \le k \le 24$ $-28 \le l \le 28$	$-14 \le h \le 14$, $-38 \le k \le 38$, $-17 \le l \le 17$	$-8 \le h \le 12$, $-32 \le k \le 32$, $-14 \le l \le 14$	$-14 \le h \le 14$, $-27 \le k \le 27$, $-23 \le l \le 22$	$-12 \le h \le 12$ $-14 \le k \le 14$ $-27 \le l \le 27$
F(000)	5296	1304	1376	1200	684
θ range	2.00−23.31	2.19−30.03	2.17−25.02	2.09−30.07	2.23−30.03
linear abs coeff (mm^{-1})	0.243	1.471	1.176	0.275	0.375
total no. of reflcns collected	146 395	60 664	16 099	44 095	44 382
no. of unique reflcns $F > 4\sigma(F)$	8772	9808	6023	9938	9596
no. of obsd reflcns	5144	6897	4145	5681	6863
R_{int}	0.1942	0.0863	0.0603	0.1723	0.0727
no. of data/params	8772/1036	9808/547	6023/553	9938/563	9596/567
R_1, wR_2 (for $I > 2\sigma(I)$)	0.0462, 0.0980	0.0402, 0.0935	0.0345, 0.0553	0.0493, 0.1138	0.0408, 0.0988
GoF	1.028	0.929	0.862	0.892	0.942
peak/hole (e/Å^{-3})	0.532, −0.337	1.948, −1.108	0.737, −0.360	0.755, −0.824	0.799, −0.431

(**X^-** = Cl, η^2-OTf,[14] and Br, Scheme 4). From the **5-Cl**, **5-OTf**, and **5-Br** derivatives only **5-OTf** was isolated in 65% yield.[14] Thermolysis of complexes **3-Cl** and **3-Br** leads to several products, from which we identified **5-Cl** and **5-Br** based solely on ^1H NMR spectroscopic comparisons with isolated samples of **5-OTf**. In contrast to **3-X** (X^- = OTf, Cl, and Br), complexes **3-I** and **3-BH_4** decompose rapidly in solution at room temperature or −35 °C to **5-I** and **5-BH_4**, respectively. In all systems the ^1H NMR spectrum for each complex also indicates that only one diastereomer is present in solution at 25 °C. This feature is signified clearly by the α-hydrogen, which was detected in the ^1H NMR spectrum (1.5−2.8 ppm) using HMQC experiments.[18] α-Hydrogen agostic interaction is also present in isolated samples of **5-OTf**, **5-I**, and **5-BH_4**, which is evident from the C−H coupling constants of the terminal olefin group (126−129 Hz).[31] The α and *β* olefinic carbon atoms display carbon NMR resonances similar to those of group 4 alkene adducts reported by Jordan and co-workers.[32] Similar α-hydrogen agostic interactions have been reported for 1-aza,1,3-diene ligands bound to titanium.[32] However, the anilide diene interaction in **5-X** can also be viewed as a delocalized charge about the NCCCH or CCH rings, where a considerable amount of rehybridization of the terminal carbon atom toward sp^3 has occurred. Therefore one cannot exclude these binding options when taking into consideration the small C−H coupling constants for the terminal olefinic group (vide supra).[32] Complexes **5-X** are formed likely by a cross-metathesis

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(31) For common J_{C-H} values of sp^2 carbons see: Strothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972.

(32) The low coupling value could also suggest considerable amount of rehybridization of the terminal carbon atom toward sp^3 hybridization. Such a spectroscopic feature has been suggested for 1-aza-1,3-diene ligands containing α-hydrogens that are bonded to titanium. Scholz, J.; Kahlert, S. *Organometallics* **1998**, *17*, 2876−2884. Stoebenau, E. J., III; Jordan, R. F. *J. Am. Chem. Soc.* **2003**, *125*, 3222−3223.

Table 4. Crystallographic Data for Complexes 5-I, 5-BH_4, 7-OTf, 7-BH_4, 9·$3CH_2Cl_2$, and 11

	5-I	**5-BH3**	**7-OTf**	**7-BH_4**	**9**·$3CH_2Cl_2$	**11**
empirical formula	$C_{34}H_{51}IN_2Ti$	$C_{34}H_{55}BN_2Ti$	$C_{30}H_{39}F_3N_2O_3STi$	$C_{29}H_{43}BTi$	$C_{75}H_{108}Cl_6F_6N_4O_{10}S_2Ti_2$	$C_{42}H_{56}F_3N_3O_3S_2Ti$
fw	662.57	550.51	612.59	478.36	1712.27	819.92
cryst system	triclinic	triclinic	monoclinic	orthorhombic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2(1)/n$	$Cmc2(1)$	$P2(1)/n$	$P\bar{1}$
a (Å)	9.091(1)	9.0020(3)	9.2570(5)	19.268(9)	14.307(7)	10.662(4)
b (Å)	11.000(2)	11.0365(4)	17.9054(9)	10.2436(9)	25.734(3)	12.7780(4)
c (Å)	17.149(8)	17.3981(6)	18.0970(9)	13.710(4)	23.411(3)	16.7565(6)
α (deg)	102.356(2)	76.626(1)		90		91.363(1)
β (deg)	92.035(3)	89.1540(1)	91.720(1)	90	90.107(3)	94.131(1)
γ (deg)	99.780(3)	78.3890(1)		90		109.029(1)
V (Å^3)	1646.2(3)	1646.31(1)	2998.2(3)	2705.9(5)	8619(7)	2149.8(3)
Z	2	2	4	4	4	2
D_c (g·cm^{-3})	1.337	1.111	1.357	1.174	1.320	1.267
T (K)	125(2)	129(2)	136(2)	117(2)	120(2)	132(2)
cryst size (mm)	0.26 × 0.25 × 0.20	0.21 × 0.18 × 0.13	0.30 × 0.30 × 0.25	0.25 × 0.25 × 0.04	0.30 × 0.30 × 0.18	0.23 × 0.23 × 0.20
solvent, color	toluene, dark red	hexane, orange-brown	Et_2O, red	Et_2O, orange-pink	CH_2Cl_2/Et_2O, orange	pentane, black
(h, k, l)	$-11 \leq h \leq 11$, $-14 \leq k \leq 14$, $-22 \leq l \leq 22$	$-12 \leq h \leq 12$, $-15 \leq k \leq 15$, $-24 \leq l \leq 24$	$-13 \leq h \leq 11$, $-25 \leq k \leq 25$, $-25 \leq l \leq 25$	$-24 \leq h \leq 24$, $-13 \leq k \leq 13$, $-17 \leq l \leq 17$	$-18 \leq h \leq 18$, $-33 \leq k \leq 33$, $-30 \leq l \leq 30$	$-13 \leq h \leq 13$, $-16 \leq k \leq 16$, $-21 \leq l \leq 21$
F(000)	688	600	1288	1032	3592	868
θ range	2.44−27.53	2.03−30.02	2.27−30.01	2.11−27.52	2.30−27.60	2.13−27.51
linear abs. coeff (mm^{-1})	1.221	0.283	0.407	0.335	0.487	0.349
total no. of reflcns collected	43 074	44 796	30 990	25 991	190 318	48 428
no. of unique reflcns $F > 4\sigma(F)$	7574	9613	8731	3192	19 935	9878
no. of obsd reflcns	6670	6795	5594	2679	13 632	8220
R_{int}	0.0413	0.0963	0.0678	0.0583	0.1067	0.0548
no. of data/params	6914/516	9613/563	8731/517	3192/274	19 935/1380	9878/711
R_1, wR_2 (for $I > 2\sigma(I)$)	0.0280, 0.0665	0.0402, 0.0935	0.0387, 0.0827	0.0398, 0.0647	0.0868, 0.2167	0.0309, 0.0791
GoF	1.022	0.972	0.917	0.961	1.107	1.037
peak/hole (e/Å^{-3})	0.766, −0.583	0.511, −0.350	0.423, −0.418	0.231, −0.242	1.417, −0.833	0.462, −0.285

reaction (or alternatively called Wittig-like) between the titanium neopentylidene and the imine aryl functionality of the Nacnac$^-$ ligand. Not surprisingly, complexes **5-X** seem to be thermodynamically driven due to formation of the strong Ti=N_{imido} bond.

The chelate ligand appears to behave "diene-like" in **5-X** since the addition of a weak Lewis base such as Et_2O to **5-OTf** affords crystals of the adduct (η^1-H^{t}BuC=C(Me)CHC(Me)N[Ar])Ti=NAr(OTf)(Et_2O) (**6-OTf**) in 80% yield (Scheme 4).[14] In complex **6-OTf** the olefinic pendent arm of amide diene ligand has been displaced completely by the Lewis base; thus we depict the supporting ligand in **5-X** as an anilide possessing a pedant olefinic arm. ^1H and ^{13}C NMR spectra in C_6D_6 are relatively unchanged for the Lewis base adduct **6-OTf** when compared to the Lewis base-free precursor **5-OTf**, thus suggesting that the coordinated Et_2O might be being displaced under these conditions. Mild heating of **6-OTf** under reduced pressure (50 °C, 2 h) regenerates **5-OTf** quantitatively, showing that this process is reversible (Scheme 4). As described in an earlier communication, inspection of the structure of **6-OTf** reveals clearly that the olefinic arm of the former Nacnac$^-$ ligand is not interacting with the metal center (Ti−C_{olefin} ≥ 4.30 Å).[14]

Single-crystal structure determinations of **5-OTf**, **5-I**, and **5-BH_4** are also consistent with the proposed connectivity suggested by the ^1H and ^{13}C NMR spectra (Figure 4). The molecular structures of **5-X** (X^- = OTf, I, and η^3-BH_4) display only one of the possible diastereomers, which is also consistent with solution NMR spectra (vide infra). In the three crystal structures of **5-X** the α-hydrogen was located in the Fourier electron map and was refined isotropically (Ti−H_α, 2.05−2.09 Å). Such an α-hydrogen agostic interaction in all three crystal structures might lock the olefinic arm, thus preventing formation of diastereomers. In the crystal structures of **5-OTf**, **5-I**, and **5-BH_4** the titanium binds to the α- and β-carbons. For instance, in the molecular structure of **5-I** the Lewis acidic metal center in turn compensates by engaging strongly with the ^{t}BuHC=C(CH_3) group (Figure 4), and as a result, the former C=C bond is elongated. This feature also correlates with complex **5-I** having the lowest α-C−H coupling constant (vide supra). Since the pendant olefin is regarded as a poor ligand, the low-coordinate titanium center also compensates by forming a very strong bond with the imido nitrogen (Ti=NAr average distance in **5-X** is ~1.72 Å). The molecular structures of complex **5-X** (X− = OTf, I, and η^3-BH_3) are also interesting since they depict a rare example of low-coordinate titanium imido complexes.[14,24,33]

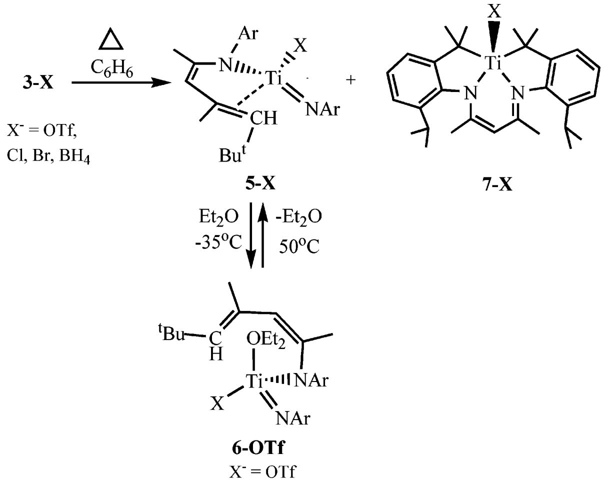
Double C−H Abstraction Reactions in the Thermolysis of 3-X (X^- = OTf, Cl, Br, and BH_4). Attempts to perform kinetic studies (60−70 °C) on the cross-metathesis reaction leading to formation of **5-X** were

Table 5. Crystallographic Data for Complexes 12·Et_2O, 13·C_5H_{12}, 14, and 15·C_5H_{12}

	12·Et_2O	**13**·C_5H_{12}	**14**	**15**·C_5H_{12}
empirical formula	$C_{50}H_{74}F_3N_3O_4STi$	$C_{45}H_{72}F_3N_3O_3Sti$	$C_{48}H_{61}F_3N_4O_3Sti$	$C_{50}H_{78}F_3N_3O_3Sti$
fw	918.08	840.02	878.97	906.11
cryst syst	triclinic	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$P2(1)/c$	$P2(1)2(1)2(1)$
a (Å)	12.152(5)	15.851(3)	12.7640(4)	14.4433(8)
b (Å)	12.208(5)	16.400(3)	17.7911(6)	17.842(1)
c (Å)	18.140(2)	18.475(3)	20.8737(7)	19.232(1)
α (deg)	77.585(3)	87.600(4)		90
β (deg)	75.257(3)	82.003(4)	98.537(1)	90
γ (deg)	81.809(3)	89.976(4)		90
V (Å^3)	2530.8(5)	4752(5)	4687.6(3)	4956.0(5)
Z	2	4	4	4
D_{calc} (g·cm^{-3})	1.205	1.174	1.245	1.214
T (K)	136(2)	136(2)	137(2)	136(2)
cryst size (mm)	0.30 × 0.18 × 0.12	0.30 × 0.30 × 0.09	0.30 × 0.30 × 0.25	0.25 × 0.25 × 0.18
solvent, color	Et_2O, orange	pentane, black	toluene, dark red	Et_2O, red-brown
(h, k, l)	$-17 \le h \le 17$, $-17 \le k \le 16$, $-25 \le l \le 25$	$0 \le h \le 22$ $-23 \le k \le 23$ $-25 \le l \le 26$	$-17 \le h \le 17$, $-25 \le k \le 25$, $-29 \le l \le 29$	$-18 \le h \le 18$, $-23 \le k \le 23$, $-25 \le l \le 24$
F(000)	984	1808	1864	1952
θ range	2.33−30.16	2.18−30.11	2.49−30.02	2.28−27.57
linear abs coeff (mm^{-1})	0.265	0.275	0.283	0.268
total no. of reflcns collected	39 113	51 532	103 943	110 696
no. of unique reflcns $F > 4\sigma(F)$	14 802	27 772	13 681	11 423
no. of obsd reflcns	8579	10 951	10 969	8317
R_{int}	0.1307	0.1200	0.0580	0.1065
no. of data/params	14 802/855	27 772/1011	13 681/812	11 423/665
R_1, wR_2 (for $I > 2\sigma(I)$)	0.0543, 0.1139	0.0896, 0.2059	0.0400, 0.1029	0.0489, 0.1305
GoF	0.927	0.835	1.017	1.005
peak/hole (e/Å^{-3})	0.778, −0.788	1.758, −0.700	0.929, −0.867	0.525, −0.338

hampered by the presence of an additional product in the mixture. Fortunately in the thermolysis of complex **3-OTf** the second product was separated conveniently from **5-OTf** due to its limited solubility in pentane. Washing of the red-brown solid with hexane and subsequent recrystallization from Et_2O at −35 °C afforded red prisms of the titanacycle $Ti[2,6\text{-}(CMe_2)(CHMe_2)\text{-}C_6H_3]NC(Me)CHC(Me)N[2,6\text{-}(CMe_2)(CHMe_2)C_6H_3]\text{-}(OTf)$, **7-OTf**, in 31% yield (Scheme 4). Thermolysis of isolated **5-OTf** under similar conditions failed to show any conversion to **7-OTf**, suggesting that complex **3-OTf** is in fact a precursor to **7-OTf**. Increasing the temperature above 70 °C in the thermolysis of **3-OTf** did not improve the yield of **7-OTf**. Consecutive thermolytic experiments yielded consistent results, thus suggesting that an impurity (e.g., Ag^+) could not be the reason for the formation of **7-OTf**. Formation of **7-OTf** was unexpected, as C−H abstraction of two methine groups (3° carbons) is exceedingly rare.[34−36] Generation of **7-OTf** from the thermolysis of **3-OTf** is selective inasmuch as it is the only new product generated as a consequence of activation of two tertiary C−H bonds of the formal Nacnac⁻ ligand. The ^1H NMR spectrum of **7-OTf** displays one methine resonance integrating to two protons, three distinctive methyl environments (one for the β-carbon methyl of Nacnac⁻ and two for the C−H activated isopropyl groups), two diastereotopic isopropyl methyls, and one aryl environment, all being consistent with the complex retaining C_s symmetry in solution. In addition, the ^{13}C NMR spectrum of **7-OTf** indicates the

Scheme 4. Thermal Transformation of the Titanium Alkylidenes (Nacnac)Ti=CH^{t}Bu(X) (X− = OTf, Cl, Br, BH_4)



