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

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Received August 3, 2004

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(CH3)2Bu2 (Nacnac = [Ar]NC(CH2)CHC-(CH3)N[Ar], Ar = 2,6-(CHMe2)2C6H3), among them (Nacnac)Ti=CH′Bu(OTf) and (Nacnac)Ti=CH′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′Bu(OTf) serves as a template for other four-coordinate titanium neopentylidene complexes such as (Nacnac)Ti=CH′Bu(X) (X = Cl, Br, and BH4). Complexes (Nacnac)Ti=CH′Bu(X) undergo cross-metathesis reactivity with the imine functionality of the Nacnac ligand forming the imido complexes (H′Bu=C(Me)CH(Me)N[Ar])Ti=NAr-X (X = OTf, Cl, Br and BH4). In addition, C–H activation of two tertiary carbons also takes place to afford the titanacycles Ti[2,6-(CMeg2)CHMe2C6H3]NC(Me)CH(Me)N[2,6-(CMeg2)-(CHMe2)C6H3])X (X = OTf, Cl, Br and BH4). Kinetic studies in C6D6 reveal the formation of (H′Bu=C(Me)CH(Me)N[Ar])Ti=NAr(1) from (Nacnac)Ti=CH′Bu(I) to be independent of solvent (C6D6, Et2O, d10, THF-d8) and the reaction to be first order in titanium (k = 8.06 × 104 s−1 at 57 °C, with activation parameters AH° = 21.3(2) kcal/mol, AS° = −8(3) cal/mol K). Compound (Nacnac)Ti=CH′Bu(OTf) reacts with various substrates to afford products in which the alkylidene functionality has been significantly transformed. When the alkylidene derivatives (NacnacBu)Ti=CH′Bu(X) (X = OTf; I; NacnacBu = [Ar]NC-(Bu)CH(C)iBu[NAr]) were prepared, the intramolecular cross-metathesis transformation observed with (Nacnac)Ti=CH′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 reviews1 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-hydrogens.3,3 Promoting α-hydrogen abstraction to yield high-oxidation-state metal alkylidenes is typically induced thermally, photochemically, or with the aid of Lewis bases.3,3–5 Hence the entry into d6-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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10.1021/am049400b CCC: $30.25 © 2005 American Chemical Society
Publication on Web 03/17/2005
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 oxophilic character 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 electrophilic metal. Hence, complexes of this type are often represented as M=−CR=C− ≈ M=CR=C ≈ M=CR2 much like ylides would resonate.8 Prototypical among nucleophilic alkylidenes are those that can readily react with Lewis acids to make zwitterionic-like complexes.76 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.8 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 d8 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.13 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 Budzelaar15a and Theopold15f on redox-active and stable early-transition-metal d4 (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=CH2Bu 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)TiCl2 (Nacnac = [Ar]NC(Me)CHC(Me)N[Ar], Ar = 2,6-(CHMe2)2C6H3) complex reported previously by Budzelaar and co-workers.15a Following Budzelaar’s procedure we recrystallized the THF base adduct (Nacnac)TiCl2(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)TiCl2.


Complex 1 was characterized by a combination of $^1$H NMR spectroscopic methods, elemental analysis, and single-crystal X-ray diffraction. Ethereal solutions of 1 react rapidly with 2 equiv of LiCH$_2$tBu to afford emerald green solutions of (Nacnac)Ti(CH$_2$tBu)$_2$ (2), which was isolated as dark green blocks in 75% yield. Complex 2 was fully characterized, and the molecular structure indicates no α-agostic interactions or remarkable features different from that of the reported dimethyl derivative. 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 coupling 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 (the $z$-axis is along the Ti–C$_g$ of the NCC, CN–Nacnac$^-$ ring).

In fact, DFT calculations on the model complex (Nacnac)$^+$TiMe$_2$(Nacnac$^-$ = [Ar]NCHCHCN[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 $d_z^0$ 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$_5$)$_3$])$_2$ to form highly reactive zwitterion Ti(III) species. 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 ($E_{\text{red}} = -0.11$ V vs FeCp/$^+$/FeCp$^+$) 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 voltamogram of a solution of 2 (THF/TBAH, TBAH = n-tetrabutylammonium hexafluorophosphate) showed one irreversible oxidation wave at $-0.99$ V (referenced vs FeCp/$^+$/FeCp$^+$) for the Ti(III)/Ti(IV) couple, thus suggesting that [CPh$_3$]$^+$ could be oxidizing the Ti(III) center.

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(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). 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 $C_s$ resonance centered at $\delta = 271$–272 with a $J_{CH}$ coupling constant of $90$–$95$ Hz is diagnostic of both complexes having a terminal alkylidene functionality. The $J_{CH}$ coupling from the $^{13}$C NMR spectral data suggests significant $\alpha$-hydrogen agostic interaction with the electron-deficient metal center, especially for complex 3-I. In compounds 3-OTf and 3-I, the $^1$H NMR CH$_4$ resonance was located and differentiated unambiguously from the CH resonance for the Nacnac$^-$ backbone using HMQC NMR methods.

Complexes 3-OTf and 3-I are likely formed from the putative five-coordinate and $d^0$ intermediate (Nacnac)Ti(CH$_2$Bu)$_2$- (X)$^-$ (X = OTf, I), which then undergoes smooth $\alpha$-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 $\alpha$-hydrogen abstraction since oxidation of 2 with [FeCp]$^+$_2[B(C$_6$F$_5$)$_3$]$_2$ affords a relatively stable of the active product was hampered by its rapid decomposition. Suspecting that electrophiles such as [CPh$_3$]+$^+$ might be good oxidants ($E_{\text{red}} = -0.11$ V vs FeCp/$^+$/FeCp$^+$) 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 voltamogram of a solution of 2 (THF/TBAH, TBAH = n-tetrabutylammonium hexafluorophosphate) showed one irreversible oxidation wave at $-0.99$ V (referenced vs FeCp/$^+$/FeCp$^+$) for the Ti(III)/Ti(IV) couple, thus suggesting that [CPh$_3$]$^+$ could be oxidizing the Ti(III) center.

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bis-alkyl cation, [(Nacnac)Ti(CH3)2Bu2][B(C6F5)4] (2), which gradually decomposes in solution at room temperature (Scheme 2). Lewis bases such as THF or PMes appear to rapidly catalyze the decomposition of (2)[B(C6F5)4]. 1H and 13C NMR spectra (CD2Cl2, 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(C6F5)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. The average Ti–C bond distance for (2)[B(C6F5)4] (∼2.03 Å) compares well with the M–C bond length of electron-deficient titanium zwitterions (2.081(5) Å). In the molecular structure for (2)[B(C6F5)4], the Ti(III) precursor, and we are currently examining this possibility.

The anion present in the oxidant must be sterically encumbering since oxidation of 2 with AgBF4 leads only to oxidation and formation of (Nacnac)Ti(CH3)2Bu2(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(CH3)215a with AgOTf does not lead to formation of the parent methyldiene but instead affords the five-coordinate Ti(IV) dimethyl triflato complex (Nacnac)Ti(CH2)(OTf) (4) in moderate yield (Scheme 2). Thermalysis 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.

The derivatives (Nacnac)Ti=CHBFu(X) (X = Cl, 3-Cl, Br, 3-Br, BH4, 3-BH4) can be readily prepared by the corresponding salt metathesis with 3-OTf as depicted in Scheme 3. Although the preparation of 3-CI and 3-BH4 is straightforward and involves simple anion exchange using MgCl2 and LiBH4, the synthesis of 3-Br was somewhat less obvious. Greater yields of 3-Br were obtained when the LiBr-ylide adduct Ph3P=CH2LiBr was used in place of MgBr2. The ylide salt adduct in moderated yield (vide infra). Table 1 lists all the relevant spectroscopic features for 3-OTf, 3-I, 3-Cl, 3-Br, and 3-BH4. Judging from the 1H and 13C NMR spectra, as well as JCH coupling constants of the α-alkylidene C–H group, it is evident that electrophilicity of the metal center increases in the order 3-BH4 < 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-BH4) thus the metal participates...
Scheme 3. Synthesis of Terminal Titanium Alkylidene Complexes (Nacnac)Ti=CH²Bu(X) (X = Cl, Br, BH₄) by Salt Metathesis

![Scheme 3](image)

Table 1. Spectroscopic Data for the Alkylidene Complexes 3-X (X = I, Br, OTf, Cl, BH₄)

<table>
<thead>
<tr>
<th>3-I</th>
<th>3-Br</th>
<th>3-OTf</th>
<th>3-Cl</th>
<th>3-BH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>J(C-H) (Hz)</td>
<td>85</td>
<td>88</td>
<td>90</td>
<td>93</td>
</tr>
</tbody>
</table>

more in α-agostic interaction with the alkylidene hydrogen. In the case of 3-BH₄, the hapticity of the BH₄⁻ ligand remains uncertain. Although the borohydride resonance was not located in the ¹H NMR, the ¹¹B NMR spectrum displayed a quintet with \( J_{B-H} = 89 \) Hz, consistent with a fluxional BH₄⁻ ligand.

Structural Comparisons of (Nacnac)-Ti=CH²Bu(X) (X = OTf, Br, I, and BH₄). The molecular structures for complexes 3-X (X = OTf, Br, I, and BH₄) 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=CH 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 \( \sigma \)-plane bisecting the \( N-Ti-N \) angle and is oriented syn with respect to the X⁻ ligand. The Ti=CH₂H₂ hydrogen was located in the Fourier electron map for all 3-X (excluding 3-I and 3-BH₄) systems and was refined isotropically (Ti-H distances are reported in Table 2). Even though there is a systematic error in detection of hydrogens by X-ray diffraction, 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 ¹H 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 spectroscopically) is also substantiated by the large Ti(1)=C(33)–C(34) angle of 160–164°. The structure of 3-BH₄ is nearly identical to that of the halide and pseudohalide derivatives. Although the BH₄⁻ protons were not observed by ¹H NMR spectroscopy,²⁹ location and refinement of the hydrogens in the X-ray structure suggest this ligand to be \( \eta^3 \).³⁰ We are however doubtful of how accurate the hapticity of the BH₄⁻ ligand really is in 3-BH₄. Solution IR and ¹¹B NMR spectroscopy are also consistent with a tetrahedraborate ligand being present.

Figure 3. Molecular structures of 3-X (X = OTf, I, Br, BH₄) 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.