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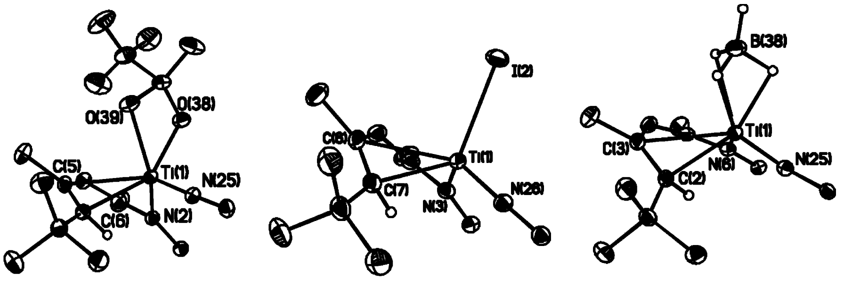
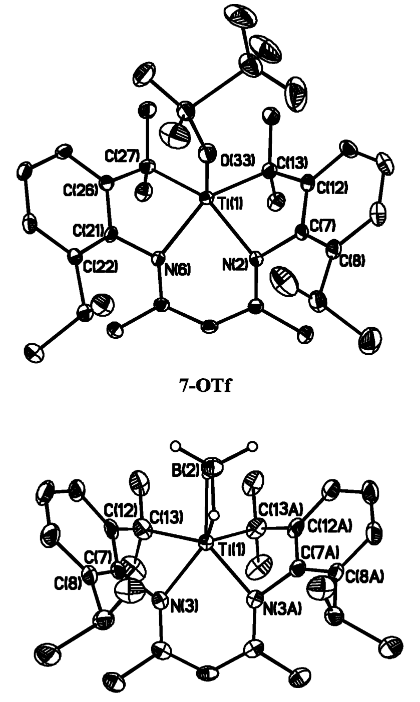


5-OTf **5-I** **5-BH$_4$**

Figure 4. Molecular structure of **5-OTf**, **5-I**, and **5-BH$_4$** with thermal ellipsoids at the 50% probability level. All H atoms with the exception of α-hydrogens and aryl groups with the exception of ipso-carbons have been omitted for clarity. Crystallographic data are reported in Table 4. Selected metrical parameters: For **5-OTf**: Ti1−N25, 1.715(1); Ti1−N2, 2.015(1); Ti1−O38, 2.213(1); Ti1−O39, 2.254(1); Ti1−C6, 2.263(4); Ti1−C5, 2.524(4); Ti1−H48, 2.09(9); C5−C6, 1.390(9) Å. For **5-I**: Ti1−N26, 1.717(7); Ti1−N3, 2.015(7); Ti1−C7, 2.205(2); Ti1−C6, 2.527(2); Ti1−H10, 2.05(2); C6−C7, 1.397(3); Ti1−I2, 2.6883(4) Å. For **5-BH$_4$**: Ti1−N25, 1.716(2); Ti1−N6, 2.032(2); Ti1−C2, 2.230(4); Ti1−C3, 2.626(4); Ti1−H39, 2.08(7); Ti1−B38, 2.265(8); C2−C3, 1.403(2) Å.

presence of one quaternary and one methine carbon environment centered at 88.78 and 106.2 ppm, respectively. We also observe formation of **7-Cl**, **7-Br**, and **7-BH$_4$** from thermolysis of their corresponding alkylidene precursors, but formation of these complexes is based only on ^{1}H NMR spectroscopic comparisons with isolated samples of **7-OTf**. Attempts to isolate these derivatives were hampered by a combination of low yield and lypophilicity. Complex **7-Cl** was also formed from thermolysis of **3-Cl**, but the reaction mixture contained a myriad of additional products including **5-Cl** (vide supra). Independent studies have shown that **7-BH$_4$** can be prepared readily in 91% yield from **7-OTf** and LiBH$_4$ in Et$_2$O. ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy, along with single-crystal X-ray diffraction studies (Figure 5, vide infra), confirmed the proposed connectivity (see Experimental Section). The BH$_4$ hydrogens were located and refined isotropically in the crystal structure for complex **7-BH$_4$** and suggest the ligand to be η^2. We have not pursued the independent synthesis of **7-Br** and **7-Cl** from anion metathesis of **7-OTf**.

Single crystals of **7-OTf** and **7-BH$_4$** were grown from a saturated Et$_2$O solution cooled to −35 °C, and the molecular representations are depicted in Figure 5. Complexes **7-OTf** and **7-BH$_4$** display a five-coordinate titanium(IV) in a distorted square pyramidal environment with the pseudohalide ligand occupying the axial site. The constrained geometry of **7-OTf** and **7-BH$_4$** is likely a consequence of the ligand being macrocyclic, and dihedral angles ($N_{Nacnac}-C-C-C_\alpha$, range is 7.3(2)° to −3.3(2)°) reflect the strain generated upon ring closure. Similarly, the average acute angles $Ti-C_\alpha-C_\beta$ of 86° also echo some strain in the metalacycle. The Ti atom sits ~0.82 Å from the mean plane bisecting the two N_{Nacnac} and C_α atoms, and the structures of both **7-OTf** and **7-BH$_4$** also reveal close arene interactions between Ti and the ortho and meta carbons of the aryl groups (average $Ti-C_{arene}$ distance is ~2.58 Å). The molecular structures for complexes **7-OTf** and **7-BH$_4$** are displayed in Figure 5.



7-OTf

7-BH$_4$

Figure 5. Molecular structure of **7-OTf** and **7-BH$_4$** with thermal ellipsoids at the 50% probability level. All H atoms with the exception of the η^2-BH$_4$ have been omitted for clarity. Crystallographic data are reported in Table 4, and complete metrical parameters are listed in the Supporting Information.

Previous work has documented C−H activation reactions 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.[37] In general C−H activation of 1° carbons in the 2,6-dialkyl substituents on the aryl rings is often encountered for the Nacnac$^-$ derivative used in the present study.[38] Recently Goldberg and co-workers reported C−H abstraction of both the methine and methyl groups of the isopropyl of Nacnac$^-$ via reductive elimination of a Pt(IV) species and subsequent oxidative addition leading to formation of an isopropenyl(hydrido)-

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(37) For the most current and complete description of chemistry concerning β-diketiminate complexes see: (a) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031−3066. (b) Harder, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 3430−3434, and references therein.

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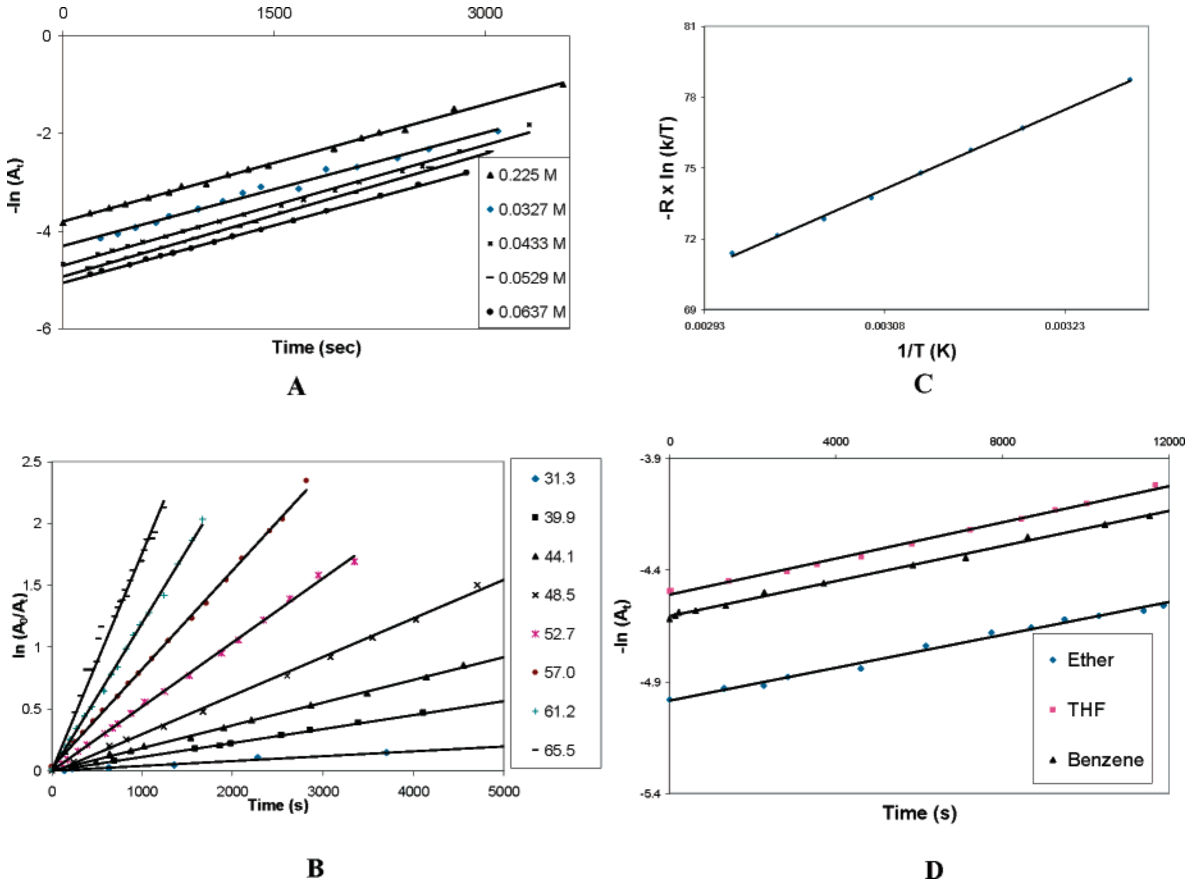
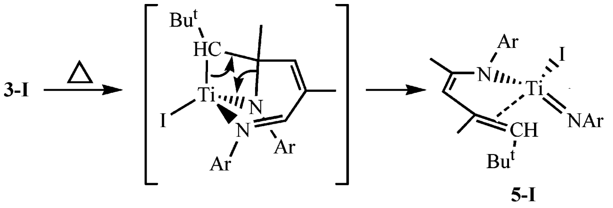


Figure 6. (A) Concentration dependence at 57 °C for the thermal transformation of the titanium alkylidene (Nacnac)Ti=CH^{t}Bu(I) **3-I**. (B) Temperature dependence plot for the thermal transformation of the titanium alkylidene (Nacnac)Ti=CH^{t}Bu(I) **3-I** (temperature reported in °C). The complete data set for the run of 31.3 °C is not shown since the reaction took over 314 min to go one half-life. (C) Eyring plot for the thermal transformation of the titanium alkylidene (Nacnac)Ti=CH^{t}Bu(I) **3-I**. (D) Solvent dependence plot for the thermal transformation of the titanium alkylidene (Nacnac)Ti=CH^{t}Bu(I) **3-I** at 31.3 °C

platinum(II) complex.[36a] In contrast our work establishes a C−H abstraction reaction by which two methine groups are selectively cleaved under relatively mild conditions.[39] In the context of group 4 metal alkylidenes, the 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 has been reported.[40]

Scheme 5. Thermal Transformation of the Titanium Alkylidene (Nacnac)Ti=CH^{t}Bu(I), 3-I



Transformation of Complex 3-I to 5-I. Mechanistic Investigation of an Intramolecular Cross-Metathesis Reaction. Remarkably it was found that complex **3-I** cleanly transforms to solely one product (31.3−65.5 °C), (H^{t}BuC=C(Me)CHC(Me)N[Ar])Ti=NAr(I), **5-I**, without any formation of the hypothetical C−H abstraction derivative **7-I** (Scheme 4). Apparently the lower activation energy to form **5-I** combined with the greater Lewis acidity of the metal precludes any secondary and indepenent side reaction from occurring. Concentration-dependent experiments (by ^{1}H NMR spectroscopy, 0.225−0.0637 M) and fitting of the data to a first-order decay plot determined the reaction to be first-order in titanium with a rate constant k = 8.1(4) × 10^{-4} s^{-1} (Figure 6A). From the rate we calculate the $t_{1/2}$ for **3-I** to be 14.4 min at 57 °C, which is relatively faster than the estimated $t_{1/2}$ values of the derivatives **3-X** (X^- = OTf, ~45.0 min at 57 °C; Cl, ~16.9 min at 57 °C; Br, ~19.2 min at 57 °C). Temperature dependence studies (Figure 6B) allowed for extraction of the activation parameters ($S^{\ddagger}$ = −8(3) cal/mol·K^{-1} and $\Delta H^{\ddagger}$ = 21.3(2) kcal/mol) from the Eyring plot (Figure 6C). Hence results indicate that *formation of* **5-I** *proceeds by an intramolecular rearrangement stemming from* **3-I**. Scheme 5 depicts a metalacyclobutane intermediate or transition state species leading to formation of **5-I**. Kinetic studies also reveal formation of **5-I** to be

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(39) Double C−H activation of two 1° carbons has been documented recently for electron-deficient Rh(III) systems: Dorta, R.; Stevens, E. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2004**, *126*, 5054−5055. Scott, N. M.; Dorta, R.; Stevens, E. D.; Correa, A.; Cavallo, L.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, ASAP article.

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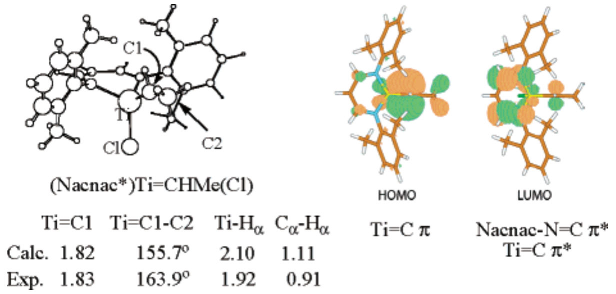


Figure 7. DFT calculations on the model complex (Nacnac*)Ti=CHMe(Cl) and structural comparisons with **3-OTf**. The HOMO and LUMO are also depicted. Complete geometrical features for the optimized geometry are included in the Supporting Information.

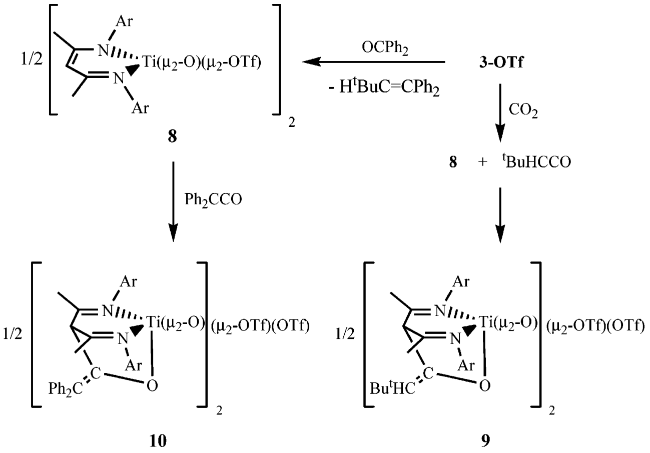
independent of solvents such as C_6H_6, THF, and Et_2O (Figure 6D). Therefore the mechanism leading to the cross-metathesis reaction observed in **3-X** (X^- = OTf, Cl, Br, I, and BH_4) does not likely involve dissociation of the Nacnac$^-$ and X^- ligand or coordination of solvent. Although enthalpy makes a favorable contribution to the chelate effect, the main source of effect is found in the entropy.[41] We cannot however rule out the possibility that a hapticity change in Nacnac$^-$ could occur during the transformation of **3-X** to **5-X**.

DFT Calculations of the Titanium Alkylidene Complexes 3-X. Theoretical calculations were performed on the titanium alkylidene model complex (Nacnac*)Ti=CHMe(Cl) (Nacnac*$^-$ = [Ar]NCHCHCHN[Ar], Ar = 2,6-$Me_2C_6H_3$) using density funtional theory (DFT) and the B3PW91 functional. The optimized geometry reproduced the key features of the solid-state structure of **3-OTf** expectedly well (Figure 7). The calculated molecular orbitals for the model (Nacnac*)Ti=CHMe(Cl) indicate the HOMO to be the π orbital in the Ti=C double bond, while the LUMO is composed predominantly of π^* character localized about the N−C bonds of the Nacnac$^-$ backbone with a node at the γ-C supplemented with some π^* character in the Ti=C bond (Figure 7).

The match in symmetry of the frontier orbitals combined with the observed chemical reactivity suggest tantalizingly that complex **3-X** has a reactive alkylidene functionality capable of both transferring the carbenoid motif to give **5-X** and activating inert carbon−hydrogen bonds to afford titanacycles such as **7-X**. Kinetic results in combination with the theoretical findings also suggest that the cross-metathesis transformation occurs by an intramolecular [2+2] cycloaddition in which the Nacnac$^-$ ligand rearranges (without dissociation) by placing the imine functionality across the Ti=C bond, yielding the putative azametallacyclobutane complex. Electron shuffling then leads to the final product **5-X** (Scheme 5).

Reactivity of the Ti=C$_{\text{alkylidene}}$ Functionality in Complex 3-OTf. Reactions of 3-OTf with Olefins. Alkylidene **3-OTf** failed to react with olefins such as ethylene, styrene, *trans*-stillbene, 1-hexene, and chlorosubstituted alkenes. Electron-rich olefins such as 2,3- and 2,5-dihydrofuran appear to react slowly with **3-OTf**, but attempts to isolate the product(s) only yielded **5-OTf** and **7-OTf**. Internal alkynes did not react cleanly with the Ti=C bond of **3-OTf**. Attempts to carry out these reactions at higher temperatures resulted only in rapid transformation of **3-OTf** to complexes **5-OTf** and **7-OTf**. Thus, it appears that the reactivity of **3-OTf** is hampered significantly by its thermal rearrangement to **5-OTf** and **7-OTf**.

Scheme 6. Cross-Metathesis Reactions of the Titanium Alkylidene (Nacnac)Ti=CH^{t}Bu(OTf), 3-OTf



Reactions of 3-OTf with Polar Molecules. Complex **3-OTf** reacts rapidly and cleanly with 1 equiv of benzophenone at room temperature to afford the olefin H^{t}BuC=CPh$_2$[42] and 0.5 equiv of the edge-sharing bioctahedra titanium oxo dimer [(Nacnac)Ti(μ_2-O)(μ_2-OTf)]$_2$ (**8**)[14,43] (Scheme 6). The reactivity observed between **3-OTf** and benzophenone follows well-established "Wittig-type" reagents studied in organic synthesis.[7] Likewise, CO_2 also reacts with **3-OTf** to yield the μ-oxo titanium dimer [$(L_1)_2Ti_2(\mu_2\text{-O})_2(\mu_2\text{-OTf})$][OTf] (**9**) ($L_1^-$ = [Ar]NC(CH_3)CHC(O)=C^{t}BuHC(CH_3)N[Ar]). Complex **9** results from a cross-metathesis reaction, leading to formation of putative **8** and the ketene ^{t}BuHC=C=O (Scheme 6). Nucleophilic attack of the ketene generated in the reaction by the γ-carbon of the Nacnac$^-$ ring yields complex **9**. The ^{19}F NMR spectrum displays two independent resonances consistent with a bridging and a nonbound OTf$^-$. The solid-state structure of **9** also confirms these spectroscopic features as well as the inferred degree of aggregation (vide infra). Independently, we have also shown that complex **8** reacts with the much more stable diphenylketene[44] derivative to yield a system analogous to **9**, namely, [$(L_2)_2Ti_2(\mu_2\text{-O})_2(\mu_2\text{-OTf})$][OTf] (**10**) ($L_2^-$ = [Ar]NC(CH_3)CHC(O)=CPh$_2$C(CH_3)N[Ar]) (Scheme 6). NMR (^{1}H and ^{13}C) spectra for **9** and **10** are broader than usual and can likely be attributed to a fluxional process occurring in solution. Precedent in the literature concerning addition of electrophiles to β-diketiminates has been described previously by us and others.[33n,45] Complexes **9** and **10** have been scrutinized by single-crystal X-ray diffraction

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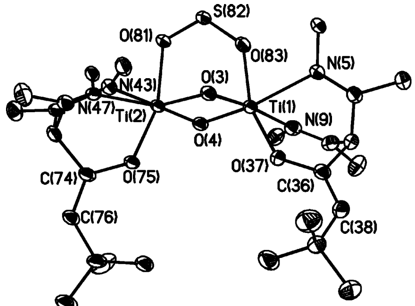
[41] Cotton, F. A.; Wilkinson, G.; Murrillo, C A. *Advanced Inorganic Chemistry*; John Wiley and Sons: New York, 1999.

[42] The formation of alkene was confirmed by spectroscopic comparison with ^{1}H NMR shifts reported in the literature. Adam, W.; Baeza, J.; Liu, J.-C. *J. Am. Chem. Soc.* **1972**, *94*, 2000−2006.

[43] The molecular structure of **8** showed an edge-sharing bioctahedra geometry composed of two bridging oxo and triflate ligands. See ref 14.

[44] Taylor, E. C.; McKillop, A.; Hawks, G. H. *Org. Synth.* **1988**, *50*, 549.



$[9]^+$

Figure 8. Molecular structure of complex **[9]**$^+$ with thermal ellipsoids at the 50% probability level. All H atoms, O and CF_3 groups of the μ_2-OTf^-, and aryl groups with the exception of ipso-carbons have been omitted for clarity. Three disordered CH_2Cl_2 molecules are omitted from the structure of complex **[9]**$^+$. Crystallographic data for **9** are reported in Table 4, and complete metrical parameters for both **9** and **10** are listed in the Supporting Information.

(Figure 8 displays the molecular structure of **[9]**$^+$), and complete structural data are included in the Supporting Information.

Alkylidene **3-OTf** was found to react with SCNPh to afford the complex (Nacnac)Ti(η^2-(*S,N*)-SC=CH^{t}BuNPh) (**11**) in 88% yield. Complex **11** results from a [2+2] cycloaddition of the S=C functionality across the Ti=C bond and subsequent Ti−C bond breaking and rotation of the S−C linkage (Scheme 7). Complex **11** is likely favored thermodynamically due to formation of a strong Ti−N bond. ^{1}H and ^{13}C NMR spectra of **11** are in accord with this molecule retaining C_1 symmetry in solution. Single-crystal X-ray diffraction studies of **11** also support η^2-(*S,N*) coordination of the ligand (Scheme 7).

The nitrile $NCCH_2Mes$ (Mes = 2,4,6-$Me_3C_6H_2$) undergoes a cross-metathesis with alkylidene **3-OTf** to afford the four-coordinate titanium imido (Nacnac)-Ti=N[C=CH^{t}Bu(CH_2Mes)](OTf) (**12**) (Scheme 7). Complex **12** forms from a putative azametalacyclobutene intermediate. This type of reaction complements Schrock's original work on the reaction of alkynes and nitriles with tantalum alkylidenes.[1a,46] On the other hand the isonitrile CN^{t}Bu inserts into the Ti=C bond of **3-OTf** to afford the azaallene or *N*-alkylketenimine complex (Nacnac)Ti(η^2-(*N,C*)-^{t}BuN=C=CH^{t}Bu)(OTf) (**13**) in 88% yield as black crystals (Scheme 7). ^{1}H and ^{13}C NMR spectra are in accord with the molecule having C_s symmetry. The η^2-(*N,C*) coordination of the *N-tert*-butylketenimine in **13** was confirmed by single-crystal X-ray diffraction studies (Scheme 7).

Perhaps the most unusual transformation of **3-OTf** involves the reaction with N_2CPh_2 to provide a titanium imide with a coordinated nitrile. Complex (Nacnac)-Ti=NCHPh$_2$(NC^{t}Bu)(OTf) (**14**) forms from N=N rupture of the diazodiphenylmethane and subsequent alkylidene and hydrogen atom transfer to yield Ti=N and C≡N bonds. These occurrences likely proceed through an azine intermediate resulting from addition of N_2CPh_2 across the Ti=C bond. Under dynamic vacuum, complex **14** readily loses CN^{t}Bu to yield the four-coordinate titanium imide complex (Nacnac)Ti=NCHPh$_2$(OTf). Scheme 7 displays the synthesis and structural diagram for the isonitrile adduct **14**.

Addition of N_3Ad to **3-OTf** results in effervescence of the mixture concomitant with formation of the four-coordinate titanium imide (Nacnac)Ti=NCH^{t}BuAd(OTf) (**15**) (Scheme 7). It is proposed that complex **15** results from nucleophilic attack of azide to the metal center, which leads to extrusion of N_2 and subsequent adamantyl (Ad) radical migration to the former alkylidene carbon. As noted previously in the thermolysis of **3-OTf**, formation of complexes **14** and **15** appears to be thermodynamically driven due to the formation of a strong Ti=N bond in a low-coordinate environment. Single-crystal X-ray structures of **14** and **15** are displayed in Scheme 7, and both systems reveal short Ti=N$_{\text{imide}}$ bonds (~1.68 Å).

Protonation of 3-OTf. The nucleophilic character of **3-OTf** was demonstrated with a Bronsted acid. Benzophenone imine cleanly reacts with **3-OTf** to afford the diphenylketiminide alkyl complex (Nacnac)Ti(CH_2^{t}Bu)-(N=CPh$_2$) (**16**) in 73% yield (Scheme 7). Diagnostic features for **16** include a ^{1}H NMR methylene resonance for the neopentyl ligand at 1.88 ppm. In addition, the former sp^2 alkylidene ^{13}C NMR resonance has now shifted to the titanium alkyl region at 53.1 ppm. Treatment of **3-OTf** with ammonium or anilinium salts as well as other weak Brϕnsted acids has resulted in a mixture of products.

Inhibiting an Intramolecular Cross-Metathesis Reaction. Synthesis of the Four-Coordinate Titanium Alkylidene Complexes (Nacnac$_{\text{tBu}}$)-Ti=CH^{t}Bu(X) (X^- = OTf, I; Nacnac$_{\text{tBu}}^-$ = [Ar]NC-(^{t}Bu)CHC(^{t}Bu)N[Ar], Ar = 2,6-($CHMe_2$)$_2$$C_6H_3$). Given the facility for **3-X** to undergo rearrangement to **5-X** we sought incorporation of a bulkier β-diketiminate ligand which would inhibit formation of the putative azametallacyclobutane complex resulting from intramolecular [2+2] cycloaddition. Substituting ^{t}Bu groups in the β-carbon positions of the Nacnac$^-$ ligand has been shown to be effective at stabilizing low coordination numbers on metal centers.[15a,37,38,47] Unfortunately attempts to incorporate the β-diketiminate ligand Li(Nacnac$_{\text{tBu}}$) (Nacnac$_{\text{tBu}}^-$ = [Ar]NC(^{t}Bu)CHC(^{t}Bu)N[Ar]) onto $TiCl_3$-(THF)$_3$ proved difficult and led instead to undesirable products.[33l,48] However, we found that room-temperature reaction of $TiCl_3$ and Li(Nacnac$_{\text{tBu}}$) in Et_2O for 2 days led to isolation of (Nacnac$_{\text{tBu}}$)$TiCl_2$ (**17**) in 23% yield. Complex **17** has been fully characterized, and the X-ray structure reveals a four-coordinate titanium center, which is protected by the steric encumbrance of the bulkier β-diketiminate ligand (see Supporting Information). The widening of the N−Ti−N angle is in turn compensated by the deviation of the metal center (~1.07 Å for **17**) from the NCCCN plane of the Nacnac$_{\text{tBu}}^-$ ligand, which is in contrast to the planar dichloro systems reported by Theopold's ([Ph]NC(Me)-

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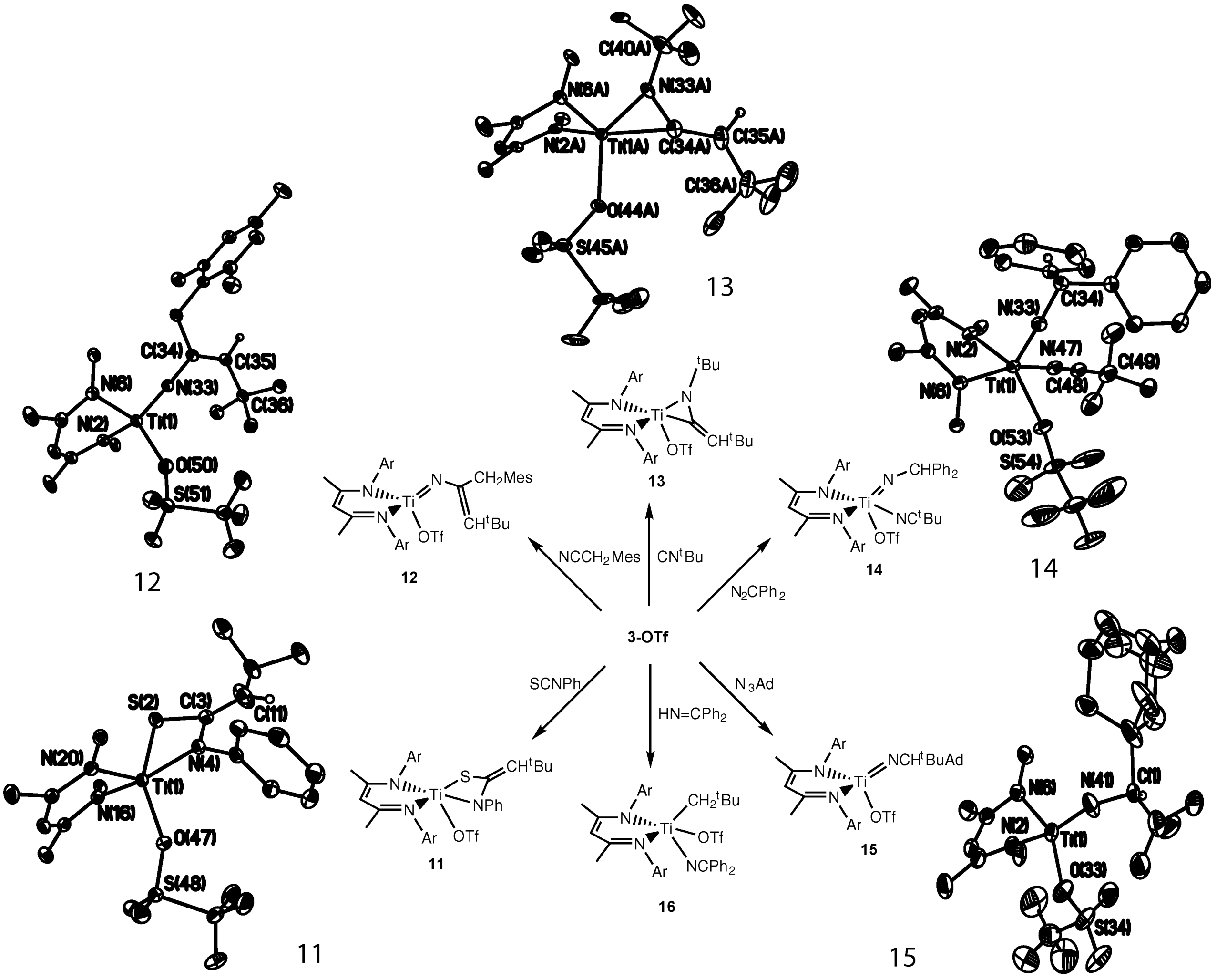
(45) Radzewich, C. E.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 9384−9385. Electrophilic substitution with Ph_2P^+ or $PhClP^+$ at the γ-carbon of the Nacnac$^-$ backbone has been recently reported. (a) Hitchcock, P. B.; Lappert, M. F.; Nycz, J. E. *Chem. Commun.* **2003**, 1142−1143. (b) Ragogna, P. J.; Burford, N.; D'eon, M.; McDonald, R. *Chem. Commun.* **2003**, 1052−1053, and references therein. In addition, α-alkoxylithium-β-diimine ligands have been prepared from the reaction of the lithium-Nacnac salt and the corresponding ketone. Carey, D. T.; Cope-Eatough, E. K.; Vilaplana-Mafé, E.; Mair, F. S.; Pritchard, R. G.; Warren, J. E.; Woods, R. J. *J. Chem. Soc., Dalton Trans.* **2003**, 1083−1093.

(46) Schrock, R. R. *Science* **1983**, *219*, 13−18.

Scheme 7. Reactivity for the Terminal Titanium Alkylidene (Nacnac)Ti=CH^{t}Bu(OTf), 3-OTf[a]



[a] Thermal ellipsoid plots are at the 50% probability level. H atoms with the exception of the formal alkylidene α-hydrogen and aryl groups with the exception of ipso carbons on the Nacnac$^-$ ligand have been omitted for clarity. Disordered solvent molecules have been omitted from the structure of complexes **12**, **13**, and **15**. Crystallographic data are reported in Tables 4 and 5, and complete metrical parameters for the molecular structure of complexes **11**–**15** are listed in the Supporting Information.

CHC(Me)N[Ph])TiCl$_2$[15f] and Budzelaar's ([Mes]NC(R)-CHC(R)N[Mes])TiCl$_2$ (Mes = 2,4,6-Me$_3$C$_6$H$_2$; R = Me or ^{t}Bu).[15a,49] Complex **17** is closely related, structurally, to d^0 scandium derivative (Nacnac$_{tBu}$)ScCl$_2$ prepared by Piers and co-workers in which the Sc atom sits 0.815 Å out of the NCCCN plane.[38] Unlike compound **1**, THF appears to catalyze the decomposition of **17**.