Thermal Transformation of the Titanium Neo-pentylidene Complexes 3-X. Although stable as solid complexes, 3-X (X = OTf, Cl, Br, I, and BH₄) are all kinetic products since these systems transform gradually in solution in the order 3-OTf < 3-Cl < 3-Br < 3-I < 3-BH₄, as evidenced by ¹H and ¹³C 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, \( (H^3BuC=C(Me)CHC(Me)N[Ar])/Ti=NaAr(X) \). 5-X

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


(29) We have not been able to locate the hydride resonance in the ¹H NMR spectrum, presumably due to broadening of the signal by coupling of the hydride to the ¹³B (I = 3/2, 80%) quadrupolar nuclei.


resonances similar to those of group 4 alkene adducts

\[
R^* \rightarrow \text{alkene}_3 \rightarrow \text{alkene}_2 \rightarrow \text{alkene}_1 \rightarrow \text{alkene}_0
\]

The decomposition rapidly in solution at room temperature or

\[\text{alkene}_0 \rightarrow \text{alkene}_1 \rightarrow \text{alkene}_2 \rightarrow \text{alkene}_3 \rightarrow \text{alkene}_4\]

which was detected in the 1H NMR spectrum (1.5 Hz).

\[\text{alkene}_0 \rightarrow \text{alkene}_1 \rightarrow \text{alkene}_2 \rightarrow \text{alkene}_3 \rightarrow \text{alkene}_4\]

interaction is also present in isolated samples of

\[\text{alkene}_0 \rightarrow \text{alkene}_1 \rightarrow \text{alkene}_2 \rightarrow \text{alkene}_3 \rightarrow \text{alkene}_4\]

parisons with isolated samples of

\[\text{alkene}_0 \rightarrow \text{alkene}_1 \rightarrow \text{alkene}_2 \rightarrow \text{alkene}_3 \rightarrow \text{alkene}_4\]

constants of the terminal olefin group (126 Hz). This feature is

\[\text{alkene}_0 \rightarrow \text{alkene}_1 \rightarrow \text{alkene}_2 \rightarrow \text{alkene}_3 \rightarrow \text{alkene}_4\]

reported by Jordan and co-workers. Similar α-hydrogen agostic interactions have been reported for 1-aza-1,3-diene ligands bound to titanium. 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 sp² 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). Complexes 5-X are formed likely by a cross-metathesis

\[\text{alkene}_0 \rightarrow \text{alkene}_1 \rightarrow \text{alkene}_2 \rightarrow \text{alkene}_3 \rightarrow \text{alkene}_4\]


(32) The low coupling value could also suggest considerable amount of rehybridization of the terminal carbon atom toward sp² 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; Stoebe, E. J., III; Jordan, R. F. J. Am. Chem. Soc. 2003, 125, 3222–3233.
reaction (or alternatively called Wittig-like) between the titanium neopentylidyne 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=NH imido bond.

The chelate ligand appears to behave "diene-like" in 5-X since the addition of a weak Lewis base such as Et2O to 5-OTf affords crystals of the adduct \((\eta^1\text{H}^+\text{BuC}=\text{C(\text{Me})CH(\text{Me})N=\text{Ar}})\text{Ti}=\text{NAr(OTf)}(\text{Et}2\text{O})\) (6-OTf) in 80% yield (Scheme 4).14 In complex 6-OTf the olefinic pendant 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. 

\(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra in CsD6 were relatively unchanged for the Lewis base adduct 6-OTf when compared to the Lewis base-free precursor 5-OTf, thus suggesting that the coordinated Et2O 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=\(\text{C}^{\text{olefin}}\) ≥ 4.30 Å).14

Table 4. Crystallographic Data for Complexes 5-I, 5-BH3, 7-OTf, 7-BH4, 9-3CH2Cl2, and 11

<table>
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<th>Empirical formula</th>
<th>C(<em>{66})H(</em>{65})N(_2)Ti</th>
<th>C(<em>{66})H(</em>{63})BH(_3)Ti</th>
<th>C(<em>{66})H(</em>{63})F(_2)N(_2)O(_2)STi</th>
<th>C(<em>{66})H(</em>{63})Ti</th>
<th>C(<em>{66})H(</em>{63})F(_2)N(_2)O(_2)S(_2)Ti</th>
<th>C(<em>{66})H(</em>{63})F(_2)N(_2)O(_2)S(_2)Ti</th>
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<td>612.59</td>
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<td>819.92</td>
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<td>orthohombic</td>
</tr>
<tr>
<td>Space group</td>
<td>P1</td>
<td>P1</td>
<td>P2(1)/n</td>
<td>P2(1)/n</td>
<td>P1</td>
<td>P1</td>
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<tr>
<td>a (Å)</td>
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<td>9.0020(3)</td>
<td>9.2570(5)</td>
<td>19.2689</td>
<td>14.3077</td>
<td>10.6624</td>
</tr>
<tr>
<td>b (Å)</td>
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<td>11.0365(4)</td>
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<td>612.59</td>
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(Figure 4). The molecular structures of 5-X (X = OTf, I, and \(\eta^3\)-BH\(_3\)) 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 \(\alpha\)-hydrogen was located in the Fourier electron map and was refined isotropically (Ti–\(\text{H}_\alpha\), 2.05–2.09 Å). Such an \(\alpha\)-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\(_3\) the titanium binds to the \(\alpha\)- and \(\beta\)-carbons. For instance, in the molecular structure of 5-I the Lewis acidic metal center in turn compensates by engaging strongly with the \(\text{BuHC} = \text{C(\text{Me})CH(\text{Me})N=\text{Ar}})\) (Figure 4). The \(\text{BuHC} = \text{C(\text{Me})CH(\text{Me})N=\text{Ar}})\) 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 \(\alpha\)-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=\(\text{N}_\text{imid} \) average distance in 5-X is ~1.72 Å). The molecular structures of complex 5-X (X = OTf, I, and \(\eta^3\)-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\(_3\)). Attempts to perform kinetic studies (60–70 °C) on the cross-metathesis reaction leading to formation of 5-X were...
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 sub-

Table 5. Crystallographic Data for Complexes 12-Et2O, 13-C5H12, 14, and 15-C5H12

| Complex | empirical formula | fw | crystal syst | space group | a (Å) | b (Å) | c (Å) | α (deg) | β (deg) | γ (deg) | V (Å³) | Dcalc (g·cm⁻³) | T (K) | crystal size (mm) | σcP | total no. of reflns collected | no. of unique reflns F > 4σ(F) | no. of obsd reflns | Rint | Rwp | GoF | peak/hole (eÅ⁻³) |
|---------|------------------|----|-------------|-------------|-------|-------|-------|--------|--------|--------|-------|----------------|-----|-----------------|-----|------------------|------------------------|----------------|-------|-------|-----|------|---------|
| 12-Et2O | C₅H₆F₂P₃N₉O₫Sti | 918.08 | triclinic | P1 | 12.152(5) | 12.208(5) | 18.140(2) | 77.585(3) | 75.257(3) | 81.809(3) | 2530.8(5) | 1.205 | 136(2) | 0.30 × 0.30 × 0.12 | 51.322 | 14 802 | 27 772 | 10 951 | 0.1200 | 0.925 | 0.778, -0.788 |
| 13-C5H12 | C₅H₆F₂P₃N₉O₫Sti | 540.02 | monoclinic | P21/c | 12.125(5) | 16.400(3) | 18.475(3) | 77.650(3) | 87.000(4) | 89.976(4) | 4752(5) | 1.174 | 137(2) | 0.30 × 0.30 × 0.09 | 50.722 | 14 802 | 27 772 | 10 951 | 0.1200 | 0.925 | 0.778, -0.788 |
| 14 | C₅H₆F₂P₃N₉O₫Sti | 878.97 | orthorhombic | P21/c | 12.125(5) | 16.400(3) | 18.475(3) | 77.650(3) | 87.000(4) | 89.976(4) | 4752(5) | 1.174 | 137(2) | 0.30 × 0.30 × 0.09 | 50.722 | 14 802 | 27 772 | 10 951 | 0.1200 | 0.925 | 0.778, -0.788 |
| 15-C5H12 | C₅H₆F₂P₃N₉O₫Sti | 906.11 | orthorhombic | P21/c | 12.125(5) | 16.400(3) | 18.475(3) | 77.650(3) | 87.000(4) | 89.976(4) | 4752(5) | 1.174 | 137(2) | 0.30 × 0.30 × 0.09 | 50.722 | 14 802 | 27 772 | 10 951 | 0.1200 | 0.925 | 0.778, -0.788 |

Scheme 4. Thermal Transformation of the Titanium Alkylidene (Nacnac)Ti(=CH₂Bu(X)) (X = OTf, Cl, Br, BH₄)

"Three-dimensional perspective structures of..."
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-BH₄ from thermolysis of their corresponding alkylidene precursors, but formation of these complexes is based only on ¹H NMR spectroscopic comparisons with isolated samples of 7-OTf. Attempts to isolate these derivatives were hampered by a combination of low yield and lypophlicity. 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 infra). Independent studies have shown that 7-BH₄ can be prepared readily in 91% yield from 7-OTf and LiBH₄ in Et₂O. ¹H, ¹³C, and ¹¹B NMR spectroscopy, along with single-crystal X-ray diffraction studies (Figure 5, vide infra), confirmed the proposed connectivity (see Experimental Section). The BH₄ hydrogen atoms were located and refined isotropically in the crystal structure for complex 7-BH₄ and suggest the ligand to be η². 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-BH₄ were grown from a saturated Et₂O solution cooled to −35 °C, and the molecular structures are depicted in Figure 5. Complexes 7-OTf and 7-BH₄ display a five-coordinate titanium(IV) in a distorted square pyramidal environ-ment with the pseudohalide ligand occupying the axial site. The constrained geometry of 7-OTf and 7-BH₄ is likely a consequence of the ligand being macrocyclic, and dihedral angles (Nacnac−C−C−C₉, range is 7.3(2)° to −3.3(2)°) reflect the strain generated upon ring closure. Similarly, the average acute angles Ti−C₉−C₅ of 86° also echo some strain in the metalacycle. The Ti atom sits ~−0.82 Å from the mean plane bisecting the two Nacnac and C₉ atoms, and the structures of both 7-OTf and 7-BH₄ also reveal close arene interactions between Ti and the ortho and meta carbons of the aryl groups (average Ti−Carene distance is ~2.58 Å). The molecular structures for complexes 7-OTf and 7-BH₄ are displayed in Figure 5.

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. 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. 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)-

Figure 5. Molecular structure of 7-OTf and 7-BH₄ with thermal ellipsoids at the 50% probability level. All H atoms with the exception of the η²-BH₄ have been omitted for clarity. Crystallographic data are reported in Table 4, and complete metrical parameters are listed in the Supporting Information.


platinum(II) complex. In contrast our work establishes a C–H abstraction reaction by which two methine groups are selectively cleaved under relatively mild conditions. 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.

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), (HtBuC=CHtBu(I)-Ti=NR(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 independent side reaction from occurring. Concentration-dependent experiments (by 1H 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 $k_{1/2} = 8.1(4) \times 10^{-4}$ 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
independent of solvents such as C₆H₆, THF, and Et₂O (Figure 6D). Therefore, the mechanism leading to the cross-metathesis reaction observed in 3-X (X = OTf, Cl, Br, I, and BH₄) 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) 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.

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.

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.