Transmetalation of **17** with 2 equiv of LiCH$_2{}^t$Bu leads to rapid formation of the bis-neopentyl complex (Nacnac$_{tBu}$)Ti(CH$_2{}^t$Bu)$_2$ (**18**) in 71% yield as green blocks. Complex **18** is a close analogue to **2** and has no unusual features. Scheme 8 depicts the reaction leading to a more congested metal center in compounds **17** and **18**, which is exacerbated by the sterically encumbering ^{t}Bu group on the β-carbon position. This feature is reflected by the more acute Ti–N–C$_{ipso}$ angle in the

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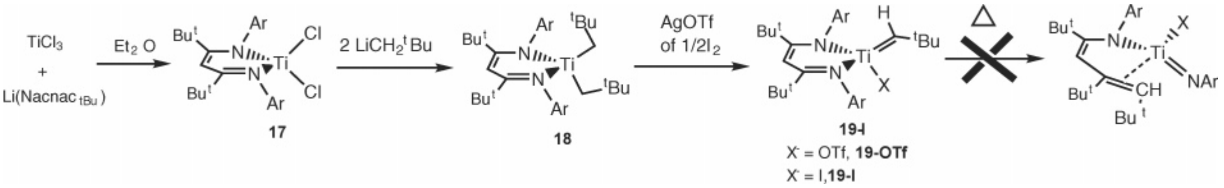
(47) (a) Smith, J. M.; Lachicotte, R. J.; Pittard, K. A.; Cundari, T. R.; Lukat-Rodgers, G.; Rodgers, K. R.; Holland, P. L. *J. Am. Chem. Soc.* **2001**, *123*, 9222–9223. (b) Smith, J. M.; Lachicotte, R. J.; Holland, P. L. *Chem. Commun.* **2001**, 1542–1543. (c) Smith, J. M.; Lachicotte, R. J.; Holland, P. L. *Organometallics* **2002**, *21*, 4808–4814. (d) Bailey, P. J.; Liddle, S. T.; Morrison, C. A.; Parsons, S. *Angew. Chem., Int. Ed.* **2001,** *40*, 4463–4466. (e) Bailey, P. J.; Coxall, R. A.; Dick, C. M.; Fabre, S.; Parsons, S. *Organometallics* **2001**, *20*, 798–801. (f) Knight, L. K.; Piers, W. E.; McDonald, R. *Chem. Eur. J.* **2000**, *6*, 4322–4326. (g) Spencer, D. J. E.; Aboelella, N. W.; Reynolds, A. M.; Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc.* **2002**, *124*, 2108–2109. (h) Hayes, P. G.; Piers, W. E.; McDonald, R. *J. Am. Chem. Soc.* **2002**, *124*, 2132–2133. (i) Andres, H.; Bominaar, E. L.; Smith, J. M.; Eckert, N. A.; Holland, P. L.; Munck, E. *J. Am. Chem. Soc.* **2002**, *124*, 3012–3025. (j) Gibson, V. C.; Marshall, E. L.; Navarro-Llobet, D.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **2002**, 4321–4322. (k) Aboelella, N. W.; Lewis, E. A.; Reynolds, A. M.; Brennessel, W. W.; Cramer, C. J.; Tolman, W. B. *J. Am. Chem. Soc.* **2002**, *124*, 10660–10661. (l) Vela, J.; Smith, J. M.; Lachicotte, R. J.; Holland, P. L. *Chem. Commun.* **2002**, 2886–2887. (m) Holland, P. L.; Cundari, T. R.; Perez, L. L.; Eckert, N. A.; Lachicotte, R. J. *J. Am. Chem. Soc.* **2002**, *124*, 14416–14424. (n) Smith, J. M.; Lachicotte, R. J.; Holland, P. L. *J. Am. Chem. Soc.* **2003**, *125*, 15752–15753. (o) Vela, J.; Vaddadi, S.; Cundari, T. R.; Smith, J. M.; Gregory, E. A.; Lachicotte, R. J.; Flaschenriem, C. J.; Holland, P. L. *Organometallics* **2004**, *23*, 5226–5239.

(48) Addition of Li(Nacnac$_{tBu}$) to TiCl$_3$(THF)$_3$ in toluene and reflux for 3 days did not lead to the desire precursor (Nacnac$_{tBu}$)TiCl$_2$, but instead afforded diamagnetic (Nacnac$_{tBu}$)Ti=NAr(Cl) in 39% yield. It has been postulated in the literature that similar C=N bond cleavage reactions using Nacnac$^-$ occur through a putative (Nacnac)$_2$TiCl intermediate (ref 33l). The organic byproducts generated from either of these reactions have not been identified. Falguni, B.; Clark, R. L.; Bailey, B. C.; Brown, D.; Huffman, J. C.; Mindiola, D. J. *Chem. Commun.*, in press.

(49) Significant deviation of the Ti atom from the NCCCN plane has been observed with less bulky β-diketiminate systems of Ti(IV). Kakaliou, L.; Scanlon IV, W. J.; Qian, B.; Baek, S. W.; Smith, M. R., III; Motry, D. H. *Inorg. Chem.* **1999**, *38*, 5964–5977. For the five-coordinate titanium complex (Nacnac)TiCl$_2$(THF), the metal atom sits ~0.778 Å from the NCCCN mean plane.

Scheme 8. Synthesis and Thermolysis of the Titanium Alkylidene (Nacnac$_{tBu}$)Ti=CH^{t}Bu(X) (X− = OTf, 19-OTf; I, 19-I)[a]



[a] Complete structural parameters for **17**, **18**, **19-OTf**, and **19-I** are included in the Supporting Information.

molecular structure of **18** (e.g., ~124° for **2** vs ~121° for **18**, see Supporting Information).

One-electron oxidation of **18** with 1 equiv of AgOTf or 0.5 equiv of I_2 promotes α-hydrogen abstraction to form the alkylidene species (Nacnac)Ti=CH^{t}Bu(X) (X^- = OTf, **19-OTf**, 83% yield; X^- = I, **19-I**, 75% yield, Scheme 8). Spectral and structural features for **19-OTf** and **19-I** are similar to their corresponding **3-OTf** and **3-I** derivatives (see Experimental Section and Supporting Information). Perhaps the most interesting feature of the four-coordinate neopentylidene systems **19-OTf** and **19-I** is the steric hindrance provided by the more encumbering β-diketiminate ligand, which bans thermodynamic rearrangement to the titanium imide products (H^{t}BuC=C(^{t}Bu)CHC(^{t}Bu)N[Ar])Ti=NAr(X) (X^- = OTf or I) (Scheme 8). In fact, exhaustive heating (40−90 °C) of **19-OTf** and **19-I** did not lead to decomposition. As a result, the putative azametalacyclobutane complex formed in the thermolysis of alkylidene **3-X** is completely inhibited in complex **19**, presumably due to the steric repulsion among the proximal ^{t}Bu groups. The molecular structures of **19-OTf** and **19-I** are examples of kinetically stable titanium complexes containing low-coordination environments as well as a terminal and highly nucleophilic neopentylidene functionality.

Concluding Remarks

In this work we have reported a facile synthetic method for generating a family of low-coordinate titanium alkylidene complexes, all of which have allowed unprecedented reactivity of the Ti=CH^{t}Bu motif. Titanium carbon double bonds were created by a one-electron oxidation and subsequent α-hydrogen abstraction reactions. We determined that the nature of the oxidant and the steric bulk of the alkyl substituent on the metal center both influence the α-abstraction process. It seems very logical to propose that the oxidatively induced α-abstraction reaction transpires in three distinct steps: Outer sphere electron transfer occurs first followed by anion binding to the electropositive metal center to generate a coordinately saturated species. The latter step leads to the rate-determining step in the reaction, which is the α-abstraction process. This process is consistent with the principle of sterically induced α-hydrogen abstraction reactions promoted by Lewis base addition. The key components facilitating these sequential steps are the use of bulky alkyl groups and congesting anions that have the ability to coordinate to the metal center. It is unlikely that the anion from the oxidant acts as a Brϕnsted base during the α-abstraction process since F^- does not appear to catalyze the formation of a neopentylidene titanium fluoride complex.

The titanium neopentylidene species (Nacnac)-Ti=CH^{t}Bu(X) are all kinetic products and have been shown to undergo intramolecular cross-metathesis as well as double tertiary carbon−hydrogen activation reactions. In addition, these reactive compounds can engage cleanly in cross-metathesis, cycloaddition, insertion, and acid−base reactions involving the alkylidene functionality.

The steric encumbrance provided by the supporting β-diketiminate ligand (Nacnac$_{tBu}^-$) has a tremendous effect in the kinetic stability of the four-coordinate titanium neopentylidene complexes by blocking the intramolecular [2+2] cycloaddition reaction. We are currently exploring what factors govern the activation of activation of 3° carbons, as well as the reactivity of titanium alkylidene complexes having the Nacnac$_{tBu}^-$ skeleton, since these systems have proven to be much more kinetically stable than the conventional Nacnac$^-$ analogues.

Experimental Section

General Considerations. Unless otherwise stated, all operations were performed in a M. Braun Lab Master double-drybox under an atmosphere of purified nitrogen or using high-vacuum standard Schlenk techniques under an argon atmosphere.[50] Anhydrous n-hexane, pentane, toluene, and benzene were purchased from Aldrich in sure-sealed reservoirs (18 L) and dried by passage through one column of activated alumina and one of Q-5.[51] Diethyl ether and CH_2Cl_2 were dried by passage through two columns of activated alumina.[51] 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. C_6D_6 and CD_2Cl_2 were purchased from Cambridge Isotope Laboratory (CIL), degassed, and dried over 4 Å molecular sieves and CaH_2, respectively. CD_2Cl_2 was vacuum transferred from the CaF_2 mixture and stored in a reaction vessel under N_2. Et_2O-d_{10} and THF-d_8 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(Nacnac)[52] (Nacnac$^-$ = [Ar]NC(Me)CHC(Me)N[Ar], Ar = 2,6-$(CHMe_2)_2C_6H_3$), (Nacnac)$TiCl_2$(THF) (**1**),[14,15a] (Nacnac)-$TiMe_2$(THF),[15a] $LiCH_2{}^t$Bu,[3b] Ph_3P=CH_2LiBr,[25] Li(Nacnac$_{tBu}$) (Nacnac$_{tBu}^-$ = [Ar]NC(^{t}Bu)CHC(^{t}Bu)N[Ar]),[15a] N_2CPh_2,[53] [FeCp*$_2$]-[B$(C_6F_5)_4$],[20−22] OC_2Ph_2,[44] (Nacnac)Ti$(CH_2{}^t Bu)_2$ (**2**),[14] (Nacnac)-Ti=CH^{t}Bu(OTf)(**3-OTf**),[14] (H^{t}BuC=C(Me)CHC(Me)N[Ar])-

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(50) For a general description of the equipment and techniques used in carrying out this chemistry see: Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society; Washington, D.C., 1987; pp 79−98.

(51) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.

(52) Stender, M.; Wright, R. J.; Eichler, B. E.; Prust, J.; Olmstead, M. M.; Roesky, H. W.; Power, P. P. *J. Chem. Soc., Dalton Trans.* **2001**, 3465−3469, and references therein.

(53) Miller, J. B. *J. Org. Chem.*, **1959**, *24*, 560−561.

Ti=NAr(OTf) (**5**),[14] (H^{t}BuC=C(Me)CHC(Me)N[Ar])Ti=NAr(OTf)(Et$_2$O) (**6**),[14] and [(Nacnac)Ti(μ_2-O)(μ_2-OTf)]$_2$ (**8**)[14] were prepared according to the literature. All other chemicals were used as received. Solution infrared spectra (CaF$_2$ plates) were measured using a Nicolet 510P FTIR spectrometer. CHN analysis was performed by Desert Analytics, Tucson, AZ. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Varian 400 or 300 MHz NMR spectrometers. ^{1}H and ^{13}C NMR are reported with reference to solvent resonances (residual C_6D_5H in C_6D_6, 7.16 and 128.0 ppm; $CHDCl_2$ in CD_2Cl_2, 5.32 ppm and 53.8; proteo THF in THF-d_8, 3.58, 1.73, and 67.4, 25.3; proteo toluene in $C_6D_5CD_3$, 7.09, 7.00, 6.98, 2.09 and 137.5, 128.9, 128.0, 125.2, 20.4; proteo Et$_2$O in Et$_2$O-d_{10}, 3.34, 1.07 and 65.3, and 14.5). ^{19}F NMR chemical shifts are reported with respect to external HOCOCF$_3$ (−78.5 ppm). ^{11}B NMR spectra were reported with respect to external BF$_3$·(OEt$_2$) (0.0 ppm). Magnetic moments were obtained by the method of Evans.[54] Cyclic voltammetry was collected with the assistance of an E2 Epsilon potentiostat/galvanostat with a PC unit controlled by Bioanalytical Systems (BAS) software. Room-temperature and liquid helium temperature X-band EPR spectra were recorded on a Bruker EMX spectrometer. Acquisition and simulation were performed using an integrated WIN-EPR software package (Bruker). X-ray diffraction data were collected on a SMART6000 (Bruker) system under a stream of N$_2$(g) at low temperatures.

Synthesis of (Nacnac)Ti=CH^{t}Bu(Cl), 3-Cl. In a vial was dissolved **3-OTf** [180 mg, 0.262 mmol] in 5 mL of THF and the solution cooled to −35 °C. To the solution was added a cold THF (~5 mL) suspension of magnesium chloride [75 mg, 0.787 mmol], which was broken into a fine powder. After 10 min the solutions turned red-violet and the reaction mixture was allowed to stir for an additional 2 h. The solution was dried, dissolved in pentane, and then filtered, leaving behind a white precipitate. The solution was concentrated, then cooled. Recrystallization from pentane at −35 °C afforded black needles of **3-Cl** [101 mg, 0.176 mmol, 67% yield]. ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.2−7.1 (m, C_6*H*$_3$, 6H), 5.54 (s, Ti=C*H*^{t}Bu, 1H), 4.82 (s, C(Me)C*H*C(Me), 1H), 3.76 (septet, C*H*Me$_2$, 2H), 3.20 (septet, C*H*Me$_2$, 2H), 1.71 (d, CH*Me*$_2$, 6H), 1.52 (s, C(*Me*)CHC(*Me*), 6H), 1.45 (d, CH*Me*$_2$, 6H), 1.19 (d, CH*Me*$_2$, 6H), 1.18 (d, CH*Me*$_2$, 6H), 0.71 (s, Ti=CH^t*Bu*, 9H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 276.0 (Ti=*C*H^{t}Bu, J_{C-H} = 92.78 Hz), 167.8 (*C*(Me)CH*C*(Me), 145.0 (*ipso*-*C*$_6$H$_3$), 143.1 (*o*-C$_6$H$_3$), 140.5 (*o*-*C*$_6$H$_3$), 127.1 (*p*-*C*$_6$H$_3$), 124.5 (*m*-*C*$_6$H$_3$), 124.2 (*m*-*C*$_6$H$_3$), 96.79 (C(Me)*C*HC(Me)), 48.91 (Ti=CH*C*Me$_3$), 31.24 (Ti=CHC*Me*$_3$), 29.01 (*C*HMe$_2$), 28.98 (*C*HMe$_2$), 26.77 (CH*Me*$_2$), 24.74 (CH*Me*$_2$), 24.65 (CH*Me*$_2$), 24.19 (CH*Me*$_2$), 23.77 (C(*Me*)CHC(*Me*)). Anal. Calcd for $C_{34}H_{51}N_2ClTi$: C, 71.50; H, 9.00; N, 4.90. Found: C, 71.15; H, 8.96; N 5.26.

Synthesis of (Nacnac)Ti=CH^{t}Bu(Br), 3-Br. In a vial was dissolved **3-OTf** [180 mg, 0.262 mmol] in 5 mL of ether and the solution cooled to −35 °C. To the solution was added a cold ether solution (5 mL) of triphenylmethylphosphonium bromide [56 mg, 0.154 mmol]. After 15 min the solutions turned red-violet and the reaction mixture was allowed to stir for an additional 2 h. A white precipitate was filtered off, and the solution was concentrated and cooled. Recrystallization from Et$_2$O at −35 °C afforded in two crops brown crystals of **3-Br** [100 mg, 0.163 mmol, 62% yield]. ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.13−7.04 (m, C_6*H*$_3$, 6H), 4.84 (s, C(Me)C*H*C(Me), 1H), 4.57 (s, Ti=C*H*^{t}Bu, 1H) 3.67 (septet, C*H*Me$_2$, 2H), 3.42 (septet, C*H*Me$_2$, 2H), 1.75 (d, CH*Me*$_2$, 6H), 1.55 (s, C(*Me*)CHC(*Me*), 6H), 1.46 (d, CH*Me*$_2$, 6H), 1.24 (d, CH*Me*$_2$, 6H), 1.19 (d, CH*Me*$_2$, 6H), 0.76 (s, Ti=CH^t*Bu*, 9H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 274.2 (Ti=*C*H^{t}Bu, J_{C-H} = 87.9 Hz), 167.6 (*C*(Me)CH*C*(Me), 145.5 (*ipso*-C$_6$H$_3$), 143.1 (*o*-*C*$_6$H$_3$), 140.5 (*o*-*C*$_6$H$_3$), 127.1 (*p*-*C*$_6$H$_3$), 124.6 (*m*-*C*$_6$H$_3$), 124.3 (*m*-*C*$_6$H$_3$), 96.64 (C(Me)*C*HC(Me)), 49.21 (Ti=CH*C*Me$_3$), 31.38, (Ti=CHC*Me*$_3$), 29.41 (*C*HMe$_2$), 28.99 (*C*HMe$_2$), 27.11 (CH*Me*$_2$), 24.76 (CH*Me*$_2$), 24.76 (CH*Me*$_2$), 24.40 (CH*Me*$_2$), 23.91 (C(*Me*)CHC(*Me*)). Anal. Calcd for $C_{34}H_{51}N_2BrTi$: C, 66.34; H, 8.35; N, 4.55. Found: C, 66.61; H, 8.35; N 4.78.