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 H₂BuC=CH₂ and 0.5 equiv of the edge-sharing biotahedra titanium oxo dimer [(Nacnac)Ti(μ₂-O)(μ₂-OTf)]₂ (8)42,43 (Scheme 6). The reactivity observed between 3-OTf and benzophenone follows well-established “Wittig-type” reagents studied in organic synthesis. 7 Likewise, CO₂ also reacts with benzophenone to yield the μ-oxo titanium dimer [(L₁)₂Ti₂(μ₂-O)(μ₂-OTf)][OTf] (9) (L₁ = [Ar]NCHCHCHN-[Ar]) (Scheme 6). Complex 9 results from a cross-metathesis reaction, leading to formation of putative 8 and the ketene BuHC=CH₂ (Scheme 6). Nucleophilic attack of the ketene generated in the reaction by the γ-carbon of the Nacnac⁻ ring yields complex 9. The ¹³C 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 derivative to yield a system analogous to 9, namely, [(L₂)₂Ti₂(μ₂-O)]₂(μ₂-OTf)][OTf] (10) (L₂ = [Ar]NCHCHCHN-[Ar]) (Scheme 6). NMR (¹H and ¹³C) 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-diketimines has been described previously by us and others. 32a,45 Complexes 9 and 10 have been scrutinized by single-crystal X-ray diffraction


(43) The molecular structure of 8 showed an edge-sharing biotahedra geometry composed of two bridging oxo and triflate ligands. See ref 14.

Figure 8. Molecular structure of complex [9]+ with thermal ellipsoids at the 50% probability level. All H atoms, O and CF₃ groups of the μ₂-OTf⁻, and aryl groups with the exception of ipso-carbons have been omitted for clarity. Three disordered CH₂Cl₂ 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(η²-(S,N)-SC=CHFBuNPh) (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 C–S linkage (Scheme 7). Complex 11 is likely favored thermodynamically due to formation of a strong Ti–N bond. ¹H and ¹³C NMR spectra of 11 are in accord with this molecule retaining C₁ symmetry in solution. Single-crystal X-ray diffraction studies of 11 also support η²-(S,N) coordination of the ligand (Scheme 7).

The nitrile NCCH₂Mes (Mes = 2,4,6-Me₃C₆H₂) undergoes a cross-metathesis with alkylidene 3-OTf to afford the four-coordinate titanium imido (Nacnac)-Ti=N[C=CHFBu(CH₂Mes)](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.¹⁵ On the other hand the isonitrile CNBu inserts into the Ti=C bond of 3-OTf to afford the azaaallenene or N-alkylketimine complex (Nacnac/Ti(η²-(N,C)-BuN)=C=CHBu)(OTf) (13) in 88% yield as black crystals (Scheme 7). ¹H and ¹³C NMR spectra are in accord with the molecule having C₂ symmetry. The η²-(N,C) coordination of the N-tert-butylketimine 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 N₂CPh₂ to provide a titanium imide with a coordinated nitrile. Complex (Nacnac)-

Ti=NCHPh₂(NCtBu)(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 N₂CPh₂ across the Ti=C bond. Under dynamic vacuum, complex 14 readily loses CNBu to yield the four-coordinate titanium imide complex (Nacnac/Ti=NCHPh₂(OTf)) (Scheme 7). It is proposed that complex 15 results from nucelophilic attack of azide to the metal center, which leads to extrusion of N₂ 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 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 diphenylketimide alkyl complex (Nacnac/Ti/CH₂Bu)(N=CPh₂) (16) in 73% yield (Scheme 7). Diagnostic features for 16 include a ¹H NMR methylene resonance for the neopentyl ligand at 1.88 ppm. In addition, the former sp² alkylidene ¹³C 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 Brønsted acids has resulted in a mixture of products.

Inhibiting an Intramolecular Cross-Metathesis Reaction. Synthesis of the Four-Coordinate Titanium Alkylidene Complexes (NacnacBu)₂Ti=CHBu(X) (X = OTf, I; NacnacBu = [Ar]NC(=Bu)CHC(Bu)N[Ar], Ar = 2,6-(CHMe₂)₂C₆H₃). 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 azametalacyclobutene complex resulting from intramolecular [2+2] cycloaddition. Substituting Bu groups in the β-position of the Nacnac ligand has been shown to be effective at stabilizing low coordination numbers on metal centers.¹⁵,²⁷,³⁸,⁴⁷ Unfortunately attempts to incorporate the β-diketiminate ligand Li[NacnacBu] (NacnacBu = [Ar]NC(=Bu)CHC(Bu)N[Ar]) onto TiCl₃(THF)$_₃$ proved difficult and led instead to undesirable products.⁵³,⁴⁸ However, we found that room-temperature reaction of TiCl₃ and Li[NacnacBu] in Et₂O for 2 days led to isolation of (NacnacBu₂)[TiCl₂] (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 NCCN plane of the NacnacBu⁻ ligand, which is in contrast to the planar dichloro systems reported by Theopold’s ([Ph]NC(=Me)-

(45) Radziewicz, C. E.; Coles, M. P.; Jordan, R. F. J. Am. Chem. Soc. 1998, 120, 9384–9385. Electrophilic substitution with Ph₃P⁺ or PhCl⁺ at the γ-carbon of the Nacnac backbone has been recently reported.


CHC(Me)N[Ph]TiCl2\textsuperscript{15f} and Budzelaar’s ([Mes]NC(R)-CHC(N[Mes])TiCl2 (Mes = 2,4,6-Me\textsubscript{3}C\textsubscript{6}H\textsubscript{2}; R = Me or \textsuperscript{1}Bu).\textsuperscript{15a,49} Complex 17 is closely related, structurally, to d\textsuperscript{0} scandium derivative (Nacnac\textsubscript{Bu})ScCl\textsubscript{2} prepared by Piers and co-workers in which the Sc atom sits 0.815 Å out of the NCCCN plane.\textsuperscript{38} Unlike compound 1, THF appears to catalyze the decomposition of 17.