Synthesis of (Nacnac)Ti=CH^{t}Bu(I), 3-I. In a vial was dissolved **2** [120 mg, 0.198 mmol] in 5 mL of toluene and the solution cooled to −35 °C. To the solution was added a cold toluene solution (5 mL) of iodine [27.6 mg, 0.109 mmol]. After 15 min the solutions turned violet and the reaction mixture was pumped dry, then redissolved in pentane. The resulting solution was filtered, concentrated, and cooled to −35 °C to afford dark violet crystals of **3-I** [80 mg, 0.121 mmol, 61% yield]. ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.24−7.04 (m, C_6*H*$_3$, 6H), 4.79 (s, C(Me)C*H*C(Me), 1H), 3.64 (septet, C*H*Me$_2$, 2H), 3.42 (septet, C*H*Me$_2$, 2H), 3.26 (s, Ti=C*H*^{t}Bu, 1H), 1.69 (d, CH*Me*$_2$, 6H), 1.50 (s, C(*Me*)CHC(*Me*), 6H), 1.38 (d, CH*Me*$_2$, 6H), 1.23 (d, CH*Me*$_2$, 6H), 1.09 (d, CH*Me*$_2$, 6H), 0.72 (s, Ti=CH^t*Bu*, 9H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 272.4 (Ti=*C*H^{t}Bu, J_{C-H} = 85.0 Hz), 167.0 (*C*(Me)CH*C*(Me), 146.1 (*ipso*-*C*$_6$H$_3$), 143.0 (*o*-*C*$_6$H$_3$), 140.5 (*o*-*C*$_6$H$_3$), 127.2 (*p*-*C*$_6$H$_3$), 124.7 (*m*-*C*$_6$H$_3$), 124.2 (*m*-*C*$_6$H$_3$), 95.83 (C(Me)*C*HC(Me)), 49.84 (Ti=CH*C*(Me)$_3$), 31.38 (Ti=CHC*Me*$_3$), 29.85 (*C*HMe$_2$), 28.76 (*C*HMe$_2$), 27.30 (CH*Me*$_2$), 24.66 (CH*Me*$_2$), 24.56 (CH*Me*$_2$), 24.51 (CH*Me*$_2$), 23.91 (C(*Me*)CHC(*Me*)). Anal. Calcd for $C_{34}H_{51}N_2ITi$: C, 61.63; H, 7.76; N, 4.23. Found: C, 61.61; H, 7.47; N, 4.40.

Synthesis of (Nacnac)Ti=CH^{t}Bu(BH$_4$), 3-BH$_4$. In a vial was dissolved **3-OTf** [200 mg, 0.29 mmol] in 10 mL of Et$_2$O and the solution cooled to −35 °C. To the cold solution was added a cold Et$_2$O suspension (5 mL) containing LiBH$_4$ [6.36 mg, 0.29 mmol]. After stirring for 10 min the solution was filtered and dried under reduced pressure. The brown powder was extracted with hexane and filtered, and the filtrate concentrated and cooled to −35 °C to afford in two crops brown crystals of **3-BH$_4$** [111.2 mg, 0.20 mmol, 68% yield]. ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.17−7.05 (m, C_6*H*$_3$, 6H), 5.32 (s, Ti=C*H*^{t}Bu, 1H), 4.96 (s, C(Me)C*H*C(Me), 1H), 4.11 (septet, C*H*Me$_2$, 2H), 2.80 (septet, C*H*Me$_2$, 2H), 1.59 (s, C(*Me*)CHC(*Me*), 6H), 1.52 (br d, CH*Me*$_2$, 12H), 1.25 (d, CH*Me*$_2$, 6H), 1.07 (d, CH*Me*$_2$, 6H), 0.71 (Ti=CH^t*Bu*, 9H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 266.7 (Ti=*C*H^{t}Bu, J_{C-H} = 95 Hz), 167.9 (*C*(Me)CH*C*(Me)), 144.4 (*ipso*-*C*$_6$H$_3$), 142.92 (*o*-*C*$_6$H$_3$), 141.1 (*o*-*C*$_6$H$_3$), 126.8 (*p*-*C*$_6$H$_3$), 124.7 (*m*-*C*$_6$H$_3$), 124.2 (*m*-*C*$_6$H$_3$), 98.23 (C(Me)*C*HC(Me)), 46.83 (Ti=CH*C*Me$_3$), 31.54 (Ti=CHC*Me*$_3$), 29.16 (*C*HMe$_2$), 27.70 (*C*HMe$_2$), 26.17 (*C*H$_3$), 25.24 (*C*H$_3$), 24.51 (*C*H$_3$), 24.23 (*C*H$_3$), 24.18 (*C*H$_3$). ^{11}B NMR (23 °C, 128.4 MHz, C_6D_6): δ −14.29 (quintet, *B*H$_4$, J_{B-H} = 89 Hz). Anal. Calcd for $C_{34}H_{55}N_2BTi$: C, 74.18; H, 10.07; N, 5.09. Found: C, 73.81; H, 9.79; N, 5.08.

Synthesis of [(Nacnac)Ti(CH$_2$^{t}Bu)$_2$][B(C$_6$F$_5$)$_4$], [2][B(C$_6$F$_5$)$_4$]. In a vial was dissolved in 10 mL of Et$_2$O complex **2** [73 mg, 0.12 mmol] and the solution cooled to −35 °C. To the cold solution was added a cold Et$_2$O suspension (~5 mL) containing [FeCp*$_2$][B(C$_6$F$_5$)$_4$] [119 mg, 0.12 mmol]. The solution rapidly turned orange and was allowed to stir for 3 min. The solution was filtered and the filtrate dried under reduced pressure. The orange powder was washed with pentane until washings were clear, extracted with Et$_2$O, and filtered. The filtrate was then concentrated, a few drops of (Me$_3$Si)$_2$O were added, and the solution was cooled to −35 °C to afford orange crystals of **[2][B(C$_6$F$_5$)$_4$]** [145 mg, 0.11 mmol, 92% yield]. Some assignments of ^{1}H and ^{13}C NMR resonances were determined by HMQC experiments.[18] ^{1}H NMR (23 °C, 399.8 MHz, CD_2Cl_2): δ 7.53−7.39 (m, C_6*H*$_3$, 6H), 6.20 (s, C(Me)C*H*C(Me), 1H), 3.33 (septet, C*H*Me$_2$, 2H), 2.95 (s, TiC*H*$_2$^{t}Bu, 2H), 2.90 (s, TiC*H*$_2$^{t}Bu, 2H), 2.44 (septet, C*H*Me$_2$, 2H), 2.33 (s, C(*Me*)CHC(*Me*), 6H), 1.59 (d, CH*Me*$_2$, 6H), 1.37 (d, CH*Me*$_2$, 6H), 1.29 (d, CH*Me*$_2$, 6H), 1.08 (d, CH*Me*$_2$, 6H), 0.95 (TiCH$_2$C*Me*$_3$, 9H), 0.62 (TiCH$_2$C*Me*$_3$, 9H). ^{13}C NMR (25 °C, 100.6 MHz, CD_2Cl_2): δ 170.9 (*C*(Me)CH*C*(Me)), 149.5 (B(*C*$_6$F$_5$)$_4$), 147.0 (B(*C*$_6$F$_5$)$_4$), 146.7 (Ti*C*H$_2$^{t}Bu, based on HMQC), 141.8 (*ipso*-*C*$_6$H$_3$), 141.6

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(54) (a) Sur, S. K. *J. Magn. Reson.* **1989**, *82*, 169−173. (b) Evans, D. F. *J. Chem. Soc.* **1959**, 2003−2005.

(o-C_6H_3), 139.7 (o-C_6H_3), 137.6 (B(C_6F_5)$_4$), 136.1 (TiCH$_2{}^t$Bu based on HMQC), 135.2 (B(C_6F_5)$_4$), 130.6 (p-C_6H_3), 126.2 (m-C_6H_3), 126.1 (m-C_6H_3), 108.1, 100.2 (C(Me)CHC(Me), J_{C-H} = 169 Hz), 43.96 (TiCH$_2C$Me$_3$), 41.80 (TiCH$_2C$Me$_3$), 32.30 (TiCH$_2$CMe_3), 31.23 (TiCH$_2$CMe_3), 29.37 (CHMe$_2$), 29.10 (CHMe$_2$), 25.28 (CH$_3$), 25.23 (CH$_3$), 25.14 (CH$_3$), 24.52 (CH$_3$), 23.93 (CH$_3$). ^{19}F NMR (23 °C, 282.3 MHz, CD_2Cl_2): δ −133.45 (B(C$_6F_5$)$_4$), −163.95 (B(C$_6F_5$)$_4$), −167.77 (B(C$_6F_5$)$_4$). ^{11}B NMR (23 °C, 128.4 MHz, CD_2Cl_2): δ −16.96 (B(C$_6$F$_5$)$_4$). Anal. Calcd for $C_{63}H_{63}N_2F_{20}BTi$: C, 58.80; H, 4.93; N, 2.18. Found: C, 58.74; H, 4.96; N, 2.43.

Synthesis of (Nacnac)Ti(CH$_2{}^t$Bu)$_2$(F), 2-F. In a vial was dissolved **2** [130 mg, 0.214 mmol] in 10 mL of THF, and the solution was cooled to −35 °C. To the cold solution was added a THF suspension (5 mL) containing $AgBF_4$ [41.7 mg, 0.214 mmol], causing precipitation of Ag^0. After stirring for 20 min the solution was filtered and the filtrate dried under vacuum. The solids were extracted with Et_2O, and the solution was filtered. The filtrate was concentrated under reduced pressure and cooled to −35 °C to afford in two crops yellow crystals of **2-F** [57.6 mg, 0.09 mmol, 43% yield]. Two minor impurities are present with the product, and an attempt to separate **2-F** from the reaction mixture was unsuccessful (judged by ^{19}F and ^{1}H NMR spectroscopy). Complete ^{1}H NMR assignment was not possible due to impurities present in the reaction mixture. ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.28−6.88. (m, C$_6H_3$, 6H), 5.11 (s, C(Me)CHC(Me), 1H), 3.31 (septet, CHMe$_2$, 2H), 3.16 (septet, CHMe$_2$, 2H), 1.73, 1.67, 1.56, 1.50, 1.39, 1.21, 1.17, 1.15 (TiCH$_2$CMe_3), 1.11, 0.79 (d, CHMe_2, 3H). ^{19}F NMR (23 °C, 282.3 MHz, C_6D_6): δ −142.0 (m, Ti-F), and two additional resonances observed at −140.5 (m) and −129.0 (m). Multiple attempts to obtain satisfactorily elemental analysis were unsuccessful.

Synthesis of (Nacnac)Ti(CH$_3$)$_2$(OTf) (4). In a vial was dissolved (Nacnac)TiMe$_2$(THF) [270 mg, 0.47 mmol] in 10 mL of pentane, and the solution was cooled to −35 °C. To the cold solution was added a pentane suspension (~5 mL) containing AgOTf [128.4 mg, 0.50 mmol], causing precipitation of product and Ag^0. After stirring for 2 h the solution was filtered. The solids were stirred in THF, and the solution was filtered. The filtrate was concentrated under reduced pressure, layered with pentane, and cooled to −35 °C to afford in two crops of orange-red crystals of **4** [197 mg, 0.30 mmol, 64% yield]. ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.20−7.12 (m, C$_6H_3$, 6H), 5.18 (s, C(Me)CHC(Me), 1H), 2.94 (septet, CHMe$_2$, 4H), 2.02 (Me_2Ti), 1.57 (s, C(Me)CHC(Me), 6H), 1.34 (d, CHMe_2, 12H), 1.03 (d, CHMe_2, 12H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 168.2 (C(Me)CHC(Me)), 141.2 (C_6H$_3$), 128.28 (C_6H$_3$), 127.4 (C_6H$_3$), 125.2 (C_6H$_3$), 101.8 (C(Me)CHC(Me), J_{C-H} = 165), 88.89 (Me_2Ti, J_{C-H} = 124), 28.89 (CHMe$_2$), 25.40 (C(Me)CHC(Me)), 24.71 (CHMe_2), 24.16 (CHMe_2). ^{19}F NMR (23 °C, 282.3 MHz, C_6D_6): δ −77.69 (s, OSO$_2$CF_3). Anal. Calcd for $C_{32}H_{47}N_2O_3SF_3Ti$: C, 59.61; H, 7.35; N, 4.35. Found: C, 59.80; H, 7.46; N, 4.53.

Synthesis of (H^{t}BuC═C(Me)CHC(Me)N[Ar])Ti═NAr(OTf), 5-OTf, and Ti[2,6-(CMe$_2$)(CHMe$_2$)C$_6$H$_3$]NC(Me)CHC(Me)N[2,6-(CMe$_2$)(CHMe$_2$)C$_6$H$_3$](OTf), 7-OTf. In a reaction vessel was dissolved **3-OTf** [100 mg, 0.15 mmol] in 15 mL of benzene, and the solution was heated at 45 °C for 2 days. The solution was then filtered and dried under reduced pressure. The red-brown solid was extracted with pentane, filtered, concentrated, and cooled overnight at −35 °C to afford in two crops red-brown crystals of **5-OTf** [74.7 mg, 0.11 mmol, 75% yield]. If the thermolysis takes place at 60 °C, complex **5-OTf** is formed over 2 h and is isolated in ~65% yield. Some assignments of ^{1}H and ^{13}C NMR resonances were determined by HMQC experiments.[18]

For **5-OTf**: ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.20−6.77 (m, C$_6H_3$, 6H), 4.67 (s, C(Me)CHC(Me), 1H), 3.87 (septet, CHMe$_2$, 2H), 2.66 (s, H^tBuC(Me)CHC(Me), 1H), 2.14 (septet, CHMe$_2$, 2H), 1.92 (s, H^{t}BuC(Me)CHC(Me), 3H), 1.57 (s, H^{t}BuC(Me)CHC(Me), 3H), 1.43 (d, CHMe_2, 6H), 1.29 (s, H^tBuC(Me)CHC(Me), 9H), 1.17 (d, CHMe_2, 6H), 1.10 (d, CHMe_2, 6H), 0.98 (d, CHMe_2, 6H). ^{13}C NMR (25 °C, 100.5 MHz, C_6D_6): δ 161.5 (C(Me)CHC(Me)), 158.0, 157.1, 147.6, 145.8 (C_6H$_3$), 143.7 (C_6H$_3$), 139.9 (C_6H$_3$), 134.2 (H^{t}BuCC(Me)CHC(Me), J_{C-H} = 129 Hz), 127.5 (C_6H$_3$), 125.5 (C_6H$_3$), 123.8 (C_6H$_3$), 123.6 (C_6H$_3$), 122.8 (br, CF$_3$), 97.25 (C(Me)CHC(Me), J_{C-H} = 159 Hz), 35.99 (H(Me$_3C$)CC(Me)CHC(Me)), 32.18 (H(Me_3C)CC(Me)CHC(Me)), 29.15 (CHMe$_2$), 28.36 (CHMe$_2$), 24.89 (CH_3), 24.67 (CH_3), 24.47 (CH_3), 24.40 (CH_3), 24.26 (CH_3), 23.66 (CH_3). ^{19}F NMR (23 °C, 282.3 MHz, C_6D_6): δ −75.6 (s, OSO$_2$CF_3). IR (C_6H_6, CaF_2): 2964 (s), 2869 (s), 1619 (w), 1517 (m), 1463 (m), 1439 (m), 1363 (s), 1338 (m), 1239 (s), 1201 (s), 1167 (m), 997 (s) cm^{-1}. Anal. Calcd for $C_{35}H_{51}N_2O_3SF_3Ti$: C, 61.39; H, 7.51; N, 4.09. Found: C, 61.36; H, 7.82; N, 4.02.

For **7-OTf**: In a reaction vessel was dissolved **3-OTf** [100 mg, 0.146 mmol] in 10 mL of C_6H_6 and the solution was heated at 70 °C for 2 h. The solution was dried under reduced pressure and the red-brown solid washed with hexane to remove **5-OTf**. Recrystallization of the solid from Et_2O at −35 °C affords in three crops brown crystals of **7-OTf** [28 mg, 0.046 mmol, 31% yield]. The hexane filtrate from the reaction mixture was concentrated and the solution cooled overnight to −35 °C to afford in two crops red-brown crystals of **5-OTf** [62 mg, 0.09 mmol, 62% yield]. When monitoring the reaction by ^{1}H NMR at 70 °C, neopentane was observed (0.992 ppm).

For **7-OTf**: ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.59 (d, C$_6H_3$, 2H), 7.52 (t, C$_6H_3$, 2H), 7.10 (d, C$_6H_3$, 2H), 5.69 (s, C(Me)CHC(Me), 1H), 2.74 (septet, CHMe$_2$, 2H), 2.58 (s, CH_3, 6H), 2.09 (s, CH_3, 6H), 1.21 (d, CH(CH_3)$_2$, 6H), 0.55 (d, CH(CH_3)$_2$, 6H), 0.51 (s, CH_3, 6H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 159.8 (C(Me)CHC(Me)), 142.7 (C_6H$_3$), 137.6 (C_6H$_3$), 137.6 (C_6H$_3$), 132.9 (C_6H$_3$), 130.9 (C_6H$_3$), 128.5 (C_6H$_3$), 127.4 (bs, CF$_3$), 126.6 (C_6H$_3$), 95.53 (C(Me)CHC(Me), J_{C-H} = 162 Hz), 88.78 (C(CH$_3$)$_2$), 27.93 (CHMe$_2$), 27.02 (CH_3), 26.76 (CH_3), 24.61 (CH_3), 22.41 (CH_3), 21.44 (CH_3). ^{19}F NMR (23 °C, 282.3 MHz, C_6D_6): δ −78.08 (s, OSO$_2$CF_3). IR (Et_2O, CaF_2): 3029 (w), 2967 (m), 2929 (m), 2867 (m), 2837 (m), 1540 (m), 1456 (w), 1420 (w), 1362 (s), 1239 (m), 1200 (s), 1069 (w), 999 (s) cm^{-1}. Anal. Calcd for $C_{30}H_{39}N_2O_3SF_3Ti$: C, 58.82; H, 6.42; N, 4.57. Found: C, 58.91; H, 6.75; N, 4.39.