Transmetalation of 17 with 2 equiv of LiCH\textsubscript{2}Bu leads to rapid formation of the bis-neopentyl complex (Nacnac\textsubscript{Bu})Ti(CH\textsubscript{2}Bu)\textsubscript{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 \textsuperscript{1}Bu group on the \textbeta-carbon position. This feature is reflected by the more acute Ti–N–Cipso angle in the.
Scheme 8. Synthesis and Thermolysis of the Titanium Alkylidene (Nacnac)Ti=CH^Bu(X) (X = OTf, 19-OTf; I, 19-I)\(^\circ\)

\(^\circ\) Complete structural parameters for 17, 18, 19-OTf, and 19-I are included in the Supporting Information.

The titanium neopentylidene species (Nacnac)Ti=CH^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^Bu^-) 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 3° carbons, as well as the reactivity of titanium alkylidene complexes having the Nacnac^Bu^- 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.\(^\circ\) 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.\(^\circ\) Diethyl ether and CH\(_2\)Cl\(_2\) were dried by passage through two columns of activated alumina.\(^\circ\) THF was distilled, under nitrogen, from white sodium benzophenone ketyl and stored over sodium metal. Distilled THF was transferred under vacuum into bombs before being pumped into a drybox. C\(_6\)D\(_6\) and C\(_6\)H\(_6\)Cl\(_2\) were purchased from Cambridge Isotope Laboratory (CIL), degassed, and dried over 4 Å molecular sieves and CaH\(_2\), respectively. C\(_6\)H\(_6\)Cl\(_2\) was vacuum transferred from the CaF\(_2\) mixture and stored in a reaction vessel under \(\text{N}_2\); Et\(_2\)O-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)\(^{22}\) (Nacnac = [Ar]NC(Me)CHC(Me)N[Ar], Ar = 2,6-(CHMe\(_2\))\(_2\)C\(_6\)H\(_3\)), Li(Nacnac)Cl(THF) (I),\(^\circ\) Li(Nacnac)THF, Li(CH\(_2\)Bu)\(_3\), Li(CH\(_2\)LiBr,\(^\circ\) Li[Nacnac^Bu^-] (Nacnac^Bu^- = [Ar]NC(Me)CHC(Me)N[Ar], Ar = 2,6-(CHMe\(_2\))\(_2\)C\(_6\)H\(_3\)), Li(Nacnac^Bu^-)Cl, N\(_2\)CPh\(_2\), (Nacnac)Ti(CH\(_2\)n-Bu)\(_2\), (Nacnac)Ti=CH\(_2\)OTf(3-OTf),\(^\circ\) (HFBu=C(Me)CHC(Me)N[Ar])^-.

\(^{50}\) 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., Darenbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, D.C., 1987; pp 79–98.


$^{13}$C, and $^{19}$F NMR spectra were recorded on Varian 400 or 300 MHz NMR spectrometers. $^1$H and $^{13}$C NMR were referenced with respect to residual solvents (residual CD$_2$C$_2$H in CD$_2$C$_2$D$_2$, 7.16 and 128.0 ppm; CHDCl$_2$ in CD$_2$Cl$_2$, 5.32 ppm and 53.8 ppm; etc.) in THF in THF-$d_8$, 3.58, 17.3, and 67.4, 25.3; or proton toluene in CD$_2$C$_2$D$_2$, 7.09, 6.0, 2.09, and 137.5, 128.9, 128.0, 125.2, 20.4; or proton Et$_2$O in Et$_2$O-$d_{18}$, 3.34, 1.07 and 65.3, and 14.5. $^{19}$F NMR chemical shifts are measured with respect to external HOCCOF$_2$ (−78.5 ppm). $^{13}$C NMR spectra were reported with respect to external BF$_3$(OEt)$_2$ (0.0 ppm). Magnetic moments were obtained by the method of Evans. $^{14}$ Cyclic voltammetry was collected with the assistance of an EG & G Princeton Applied Research (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$^-$ TiFBU(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 $-35^\circ$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 $-35^\circ$C afforded black needles of 3-Cl [101 mg, 0.176 mmol, 67% yield]. $^1$H NMR (23 °C, 399.8 MHz, CD$_2$D$_2$): δ 7.2−7.1 (m, C$_6$H$_5$, 6H), 5.54 (s, Ti=CFBu, 1H), 4.82 (s, (CMe)CHC(Me), 1H), 3.76 (septet, CHMe$_2$, 2H), 3.20 (septet, CHMe$_2$, 2H), 1.71 (d, CHMe$_2$, 6H), 1.52 (s, (CMe)CHC(Me), 6H), 1.45 (d, CHMe$_2$, 6H), 1.19 (d, CHMe$_2$, 6H), 1.18 (d, CHMe$_2$, 6H), 0.71 (s, Ti=CFBu, 9H). $^{13}$C NMR (25 °C, 100.6 MHz, CD$_2$D$_2$): δ 276.0 (Ti=CFBu, J$_{CF-CF}$ = 92.78 Hz), 167.6 (C=O(CHC(Me)), 145.0 (ipso-CH$_2$), 143.1 (o-CH$_2$), 140.5 (o-CH$_2$), 127.1 (p-CH$_3$), 124.5 (m-CH$_3$), 124.2 (m-CH$_3$), 96.79 (C(=O)CHC(Me)), 48.91 (Ti=CFBu), 31.24 (Ti=CHMe$_2$), 29.01 (CHMe$_2$), 28.98 (CHMe$_2$), 26.77 (CHMe$_2$), 24.74 (CHMe$_2$), 24.65 (CHMe$_2$), 24.19 (CHMe$_2$), 23.77 (C(Me)$_2$CHC(Me)). Anal. Calcd for C$_{32}$H$_{53}$N$_2$BrTi: C, 67.4; H, 8.36; N, 4.90. Found: C, 71.71; H, 8.96; N, 5.26.