Thermolysis of 5-OTf. In a NMR tube was loaded complex **5-OTf** [27 mg, 0.039 mmol] in 0.8 mL of C_6D_6. The tube was sealed under vacuum and the solution heated to 70 °C for 2 days. No decomposition of **5-OTf** nor traces of **7-OTf** were observed to form based on ^{1}H NMR spectroscopy.

Synthesis of (H^{t}BuC═C(Me)CHC(Me)N[Ar])Ti═NAr(Cl), 5-Cl, and Ti[2,6-(CMe$_2$)(CHMe$_2$)C$_6$H$_3$]NC(Me)CHC(Me)N[2,6-(CMe$_2$)(CHMe$_2$)C$_6$H$_3$](Cl), 7-Cl. 3-Cl [20 mg, 0.0350 mmol] was dissolved in benzene (~675 mg) and the solution placed in an NMR tube equipped with a Teflon vacuum adapter. The NMR tube was heated to 45 °C in an oil bath for 12 h, at which point no starting material remained, as evidenced by ^{1}H NMR. Although there are two major products seen by NMR which are consistent with **5-Cl** and **7-Cl**, assignments of the resonances was difficult due to the presence of several other impurities in the reaction mixture. Attempts to isolate either product were unsuccessful.

Synthesis of (H^{t}BuC═C(Me)CHC(Me)N[Ar])Ti═NAr(Br), 5-Br, and Ti[2,6-(CMe$_2$)(CHMe$_2$)C$_6$H$_3$]NC(Me)CHC(Me)N[2,6-(CMe$_2$)(CHMe$_2$)C$_6$H$_3$](Br), 7-Br. 3-Br [20 mg, 0.0325 mmol] was dissolved in benzene (~675 mg) and the solution transferred to an NMR tube equipped with a Teflon vacuum valve. The NMR tube was heated to 45 °C in an oil bath for 12 h, at which point no starting material remained based on ^{1}H NMR. Two products are observed by NMR, and attempts to separate the two were hampered by their similar solubilities. Integration is consistent with a ~3:1 mixture of **5-Br** and **7-Br**.

For **5-Br**: ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.50−6.79 (m, C$_6H_3$, 6H), 4.90 (s, C(Me)CHC(Me), 1H), 3.87 (septet, C*H*Me$_2$, 2H), 2.49 (s, 3H), 2.16 (septet, C*H*Me$_2$, 2H), 1.92 (s, C*H*$_3$, 3H), 1.88 (s, Ti-*H*^{t}BuCCMeCH, 1H), 1.48 (s, C*H*$_3$, 3H), 1.39 (d, CH*Me*$_2$, 6H), 1.21 (s, ^{t}*Bu*, 9H), 1.08 (d, CH*Me*$_2$, 6H), 1.01 (d, CH*Me*$_2$, 6H), 0.93 (d, CH*Me*$_2$, 6H).

For **7-Br**: ^{1}H NMR (23 °C, 399.8 MHz, C$_6$D$_6$): δ 7.50−6.79 (m, C$_6$*H*$_3$, 6H), 5.60 (s, C(Me)C*H*C(Me), 1H), 2.72 (septet, C*H*Me$_2$, 2H), 2.49 (s, C*H*$_3$, 6H), 2.08 (s, C*H*$_3$, 6H), 1.18 (d, CH*Me*$_2$, 6H), 0.53 (d, CH*Me*$_2$, 6H), 0.58 (s, C*H*$_3$, 6H).

Synthesis of (H^{t}BuC=C(Me)CHC(Me)N[Ar])Ti=NAr(η^3-BH$_4$), 5-BH$_4$, and Ti[2,6-(CMe$_2$)(CHMe$_2$)C$_6$H$_3$]NC(Me)CHC(Me)N[2,6-(CMe$_2$)(CHMe$_2$)C$_6$H$_3$](η^2-BH$_4$), 7-BH$_4$. In a vial was dissolved in 10 mL of hexane **3-BH$_4$** [120 mg, 0.22 mmol] and the solution stirred for 24 h. The solution was concentrated until solid began to form and cooled to −35 °C to afford in two crops red crystals of **5-BH$_4$** [69.4 mg, 0.126 mmol, 58% yield]. Attempts to isolate pure **7-BH$_4$** were unsuccessful due to the presence of traces of **5-BH$_4$**. However, complex **7-BH$_4$** was prepared independently by reaction of **7-OTf** with LiBH$_4$ in Et$_2$O. In a vial was dissolved **7-OTf** [100 mg, 0.16 mmol] in 10 mL of Et$_2$O and the solution cooled to −35 °C. To the cold solution was added a cold Et$_2$O suspension (~5 mL) of LiBH$_4$ [3.50 mg, 0.16 mmol]. After stirring for 40 min the solution was filtered, the filtrate concentrated, and the solution cooled to −35 °C to afford in two crops red crystals of **7-BH$_4$** [71.3 mg, 0.15 mmol, 91% yield].

For **5-BH$_4$**: ^{1}H NMR (23 °C, 399.8 MHz, C$_6$D$_6$): δ 7.07−6.85 (m, C$_6$*H*$_3$, 6H), 4.89 (s, Ti−H^{t}BuCCMeC*H*, 1H), 3.81 (septet, C*H*Me$_2$, 2H), 2.77 (s, Ti-*H*^{t}BuCCMeCH, 1H), 2.26 (septet, C*H*Me$_2$, 2H), 1.93 (s, C(*Me*)CHC(Me), 3H), 1.54 (s, C(Me)CHC(*Me*), 3H), 1.40 (d, CH*Me*$_2$, 6H), 1.26 (s, *Me$_3$*CHCC(Me)CHC(Me)N[Ar], 9H), 1.11 (d, CH*Me*$_2$, 6H), 1.06 (d, CH*Me*$_2$, 6H), 1.01 (d, CH*Me*$_2$, 6H). ^{13}C NMR (25 °C, 100.6 MHz, C$_6$D$_6$): δ 161.5 (Ti−H^{t}BuCCMeCH*C*Me), 158.6 (Ti−H^{t}BuC*C*MeCHCMe), 157.8, 145.6, 142.7, 139.7 (*C*$_6$H$_6$), 132.6 (^{t}BuH*C*C(Me)CHC(Me)N[Ar], J_{C-H} = 129 Hz), 127.1, 125.1, 123.6, 122.7 (C$_6$H$_6$), 101.7 (^{t}BuHCC(Me)*C*HC(Me)N[Ar]), 35.99 (Me$_3$*C*HCC(Me)CHC(Me)N[Ar]), 32.27 ((*Me$_3$*CHCC(Me)CHC(Me)N[Ar]), 29.47 (*C*HMe$_2$), 28.39 (*C*HMe$_2$), 24.94 (*C*H$_3$), 24.59 (*C*H$_3$), 24.45 (*C*H$_3$), 23.99 (*C*H$_3$), 23.81 (*C*H$_3$), 23.41 (*C*H$_3$). ^{11}B NMR (23 °C, 128.4 MHz, C$_6$D$_6$): δ −13.5 (br, *B*H$_4$). Anal. Calcd for C$_{34}$H$_{55}$N$_2$BTi: C, 74.18; H, 10.07; N, 5.09. Found: C, 74.16; H, 10.23; N, 5.01.

For **7-BH$_4$**: ^{1}H NMR (23 °C, 399.8 MHz, C$_6$D$_6$): δ 7.50−7.09 (m, C$_6$*H*$_3$, 6H), 5.66 (s, C(Me)C*H*C(Me), 1H), 2.67 (septet, C*H*Me$_2$, 2H), 2.52 (s, C*H*$_3$, 3H), 2.08 (s, C*H*$_3$, 3H), 1.18 (d, CH*Me*$_2$, 6H), 0.51 (s, C*H*$_3$, 3H), 0.48 (d, CH*Me*$_2$, 3H), −1.82 (br, B*H*$_4$, 4H). ^{13}C NMR (25 °C, 100.6 MHz, C$_6$D$_6$): δ 158.4 (*C*(Me)CH*C*(Me)), 142.8 (*C*$_6$H$_3$), 136.6 (*C*$_6$H$_3$), 132.4 (*C*$_6$H$_3$), 129.0 (*C*$_6$H$_3$), 127.9 (*C*$_6$H$_3$), 125.9 (*C*$_6$H$_3$), 105.1 (C(Me)*C*HC(Me), J_{C-H} = 162 Hz), 83.42 (*C*Me$_2$), 29.02 (*C*HMe$_2$), 27.86 (*C*H$_3$), 27.04 (*C*H$_3$), 24.31 (*C*H$_3$), 22.63 (*C*H$_3$), 21.90 (*C*H$_3$). ^{11}B NMR (25 °C, 128.4 MHz, C$_6$D$_6$): δ −12.3 (br quintet, *B*H$_4$, J_{B-H} = 80 Hz). IR (C$_6$H$_6$, CaF$_2$): 2967 (s), 2831 (s), 2445 (w), 2398 (m), 2324 (w, ν_{B-H}), 2210 (w, ν_{B-H}), 2103 (w), 1960 (m), 1830 (s), 1537 (s), 1476 (s), 1376 (s), 1361 (s), 1352 (s), 1116 (m). Anal. Calcd for C$_{29}$H$_{43}$N$_2$BTi: C, 72.81; H, 9.06; N, 5.86. Found: C, 71.79; H, 8.69; N, 5.62.

Thermolysis of (Nacnac)Ti=CH^{t}Bu(I), 3-I. Synthesis of (H^{t}BuC=C(Me)CHC(Me)N[Ar])Ti=NAr(I), 5-I. In a vial was dissolved **3-I** (248 mg, 0.374 mmol) in 10 mL of hexane. The solution was allowed to stir for 24 h, upon which a hexane-insoluble precipitate emerged. The solution was filtered and the precipitate collected. Recrystallization from toluene afforded dark red crystals of **5-I** [165 mg, 0.249 mmol, 67% yield]. ^{1}H NMR (23 °C, 399.8 MHz, C$_6$D$_6$): δ 7.10−6.83 (m, C$_6$*H*$_3$, 6H), 5.06 (s, C(Me)C*H*C(Me), 1H), 4.04 (septet, C*H*Me$_2$, 2H), 2.13 (septet, C*H*Me$_2$, 2H), 1.98 (s, C(Me)CHC(*Me*), 3H), 1.58 (s, Ti−C*H*^{t}BuCMeCH, 1H), 1.55 (s, C(*Me*)CHC(Me), 3H), 1.44 (d, CH*Me*$_2$, 6H), 1.25 (s, Ti−CH^t*Bu*CMeCH, 9H), 1.14 (d, CH*Me*$_2$, 6H), 1.03 (d, CH*Me*$_2$, 6H), 0.98 (d, CH*Me*$_2$, 6H). ^{13}C NMR (25 °C, 100.6 MHz, C$_6$D$_6$): δ 160.1 (C(Me)CH*C*(Me), 158.6 (*C*$_6$H$_3$), 157.3 (*C*(Me)CHC(Me), 145.8 (*C*$_6$H$_3$), 143.0 (*C*$_6$H$_3$), 139.1 (Ti-*C*H^{t}BuC(Me)CH, J_{C-H} = 126 Hz), 127.4 (*C*$_6$H$_3$), 125.3 (*C*$_6$H$_3$), 123.42 (*C*$_6$H$_3$), 123.2 (*C*$_6$H$_3$), 122.7 (*C*$_6$H$_3$), 101.0 (C(Me)*C*HC(Me), J_{C-H} = 162 Hz), 35.94 (Ti−CH*C*Me$_3$), 32.38 (Ti−CHC*Me*$_3$), 30.39 (*C*HMe$_2$), 28.46 (*C*HMe$_2$), 25.26 (*C*H$_3$), 24.88 (*C*H$_3$), 24.61 (*C*H$_3$), 23.88 (*C*H$_3$), 23.16 (*C*H$_3$), 22.14 (*C*H$_3$). Anal. Calcd for C$_{34}$H$_{51}$N$_2$ITi: C, 61.63; H, 7.76; N, 4.23. Found: C, 61.61; H, 7.47; N, 4.40.

Treatment of 3-OTf with CO$_2$. Synthesis of [(L$_1$)$_2$Ti$_2$(μ_2-O)$_2$(μ_2-OTf)][OTf] (9). In a reaction vessel was dissolved in 10 mL of Et$_2$O **3-OTf** [100 mg, 0.15 mmol] and the solution cooled to −78 °C. To the cold and degassed solution was syringed CO$_2$ gas [3.9 mL, 0.16 mmol]. After stirring for 20 min an orange precipitate formed and the solution was allowed to stir for an additional 20 min. The precipitate was collected via filtration, washed with cold Et$_2$O, and dried under reduced pressure. The orange powder was crystallized form dichloromethane−Et$_2$O at −35 °C to afford in two crops orange crystals of **9** [84 mg, 0.06 mmol, 82% yield]. Some assignments of ^{1}H and ^{13}C NMR resonances were determined by HMQC experiments.[18] ^{1}H NMR (23 °C, 399.8 MHz, CD$_2$Cl$_2$): δ 7.23−7.05 (m, C$_6$*H*$_3$, 12H), 4.79 (s, C(Me)C*H*C(O)=CH^{t}BuC(Me), 2H), 4.71 (s, C(Me)CHC(O)=C*H*^{t}BuC(Me), 2H), 2.52 (overlapping septets, C*H*Me$_2$, 8H), 2.05 (s, C(*Me*)CHC(O)=CH^{t}BuC(Me), 6H), 2.00 (s, C(Me)CHC(O)=CH^{t}BuC(*Me*), 6H), 1.19 (s, C(Me)CHC(O)=CH^t*Bu*C(Me), 18H), 1.17 (br, CH*Me*$_2$, 12H), 1.07 (br, CH*Me*$_2$, 12H), 0.97 (br, CH*Me*$_2$, 12H), 0.89 (br, CH*Me*$_2$, 12H). ^{13}C NMR (25 °C, 100.6 MHz, CD$_2$Cl$_2$): δ 178.83 (C(Me)CH*C*(O)=CH^{t}BuC(Me)), 145.42 (*C*$_6$H$_3$), 140.47 (*C*$_6$H$_3$), 140.43 (*C*$_6$H$_3$), 140.37 (*C*$_6$H$_3$), 127.93 (*C*$_6$H$_3$), 127.59 (*C*$_6$H$_3$), 125.05 (*C*$_6$H$_3$), 124.1 (*C*$_6$H$_3$), 119.4 (C(Me)CHC(O)=*C*H^{t}BuC(Me), based on HMQC, J_{C-H} = 157 Hz), 67.05 (C(Me)*C*HC(O)=CH^{t}BuC(Me), based on HMQC, J_{C-H} = 139 Hz), 32.69 (C(Me)CHC(O)=CH^t*C*Me$_3$C(Me)), 30.43 (C(Me)CHC(O)=CH^{t}C*Me*$_3$C(Me)), 28.46 (*C*HMe$_2$), 28.20 (*C*HMe$_2$), 27.39 (*C*H$_3$), 27.30 (*C*H$_3$), 25.36 (*C*H$_3$), 24.95 (*C*H$_3$), 24.77 (*C*H$_3$), 23.66 (*C*H$_3$). ^{19}F NMR (23 °C, 282.3 MHz, C$_6$D$_6$): δ −75.71 (s, OSO$_2$C*F*$_3$), −79.72 (s, OSO$_2$C*F*$_3$). Anal. Calcd for C$_{72}$H$_{102}$N$_4$O$_{10}$S$_2$F$_6$Ti$_2$: C, 59.33; H, 7.05; N, 3.84. Found: C, 59.26; H, 7.23; N, 3.94.

Treatment of [(Nacnac)Ti(μ_2-O)(μ_2-OTf)]$_2$ (8) with OC$_2$Ph$_2$. Synthesis of [(L$_1$)$_2$Ti$_2$(μ_2-O)$_2$(μ_2-OTf)][OTf] (10). To a vial was added **8** [50 mg, 0.040 mmol], and the solid was dissolved in 2 mL of ether. In a separate vial was added diphenylketene [9 mg, 0.046 mmol] and the oil dissolved in 2 mL of ether. Both solutions were cooled to −35 °C, and the diphenylketene solution was slowly added to the stirring solution of **8**. The mixture was allowed to stir for 2 h. After this time the solution changed to a dark red-brown and a precipitate formed. The solution was filtered through a frit and the precipitate washed with ether until washings were clear. The orange solid was dissolved in CH$_2$Cl$_2$, concentrated, and cooled to −35 °C to yield orange blocks of **10** [47 mg, 0.0284 mmol, 73% yield]. ^{1}H NMR (23 °C, 400 MHz, C$_6$D$_6$): δ 6.85−7.31 (br, aryl, 32 H), 4.78 (s, C(Me)C*H*C(Me), 2H), 2.26−2.53 (br, C*H*Me$_2$, 8H), 1.73 (s, C(*Me*)CHC(*Me*), 6H), 1.66 (s, C(*Me*)CHC(*Me*), 6H), 0.66−1.09 (br, CH*Me*$_2$, 48H). ^{13}C NMR (25 °C, 100.6 MHz, C$_6$D$_6$): δ 178.0, 144.4, 140.4, 140.1, 138.4, 129.6, 129.5, 128.6, 128.4, 128.2, 127.9, 127.2, 124.4, 63.0, 28.46, 28.30, 28.24, 27.5, 25.3, 24.7, 24.6, 23.1. ^{19}F NMR (23 °C, 282.3 MHz, C$_6$D$_6$): δ −75.6 (s, OSO$_2$C*F*$_3$), −79.7 (s, OSO$_2$C*F*$_3$). Anal. Calcd for C$_{88}$H$_{102}$N$_4$O$_{10}$S$_2$F$_6$Ti$_2$: C, 64.07; H, 6.23; N, 3.40. Found: C, 63.74; H, 6.29; N, 3.55.