**Synthesis of (Nacnac)Ti$^-$ TiFBU(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 $-35^\circ$C. To the solution was added a cold Et$_2$O suspension (5 mL) containing LiBr [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 to $-35^\circ$C to afford two crops brown crystals of 3-Br$_2$ [112.1 mg, 0.20 mmol, 68% yield]. $^1$H NMR (23 °C, 399.8 MHz, CD$_2$D$_2$): δ 7.17−7.05 (m, C$_6$H$_5$, 6H), 5.32 (s, Ti=CFBu, 1H), 4.96 (s, (CMe)CHC(Me), 1H), 4.11 (septet, CHMe$_2$, 2H), 2.80 (septet, CHMe$_2$, 2H), 1.59 (s, (CMe)CHC(Me), 6H), 1.52 (d, CHMe$_2$, 12H), 1.25 (d, CHMe$_2$, 6H), 1.07 (d, CHMe$_2$, 6H), 0.71 (Ti=CFBu, 9H). $^{13}$C NMR (25 °C, 100.6 MHz, CD$_2$D$_2$): δ 266.7 (Ti=CFBu, J$_{CF-CF}$ = 95 Hz), 167.9 (C=O(CHC(Me)), 144.4 (ipso-CH$_2$), 142.92 (o-CH$_2$), 141.1 (o-CH$_2$), 126.8 (p-CH$_3$), 124.7 (m-CH$_3$), 124.2 (m-CH$_3$), 98.3 (C=O(CHC(Me)), 46.83 (Ti=CHMe$_2$), 31.54 (Ti=CHMe$_2$), 29.16 (CHMe$_2$), 27.70 (CH$_3$), 25.24 (CH$_3$), 24.51 (CH$_3$), 24.23 (CH$_3$), 24.18 (CH$_3$). $^{13}$B NMR (23 °C, 125.4 MHz, CD$_2$D$_2$): δ −14.29 (quintet, BH$_2$, J$_{BH-BH}$ = 89 Hz). Anal. Calcd for C$_{32}$H$_{53}$N$_2$TiBr: C, 74.18; H, 10.07; N, 5.09. Found: C, 73.81; H, 9.79; N, 5.08.

**Synthesis of [Nacnac]Ti(CH$_2$Br)$_2$[B(C$_6$F$_5$)$_4$], 2-B.[B(C$_6$F$_5$)$_4$].** In a vial was dissolved 10 mL of Et$_2$O complex 2 [73 mg, 0.12 mmol] and the solution cooled to $-35^\circ$C. To the cold solution was added a cold Et$_2$O suspension (−5 mL) containing [FeCP$_2$]$_2$[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 $-35^\circ$C to afford orange crystals of [2-B][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 HMBC experiments. $^{18}$ $^1$H NMR (23 °C, 399.8 MHz, CD$_2$Cl$_2$): δ 7.53−7.39 (m, C$_6$H$_5$, 6H), 6.20 (s, (CMe)CHC(Me), 1H), 3.33 (septet, CHMe$_2$, 2H), 2.95 (s, Ti=CH$_2$Bu, 2H), 2.44 (septet, CHMe$_2$, 2H), 2.33 (s, (CMe)CHC(Me), 6H), 1.59 (d, CHMe$_2$, 6H), 1.37 (d, CHMe$_2$, 6H), 1.29 (d, CHMe$_2$, 6H), 1.08 (d, CHMe$_2$, 6H), 0.95 (Ti=CHCH$_2$Me$_3$, 9H), 0.62 (Ti=CH$_2$CH$_2$Me, 5H). $^{13}$C NMR (25 °C, 100.6 MHz, CD$_2$Cl$_2$): δ 170.9 (C=O(CHC(Me)), 149.5 (B(C$_6$F$_5$)$_4$), 147.0 (B(C$_6$F$_5$)$_4$), 146.7 (Ti=CH$_2$Bu, based on HMBC), 141.8 (ipso-CH$_2$), 141.6 Reference 18
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H^1NMR (23 °C, 282.3 MHz, C6D6): 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(OTf)2 (4). In a vial was dissolved (Nacnac)TiMe2(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 Ti(OTf)4 suspension (15 mL containing AgOTf, 61.7 mg, 0.214 mmol), causing precipitation of Ag^+Ag. After stirring for 20 min the solution was filtered and the filtrate dried under vacuum. The solids were extracted with Et2O, 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 ^13C and ^3H NMR spectroscopy).

The final 1H NMR assignment was not possible due to impurities present in the reaction mixture. ^1H NMR (23 °C, 399.8 MHz, CD2Cl2): δ 7.28−6.86 (m, C6H3, 6H), 5.11 (s, C(Me)CH2C(Me), 1H), 3.31 (septet, CH2Me2, 2H), 3.16 (septet, CH2Me2, 2H), 1.73, 1.67, 1.56, 1.50, 1.59, 1.21, 1.17, 1.15 (C(CH3)3), 1.11 0.79 (d, C(CH3)3, 3H).[ ^19F NMR (23 °C, 282.3 MHz, C6D6): 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.]