Treatment of 3-OTf with SCNPh. Synthesis of (Nacnac)Ti(η^2-(*S,N*)-SC=CH^{t}BuNPh) (11). In a vial was dissolved in 10 mL of pentane **3-OTf** [100 mg, 0.15 mmol] and the solution cooled to −35 °C. To the solution was added a cold pentane solution (5 mL) of SCNPh [20 mg, 0.15 mmol]. After stirring for 2 h the solution was filtered, the filtrate concentrated, and the solution cooled overnight at −35 °C to afford in two crops dark blocks of **11** [105 mg, 0.13 mmol, 88% yield]. ^{1}H NMR (23 °C, 399.8 MHz, C$_6$D$_6$): δ 7.17−6.91 (m, aryl, 9H), 6.19 (d, aryl, 2H), 5.28 (PhNCC*H*^{t}BuS, 1H), 4.29 (s, C(Me)C*H*C(Me), 1H), 3.27 (br, C*H*Me$_2$, 2H), 2.95 (septet, C*H*Me$_2$, 2H), 1.63 (s, C(*Me*)CHC(*Me*), 6H), 1.48 (br, CH*Me*$_2$, 6H), 1.27 (d, CH*Me*$_2$, 6H), 1.07 (d, CH*Me*$_2$, 6H), 1.01 (d, CH*Me*$_2$, 6H), 0.96 (s, PhNCCHC*Me*$_3$S, 9H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 170.0 (*C*(Me)CH*C*(Me)), 149.1 (aryl), 146.3 (aryl), 145.6 (aryl), 142.3 (PhN*C*CH^{t}BuS), 142.12 (aryl), 129.2 (aryl), 128.2 (aryl), 126.9 (aryl), 125.2 (aryl), 124.6 (aryl), 124.0 (aryl), 112.9 (PhNC*C*H^{t}BuS, J_{C-H} = 152 Hz), 100.3 (C(Me)*C*HC(Me), J_{C-H} = 162 Hz), 31.69 (PhNCCH*C*Me$_3$S), 31.16 (PhNCCHC*Me*$_3$S), 29.83 (*C*HMe$_2$), 28.95 (*C*HMe$_2$), 25.25 (*C*H$_3$), 25.02 (*C*H$_3$), 24.78 (*C*H$_3$), 24.75 (*C*H$_3$), 24.02 (*C*H$_3$). ^{19}F NMR (23 °C, 282.3 MHz, C_6D_6): δ −77.52 (s, OSO$_2$C*F*$_3$). Anal. Calcd for $C_{42}H_{56}N_3O_3F_3S_2Ti$: C, 61.52; H, 6.88; N, 5.13. Found: C, 59.7; H, 6.88; N, 5.13.

Treatment of 3-OTf with NCCH$_2$Mes. Synthesis of (Nacnac)Ti=N[C=CH^{t}Bu(CH$_2$Mes)](OTf) (12). In a vial was dissolved **3-OTf** [100 mg, 0.15 mmol] in 10 mL of pentane and the solution cooled to −35 °C. To the solution was added a cold pentane solution (5 mL) of NCCH$_2$Mes [23.25 mg, 0.15 mmol]. After 5 min a red precipitate began to form and the reaction mixture was allowed to stir for an additional 30 min. The solid was collected by filtration and washed with cold pentane. Recrystallization from Et$_2$O at −35 °C afforded in two crops red crystals of **12** [92 mg, 0.11 mmol, 73% yield]. ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.06−7.19 (m, C$_6$*H*$_3$, 6H), 6.67 (s, C$_6$*H*$_2$, 2H), 4.96 (s, C(Me)C*H*C(Me), 1H), 3.41 (s, NCC*H*^{t}BuCH$_2$C$_6$H$_2$Me$_3$, 1H), 3.2−3.1 (overlapping septets, C*H*Me$_2$, 4H), 2.94 (s, NCCH^{t}BuC*H*$_2$C$_6$H$_2$Me$_3$, 2H), 2.04 (s, *p-Me*$_3$C$_6$H$_2$, 3H), 2.01 (s, *o-Me*$_3$C$_6$H$_2$, 6H),), 1.73 (d, CH*Me*$_2$, 6H), 1.57 (s, C(*Me*)CHC(*Me*), 6H), 1.39 (d, CH*Me*$_2$, 6H), 1.33 (d, CH*Me*$_2$, 6H), 0.93 (s, NCCHC*Me*$_3$, 9H), 0.91 (d, CH*Me*$_2$, 6H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 168.2 (*C*(Me)CH*C*(Me)), 158.1 (N*C*CH^{t}BuCH$_2$C$_6$H$_2$Me$_3$), 144.7 (aryl), 142.5 (aryl), 140.6 (aryl), 136.9 (aryl), 135.3 (aryl), 132.6 (aryl), 129.0 (aryl), 127.9 (aryl), 124.9 (aryl), 124.1 (aryl), 120.1 (NC*C*H^{t}BuCH$_2$C$_6$H$_2$Me$_3$, J_{C-H} = 151 Hz), 93.31 (C(Me)*C*HC(Me), J_{C-H} = 163 Hz), 37.79 (NCCH^{t}Bu*C*H$_2$C$_6$H$_2$Me$_3$, J_{C-H} = 130 Hz) 31.92 (NCCH*C*Me$_3$-BuCH$_2$C$_6$H$_2$Me$_3$), 30.97 (NCCHC*Me*$_3$CH$_2$C$_6$H$_2$Me$_3$), 29.57 (*C*HMe$_2$), 28.86 (*C*HMe$_2$), 26.13 (*C*H$_3$), 24.43 (*C*H$_3$), 24.26 (*C*H$_3$), 24.03 (*C*H$_3$), 23.96 (*C*H$_3$), 19.87 (*C*H$_3$). ^{19}F NMR (23 °C, 282.3 MHz, C_6D_6): δ −78.19 (s, OSO$_2$C*F*$_3$). Anal. Calcd for $C_{46}H_{64}N_3O_3F_3STi$: C, 65.46; H, 7.64; N, 4.98. Found: C, 65.43; H, 7.77; N, 5.04.

Treatment of 3-OTf with CN^{t}Bu. Synthesis of (Nacnac)Ti(η^2-(N,C)-^{t}BuN=C=CH^{t}Bu)(OTf) (13). In a vial was dissolved **3-OTf** [100 mg, 0.15 mmol] in 10 mL of pentane and the solution cooled to −35 °C. To the solution was added a cold pentane solution (5 mL) of ^{t}BuNC [12.75 mg, 0.15 mmol]. After stirring for 2 h the solution was filtered, the filtrate concentrated, and the solution cooled overnight at −35 °C to afford in two crops dark blocks of **13** [99 mg, 0.13 mmol, 88% yield]. ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 6.96−7.05 (m, C$_6$*H*$_3$, 6H), 5.82 (s, C(Me)C*H*C(Me), 1H), 5.81 (s, ^{t}BuC*H*CN^{t}Bu, 1H) 2.65 (septet, C*H*Me$_2$, 2H), 2.54 (septet, C*H*Me$_2$, 2H), 1.78 (s, C(*Me*)CHC(*Me*), 6H), 1.48 (s, ^{t}BuCHCN*^{t}Bu*, 9H), 1.38 (d, CH*Me*$_2$, 6H), 1.31 (d, CH*Me*$_2$, 6H), 1.16 (d, CH*Me*$_2$, 6H), 0.96 (d, CH*Me*$_2$, 6H), (0.83 *^{t}Bu*CHCN^{t}Bu, 9H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 170.0 (^{t}BuCH*C*N^{t}Bu), 168.2 (*C*(Me)CH*C*(Me)), 146.5 (*ipso-C*$_6$H$_3$), 142.1 (*o-C*$_6$H$_3$), 139.8 (*o-C*$_6$H$_3$), 127.7 (*p-C*$_6$H$_3$), 125.0 (*m-C*$_6$H$_3$), 124.8 (*m-C*$_6$H$_3$), 122.6 (^{t}BuNC*C*H^{t}Bu), 100.4 (C(Me)*C*HC(Me), 65.38 (Me$_3$*C*NCCH^{t}Bu), 34.99 (^{t}BuNCCH*C*Me$_3$), 32.25 (*Me*$_3$CNCCHCMe$_3$), 31.88 (*C*HMe$_2$), 28.59 (^{t}BuNCCH-C*Me*$_3$), 28.33 (*C*HMe$_2$), 25.64 (*C*H$_3$), 25.47 (*C*H$_3$), 25.16 (*C*H$_3$), 24.76 (*C*H$_3$), 24.38 (*C*H$_3$). ^{19}F NMR (23 °C, 282.3 MHz, C_6D_6): δ −77.80 (s, OSO$_2$C*F*$_3$). Anal. Calcd for $C_{40}H_{60}N_3O_3F_3STi$: C, 62.56; H, 7.88; N, 5.47. Found: C, 61.12; H, 7.97; N, 5.35.

Treatment of 3-OTf with N$_2$CPh$_2$. Synthesis of (Nacnac)Ti=NCHPh$_2$(NC^{t}Bu)(OTf) (14). In a vial was dissolved **3-OTf** [100 mg, 0.15 mmol] in 10 mL of Et$_2$O and the solution cooled to −35 °C. To the cold solution was added a similarly cold Et$_2$O solution (~5 mL) containing N$_2$CPh$_2$ [28.64 mg, 0.15 mmol]. After stirring for 1 h the solution was filtered and dried under reduced pressure. The orange powder was washed with cold pentane, extracted with Et$_2$O, and filtered. The filtrate was then concentrated and the solution cooled to −35 °C to afford in one crop orange crystals of **14** [97 mg, 0.11 mmol, 73% yield]. Some assignments of ^{1}H and ^{13}C NMR resonances were determined by HMQC experiments.[18] ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.4−6.8 (m, aryl, 16H), 6.23 (s, NC*H*Ph$_2$, 1H), 5.43 (s, C(Me)C*H*C(Me), 1H), 3.70 (septet, C*H*Me$_2$, 2H), 2.51 (septet, C*H*Me$_2$, 2H), 1.71 (s, C(*Me*)-CHC(*Me*), 6H), 1.24 (d, CH*Me*$_2$, 6H), 1.21 (d, CH*Me*$_2$, 6H), 1.09 (d, CH*Me*$_2$, 6H), 1.02 (d, CH*Me*$_2$, 6H), 0.788 (s, NC*^{t}Bu,* 9H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 167.1 (*C*(Me)CH*C*(Me)), 147.3 (aryl), 143.7 (aryl), 143.1 (aryl), 142.4 (aryl), 128.8 (aryl), 128.2 (aryl), 126.7 (aryl), 126.6 (aryl), 124.8 (aryl), 123.9 (aryl), 101.1 (C(Me)*C*HC(Me)), 85.46 (N*C*HPh$_2$) 29.00 (NCC*Me*$_3$), 28.01 (*C*H$_3$) 26.81 (*C*H$_3$), 25.81 (*C*H$_3$), 25.32 (*C*H$_3$), 24.88 (*C*H$_3$), 24.41 (*C*H$_3$), 24.31 (*C*H$_3$), 23.95 (*C*H$_3$). ^{19}F NMR (23 °C, 282.3 MHz, C_6D_6): δ −78.22 (s, OSO$_2$C*F*$_3$). Anal. Calcd for $C_{48}H_{61}N_4O_3SF_3Ti$: C, 65.58; H, 6.99; N, 6.38. Found: C, 65.28; H, 7.11; N, 6.29.

Treatment of 3-OTf with N$_3$(1-adamantyl). Synthesis of (Nacnac)Ti=NCH^{t}BuAd(OTf) (15). In a vial was dissolved in 10 mL of pentane **3-OTf** [100 mg, 0.15 mmol] and the solution cooled to −35 °C. To the solution was added a cold pentane solution (5 mL) of N$_3$Ad [28.5 mg, 0.16 mmol]. After stirring for 2 h the solution was filtered, the filtrate concentrated, and the solution cooled overnight at −35 °C to afford in three crops yellow crystals of **15** [100 mg, 0.12 mmol, 82% yield]. For **15**: ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.2−7.11 (m, C$_6$*H*$_3$, 6H), 4.92 (s, C(Me)C*H*C(Me), 1H), 3.34 (septet, C*H*Me$_2$, 1H), 3.23 (septet, C*H*Me$_2$, 1H), 3.12 (septet, C*H*Me$_2$, 1H), 2.92 (septet, C*H*Me$_2$, 1H), 2.71 (s, Ti=N−CH^{t}BuAd, 1H), 1.91 (s, Ad, 3H), 1.74−0.86 (Ad and CH$_3$ groups, 42H), 0.73 (s, CH$_2$C*Me*$_3$, 9H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 168.9 (*C*(Me)CHC(Me)), 167.7 (C(Me)CH*C*(Me)) 145.4 (*C*$_6$H$_3$), 145.2 (*C*$_6$H$_3$), 142.5 (*C*$_6$H$_3$), 142.4 (*C*$_6$H$_3$), 140.9 (*C*$_6$H$_3$), 140.7 (*C*$_6$H$_3$), 127.6 (*C*$_6$H$_3$), 127.5 (*C*$_6$H$_3$), 124.8 (*C*$_6$H$_3$), 124.7 (*C*$_6$H$_3$), 124.1 (*C*$_6$H$_3$), 123.9 (*C*$_6$H$_3$), 100.8 (C(Me)*C*HC(Me)), 93.49 (N*C*H^{t}BuAd), 41.47 (*Ad*), 41.35 (*Ad*), 38.46 (NCH*C*Me$_3$Ad), 37.25 (*Ad*), 30.35 (*Ad*), 30.15 (*C*HMe$_2$), 29.46 (28.95 (NCHC*Me*$_3$Ad), 28.91 (*C*HMe$_2$), 28.71 (*C*HMe$_2$), 25.85 (*C*H$_3$), 25.74 (*C*H$_3$), 24.95 (*C*H$_3$), 24.74 (*C*H$_3$), 24.62 (*C*H$_3$), 24.54 (*C*H$_3$), 24.51 (*C*H$_3$), 24.47 (*C*H$_3$), 24.18 (*C*H$_3$), 23.62. ^{19}F NMR (23 °C, 282.3 MHz, C_6D_6): δ −78.54 (s, OSO$_2$C*F*$_3$). Anal. Calcd for $C_{45}H_6N_3O_3F_3STi$: C, 63.38; H, 7.40; N, 5.41. Found: C, 64.80; H, 7.98; N, 5.03.

Treatment of 3-OTf with HNCPh$_2$. Synthesis of (Nacnac)Ti(CH$_2$^{t}Bu)(N=CPh$_2$)(OTf) (16). In a vial was dissolved in 10 mL of pentane **3-OTf** [50 mg, 0.07 mmol] and the solution cooled to −35 °C. To the solution was added a cold pentane solution (5 mL) of Ph$_2$CNH [14 mg, 0.08 mmol]. After stirring for 2 h the solution was filtered, the filtrate concentrated, and the solution cooled overnight at −35 °C to afford in two crops light green crystals of **16** [46 mg, 0.05 mmol, 73% yield]. ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.15−6.86 (m, aryl, 16H), 4.92 (s, C(Me)C*H*C(Me), 1H), 3.07 (septet, C*H*Me$_2$, 2H), 2.78 (septet, C*H*Me$_2$, 2H), 1.88 (s, C*H*$_2$^{t}Bu, 2H), 1.51 (s, C(*Me*)CHC(*Me*), 6H), 1.30 (d, CH*Me*$_2$, 6H), 1.25 (d, CH*Me*$_2$, 6H), 1.19 (d, CH*Me*$_2$, 6H), 0.80 (d, CH*Me*$_2$, 6H), 0.46 (s, CH$_2$C*Me*$_3$, 9H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 168.0 (*C*(Me)CH*C*(Me)), 146.9 (aryl), 145.1 (aryl), 142.6 (aryl), 140.7 (aryl), 128.64 (aryl), 127.6 (aryl), 127.5 (aryl), 126.1 (aryl), 124.8 (aryl), 124.1 (aryl), 93.57 (C(Me)*C*HC(Me), J_{C-H} = 162), 88.76 (N*C*Ph$_2$), 53.12 (*C*H$_2$^{t}Bu, J_{C-H} = 127), 31.81 (CH$_2$C*Me*$_3$), 31.14 (CH$_2$*C*Me$_3$), 29.83 (*C*HMe$_2$), 28.95 (*C*HMe$_2$), 25.24 (*C*H$_3$), 24.44 (*C*H$_3$), 24.38 (*C*H$_3$), 24.26 (*C*H$_3$), 23.89 (*C*H$_3$). ^{19}F NMR (23 °C, 282.3 MHz, C_6D_6): δ −78.23 (s, OSO$_2$C*F*$_3$). Anal. Calcd for $C_{48}H_{62}N_3O_3F_3STi$: C, 66.57; H, 7.22; N, 4.85. Found: C, 65.24; H, 7.91; N, 5.44.

Synthesis of (Nacnac$_{tBu}$)TiCl$_2$ (17). In a reaction vessel was suspended $TiCl_3$ [1 g, 6.5 mmol] in Et_2O (100 mL), and to the solution was added an Et_2O solution (20 mL) containing Li(Nacnac$_{tBu}$) [3.6 g, 7.1 mmol]. After stirring for 2 days the solution was filtered and concentrated, and the filtrate was again filtered and cooled to −35 °C to afford green crystals of **17** [930 mg, 1.5 mmol, 23% yield]. ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 8.53 ($\Delta\nu_{1/2}$ = 21 Hz), 5.06 ($\Delta\nu_{1/2}$ = 38 Hz), 1.99 ($\Delta\nu_{1/2}$ = 103 Hz). μ_{eff} = 1.89 m$_B$ (C_6D_6, 23 °C, Evans' method). Anal. Calcd for $C_{35}H_{53}N_2Cl_2Ti$: C, 67.73; H, 8.61; N, 4.51. Found: C, 66.19; H, 8.63; N, 4.40.

Synthesis of (Nacnac$_{tBu}$)Ti(CH$_2{}^t$Bu)$_2$ (18). In a reaction vessel was dissolved **17** [662 mg, 1.07 mmol] in 30 mL of Et_2O and the solution cooled to −35 °C. To the cold solution was added a cold Et_2O solution (10 mL) of LiCH$_2{}^t$Bu [175 mg, 2.24 mmol]. After stirring for 30 min the solution was filtered and dried under reduced pressure. The green powder was extracted with hexane and filtered, and the filtrate was concentrated and cooled to −35 °C to afford in two crops green crystals of **18** [526 mg, 0.76 mmol, 71% yield]. ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.26 ($\Delta\nu_{1/2}$ = 13 Hz), 7.11 ($\Delta\nu_{1/2}$ = 45 Hz), 5.57 ($\Delta\nu_{1/2}$ = 125 Hz), 2.98 ($\Delta\nu_{1/2}$ = 163 Hz), −0.06 ($\Delta\nu_{1/2}$ = 241 Hz). μ_{eff} = 1.96 m$_B$ (C_6D_6, 23 °C, Evans' method). Multiple attempts to obtain satisfactory elemental analysis failed due to the thermal instability of complex **18**.

Synthesis of (Nacnac$_{tBu}$)Ti=CH^{t}Bu(OTf), 19-OTf. In a vial was dissolved **18** [400 mg, 0.58 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) of AgOTf [147.69 mg, 0.57 mmol]. After stirring for 20 min the solution was filtered and the filtrate dried under reduced pressure. The brown powder was extracted with hexane and filtered, and the filtrate was concentrated and cooled to −35 °C to afford in two crops dark large blocks of **19-OTf** [370.2 mg, 0.48 mmol, 83% yield]. ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.08−7.01 (m, C_6H_3, 6H), 5.50 (s, C(^{t}Bu)C*H*C(^{t}Bu), 1H), 4.06 (s, Ti=C*H*^{t}Bu, 1H), 3.40 (septet, C*H*Me$_2$, 2H), 3.06 (septet, C*H*Me$_2$, 2H), 1.86 (d, CH*Me*$_2$, 6H), 1.46 (d, CH*Me*$_2$, 6H), 1.38 (d, CH*Me*$_2$, 6H), 1.26 (d, CH*Me*$_2$, 6H), 1.04 (s, C(^{t}*Bu*)CHC(^{t}*Bu*), 18H), 0.46 (Ti=CH^t*Bu*, 9H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 259.6 (Ti=*C*H^{t}Bu, J_{C-H} = 92 Hz), 175.9 (*C*(^{t}Bu)CH*C*(^{t}Bu)), 147.2, 143.3, 138.7, 127.0, 124.3, 123.9 (*C*$_6$H$_3$), 92.43 (C(^{t}Bu)*C*HC(^{t}Bu), J_{C-H} = 154 Hz), 50.43 (Ti=CH*C*Me$_3$), 44.52 (C(*C*Me$_3$)CHC(*C*Me$_3$)), 31.98, 31.61, 30.27, 29.78, 28.98, 26.97, 26.11, 24.35 (*C*H$_3$). ^{19}F NMR (23 °C, 282.3 MHz, C_6D_6): δ −77.05 (s, OSO$_2$C*F*$_3$). Anal. Calcd for $C_{41}H_{63}N_2O_3SF_3Ti$: C, 64.04; H, 8.25; N, 3.64. Found: C, 62.78; H, 7.94; N, 3.60.

Synthesis of (Nacnac$_{tBu}$)Ti=CH^{t}Bu(I), 19-I. In a vial was dissolved **18** [54 mg, 0.08 mmol] in 10 mL of toluene and the solution cooled to −35 °C. To the solution was added a cold toluene solution (~5 mL) of I_2 [9.9 mg, 0.04 mmol]. After stirring for 21 min the solution was filtered and dried under reduced pressure. The solid was extracted with pentane and filtered, and the filtrate was concentrated and cooled to −35 °C to afford dark large blocks of **19-I** [47 mg, 0.06 mmol, 75% yield]. ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.13−7.03 (m, C_6H_3, 6H), 5.56 (s, C(^{t}Bu)C*H*C(^{t}Bu), 1H), 3.97 (septet, C*H*Me$_2$, 2H), 3.24 (septet, C*H*Me$_2$, 2H), 2.33 (s, Ti=C*H*^{t}Bu, 1H), 1.80 (d, CH*Me*$_2$, 6H), 1.40 (d, CH*Me*$_2$, 6H), 1.35 (d, CH*Me*$_2$, 6H), 1.27 (d, CH*Me*$_2$, 6H), 1.10 (s, C(^{t}*Bu*)CHC(^{t}*Bu*), 18H), 0.11 (Ti=CH^t*Bu*, 9H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 259.6 (Ti=*C*H^{t}Bu, J_{C-H} = 92 Hz), 173.45 (*C*(^{t}Bu)CH*C*(^{t}Bu)), 148.5, 143.1, 139.2, 126.7, 124.7, 123.8 (*C*$_6$H$_3$), 92.33 (C(^{t}Bu)*C*HC(^{t}Bu), J_{C-H} = 152 Hz), 49.68 (Ti=CH*C*Me$_3$), 44.89 (C(*C*Me$_3$)CHC(*C*Me$_3$)), 32.05, 31.01, 29.95, 28.73, 28.65, 26.01, 24.67, 24.57 (*Me*). Anal. Calcd for $C_{40}H_{63}N_2ITi$: C, 60.82; H, 7.84; N, 3.45. Found: C, 60.90; H, 8.03; N, 3.46.

DFT Calculations for (Nacnac)Ti(CH$_2{}^t$Bu)$_2$ (2) and (Nacnac)Ti=CH^{t}Bu(OTf), 3-OTf. All calculations were performed with the Gaussian 98 package[55] at the B3PW91[56] level of theory. Basis sets used included LANL2DZ for Ti and Cl and 6-31G* for C and N, and all hydrogens.[57] The basis set LANL2DZ is the Los Alamos National Laboratory ECP plus a double-ζ valence on Ti and Cl;[58] additional d polarization functions were added to the Cl atom in all DFT calculations for model complex **3-OTf**.[59] All optimizations were performed with C_1 symmetry, and all minima were confirmed by analytical calculation of frequencies, which were also used to compute zero-point energy corrections without scaling. All initial geometries were adapted from the refined crystal structure of the analogous compounds **2** and **3-OTf**. For complex **2**, the neopentyls were replaced with methyls, and in complex **3-OTf** the triflate was replaced by a chloride atom. In both models the hydrocarbon chains were replaced by CH_3 or H where indicated. Isopropyl groups on the 2,6-aryl positions of the aryl rings attached to the β-diketiminate nitrogens were also replaced with methyls to give the model complexes ([2,6-Me$_2$C$_6$H$_3$]NC(H)CHC(H)N[2,6-Me$_2$C$_6$H$_3$])Ti(CH$_3$)$_2$ and ([2,6-Me$_2$C$_6$H$_3$]NC(H)CHC(H)N[2,6-Me$_2$C$_6$H$_3$])Ti=CHMe(Cl).

Kinetic Measurements. In a typical experiment, 10−30 mg of **3-I** was dissolved in 675 mg of a stock solution (3 μL of hexamethyldisiloxane, TMS$_2$O, as an internal standard in 675 mg of C_6D_6) and placed in an oven-dried NMR tube. The NMR tube is then placed into a temperature-equilibrated NMR probe (30−70 °C) and observed until ~90% conversion to the metathesis product **5-I** occurred. No side products were observed, as evidenced by ^{1}H NMR spectroscopy. The NMR probe temperature was calibrated using an ethylene glycol standard. The TMS$_2$O resonance was integrated to 1000, and the decay of the hydrogen resonance for the γ-carbon of the Nacnac$^-$ backbone (5.08 ppm) was monitored over time. The resulting data were fit to a first-order decay plot of the alkylidene species **3-I**. The rate constant is an average of 11 trials (8.06×10^{-4} s^{-1} ± 4.06×10^{-5} s^{-1}) performed at 57.0 °C. Activation parameters were performed in triplicate for each temperature run ($\Delta H^\ddagger$ = 21.3 ± 0.2 kcal/mol, $\Delta S^\ddagger$ = −8 ± 3 cal/mol K). Solvent dependence tests were determined by performing the above experiment with ~20 mg of compound in THF-d_8 and Et$_2$O-d_{10} at 31.3 °C, and at approximately the same concentration. Results for the calculated rates obtained from the THF-d_8 and Et$_2$O-d_{10} trials were within experimental error of the C_6D_6 trials.

Crystal Structure Determinations. Data Collection and Refinement. Inert atmosphere techniques were used to place the crystal onto the tip of a diameter glass capillary (0.03−0.20 mm) and mounted on a SMART6000 (Bruker) at 113−140 K. A preliminary set of cell constants was calculated from reflections obtained from three nearly orthogonal sets of 20−30 frames. Data collection was carried out using graphite-

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monochromated Mo Kα radiation with a frame time of 3 s with 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).[60] The structure was solved using SHELXS-97 and refined with SHELXL-97.[61] A direct-methods solution was calculated that 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, and all hydrogen atoms were refined with isotropic displacement parameters (unless otherwise specified, vide infra). We have avoided using the SQUEEZE algorithm in some structures containing poorly modeled and ambiguous solvent contributions in order to alter the original *hkl* data.[62] Most of the crystals examined are exceedingly reactive to O_2 and moisture and often suffer from degradation during the mounting process and in some cases during the data collection.

For **3-I**: Intensity statistics and systematic absences suggested the centrosymmetric space group $P2_1/c$, and subsequent solution and refinement confirmed this choice. A large peak (ca. 3 e/A^3) appeared in the difference map near C(34). Initially it was thought that this might be a disorder in the $-$CH^{t}Bu group, but it was finally recognized that there was a second form of the molecule superimposed in the lattice. Careful examination located two alternate iodine positions and the alternate titanium position. Hence, the structure consists of two molecules occupying the same site. The primary component is $C_{34}H_{51}IN_2Ti$ (95%) and the minor component is $C_{29}H_{41}I_2N_2Ti$ (5%). Several models were refined in which the minor component occupancies were varied with and without constraints. Model reported constrained occupancies of Ti1A, I33A, and I33B have the same occupancy, while Ti1, I33, and the $-$CH^{t}Bu group have 1 minus the occupancy of the minor component. When all hydrogens were allowed to vary, those on C36, C37, and C38 refined near reasonable positions but with C$-$H distances of up to 1.28 Å. The model reported fixed the hydrogen atoms on these three carbons during the refinement. The largest peak in a difference Fourier at this point was located adjacent to C34 and was assigned H80. The refinement converged satisfactorily with this model. It should be noted that the presence of the secondary form has distorted some of the hydrogen positions, so the positions, while qualitatively correct, are not highly accurate.

For **[2][B(C$_6$F$_5$)$_4$]**: Small orange crystals of this complex are exceedingly reactive to traces of moisture and oxygen and rapidly decompose at room temperature. For this reason, crystal data suffer from a combination of crystal decay (during crystal mounting) as well as weak diffraction of the single crystal.

For **3-Br**: Intensity statistics and systematic absences were consistent with the centrosymmetric space group $P2_1/n$. Subsequent solution and refinement confirmed this choice. All hydrogen atoms were located in subsequent Fourier maps and were refined as isotropic contributors. The final difference Fourier was featureless with the exception of one peak of 1.95 e/A^3 located in the vicinity of the Br atom. This may indicate that there is a minor (less than 10%) substitution of another ligand present in the lattice. The remaining electron density is located on bonds.

For **5-I**: Intensity statistics and systematic absences suggested the centrosymmetric space group $P\bar{1}$, and subsequent solution and refinement confirmed this choice. A slight disorder was present in two isopropyl groups, but was readily modeled. With the exception of those associated with the above-described disorder, all hydrogen atoms were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement. The disordered hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

For **7-BH$_4$**: Intensity statistics and systematic absences suggested the non-centrosymmetric space group $Cmc2_1$, and subsequent solution and refinement confirmed this choice. A disorder was located in one of the ^{i}Pr groups. All non-hydrogen atoms were refined with anisotropic displacement parameters. The molecule lies on a mirror plane, and all hydrogen atoms were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement.

For **9·3CH$_2$Cl$_2$**: Intensity statistics and systematic absences suggested the centrosymmetric space group $P2_1/n$, and subsequent solution and refinement confirmed this choice. The cation and anion are well defined, but there are three disordered dichloromethane solvent molecules in the cell. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The remaining electron density is located in the vicinity of three dichloromethane solvent molecules.

For **12·Et$_2$O**: Intensity statistics and lack of systematic absences suggested the centrosymmetric space group $P\bar{1}$, and subsequent solution and refinement confirmed this choice. A disordered solvent molecule (Et$_2$O) was located and refined as well. All hydrogen atoms with the exception of those associated with the solvent were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement. All solvent hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The remaining electron density is located primarily on bonds.

For **13·C$_5$H$_{12}$**: Intensity statistics and systematic absences suggested the centrosymmetric space group $P\bar{1}$, and subsequent solution and refinement utilized this choice. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Two crystallographically independent molecules were located in the asymmetric unit along with two pentane molecules. A "ghost image" corresponding to the two metal and two sulfur atoms was present in difference maps translated ca. one-third along *b*. In the final model the four atoms were included at 20% occupancy. It is assumed that the ghost was due to the twinning, but may be indicative of other problems in the analysis. There is little doubt as to the structure of the sample, but one should use caution in interpreting bond lengths. The remaining electron density is located on bonds.

For **14**: Intensity statistics and lack of systematic absences suggested the centrosymmetric space group $P2_1/c$, and subsequent solution and refinement confirmed this choice. A disorder was present in the O$_3$SCF$_3$ ligand. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were located and refined isotropically.

For **15·C$_5$H$_{12}$**: Intensity statistics and systematic absences suggested the noncentrosymmetric space group $P2_12_12_1$, and subsequent solution and refinement led to satisfactory results. It became apparent that a severe disorder was present in the adamantane as well as the ^{t}Bu group. The disorder was well

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(60) *SAINT 6.1*; Bruker Analytical X-Ray Systems: Madison, WI.

(61) *SHELXTL-Plus V5.10*; Bruker Analytical X-Ray Systems: Madison, WI.

(62) There is no consensus in the crystallographic community about the propriety of using SQUEEZE in the process of solving and refining structures intended for publication. It is our own opinion that refinements based on SQUEEZE data are rarely, if ever, appropriate for publication, as the SQUEEZE procedure utilizes parameters derived only from the experimental observations to produce a modified version of the same observations. At best, this transformation introduces no new information. In our view it is superior to provide an entirely explicit model of the electron density, even if that model cannot be interpreted exclusively in terms of discrete chemical moieties. We do not see any value to the scientific community in disguising our results so that they superficially appear more attractive.

resolved, however. In addition there is a disordered solvent (pentane), which was modeled with partial occupancy on the carbon atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The remaining electron density is located on bonds.

For **19-OTf·C_6H_{14}**: Intensity statistics and systematic absences suggested the centrosymmetric space group $P2_1/n$, and subsequent solution and refinement confirmed this choice. A disordered solvent (possibly hexane) was present, lying at a center of inversion in the cell. 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 remaining electron density is located on bonds.

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Supporting Information Available: Complete crystallographic data for compounds **[2][B(C_6F_5)$_4$]**, **2-F**, **3-I**, **3-Br**, **3-BH$_4$**, **4**, **5-I**, **5-BH$_4$**, **7-OTf**, **7-BH$_4$**, **9–15**, and **17–19** (CIF), and complete geometrical parameters for the optimized geometries of ([2,6-$Me_2C_6H_3$]NC(H)CHC(H)N[2,6-$Me_2C_6H_3$])-Ti(CH_3)$_2$ and ([2,6-$Me_2C_6H_3$]NC(H)CHC(H)N[2,6-$Me_2C_6H_3$])-Ti=CHMe(Cl) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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