Thermolysis of 5-OTf. In a NMR tube was loaded complex 5-OTf [27 mg, 0.039 mmol] in 0.8 mL of C6D6. The tube was sealed under vacuum and the solution heated at 60 °C for 2 days. No decomposition of 5-OTf nor traces of 7-OTf were observed to form based on 1H NMR spectroscopy.

Synthesis of (H^2BuC=C(Me)CH(Me)N[Ar]Ti)N=Ar(CN)(5-Cl), and Ti(2,6-C6Me3)2(C6H4Me)NC(Me)CH(Me)(2,6-C6Me3)2(C6H4Me)(CN)(7-Cl). 5-Cl and 7-Cl can be isolated in pure form as white crystalline solids by slow evaporation of the reaction mixture after addition of a small amount of DCM. The yield of 5-Cl and 7-Cl was determined to be 85%. The reaction mixture was then concentrated and the solution kept at −5 °C for 2 days. The product was then filtered and dried under vacuum. The solid was extracted with pentane, filtered, concentrated, and cooled overnight at −35 °C to afford in two crops red-brown crystals of 5-OTf [7.47 mg, 0.11 mmol, 75% yield]. 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 [7.47 mg, 0.11 mmol, 75% yield]. If the solution was taken at place 60 °C, complex 5-OTf is formed over 2 h and is isolated in ~65% yield. Some assignments of ^1H and ^13C NMR resonances were determined by HMRC experiments.

For 5-OTf: ^1H NMR (23 °C, 399.8 MHz, C6D6): δ 7.20−6.77 (m, C6H3, 6H), 4.67 (s, C(Me)CH2C(Me), 1H), 3.87 (septet, CH2Me2, 2H), 2.66 (s, H^1BuC=C(Me)CH(Me), 1H), 1.24 (septet, CH2Me2, 2H), 1.92 (s, H^1BuC=C(Me)CH(Me), 3H), 1.57 (s, H^1BuC=C(Me)CH(Me), 3H), 1.43 (d, CH2Me2, 6H), 1.29 (s, H^1BuC=C(Me)CH(Me), 9H), 1.17 (d, CH2Me2, 6H), 1.10 (d, CH2Me2, 6H), 0.98 (d, CH2Me2, 6H). ^13C NMR (23 °C, 100.5 MHz, C6D6): δ 161.5 (C(Me)CH(Me)), 158.0, 157.1, 147.6, 145.8 (C6H3), 143.7 (C6H3), 139.9 (C6H3), 134.2 (H^1BuC=C(Me)CH-(Me), J=19 Hz), 127.5 (C6H3), 125.4 (C6H3), 123.8 (C6H3), 123.6 (C6H3), 122.8 (br, CF3), 97.25 (C(Me)CH(Me), J=19 Hz), 35.99 (H^1BuC=C(Me)CH(Me)), 32.18 (H(Me)C(Me)CC(Me)CH(Me)), 29.15 (CH2Me2), 24.89 (CH3), 24.67 (CH3), 24.47 (CH2), 24.40 (CH2), 24.26 (CH3), 23.76 (CH3).

^19F NMR (23 °C, 282.3 MHz, C6D6): δ −75.6 (s, OSO2CF3). IR (C6D6, CaF2): 2964 (s), 2869 (s), 1619 (m), 1463 (m), 1439 (m), 1369 (s), 1358 (m), 1209 (s), 1201 (s), 1187 (m), 997 (m). Anal. Calcd: C, 61.36; H, 7.82; N, 4.02. 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 C6H6 and the solution was heated at 70 °C for 2 h. The solution was cooled under reduced pressure and the red-brown solid washed with hexane to remove 5-OTf. Recrystallization of the solid from Et2O 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 ^1H NMR at 70 °C, neopentane was observed (0.992 ppm).

For 7-OTf: ^1H NMR (23 °C, 399.8 MHz, C6D6): δ 7.59 (d, CH2Me2, 2H), 7.52 (d, CH2Me2, 2H), 7.10 (d, CH2Me2, 2H), 5.69 (s, C(Me)CH2C(Me)), 1H), 2.74 (septet, CH2Me2, 2H), 2.58 (s, CH2Me2, 6H), 2.09 (s, CH2Me2, 6H), 1.21 (d, CH2Me2, 6H), 0.55 (d, CH2Me2, 6H), 0.51 (s, CH2Me2, 6H). ^13C NMR (23 °C, 100.5 MHz, C6D6): δ 159.8 (C(Me)CH2C(Me)), 142.7 (C6H3), 137.6 (C6H3), 137.6 (C6H3), 132.9 (C6H3), 130.9 (C6H3), 128.5 (C6H3), 127.4 (bs, CF3), 126.6 (C6H3), 95.53 (C(Me)CH2C(Me)), J=162 Hz, 88.78 (C6H3), 27.93 (CH2Me2), 27.02 (CH2), 26.74 (CH2), 24.61 (22.44, CH2), 21.44 (CH3). ^19F NMR (23 °C, 282.3 MHz, C6D6): δ −78.08 (s, OSO2CF3). IR (Et2O, CaF2): 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 C30H33N2O4S3P2Ti: 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 C6D6. The tube was sealed under vacuum and the solution heated at 70 °C for 2 days. No decomposition of 5-OTf nor traces of 7-OTf were observed to form based on ^1H NMR spectroscopy.
CHMe₂, 2H), 2.49 (s, 3H), 2.16 (septet, CHMe₂, 2H), 1.92 (s, CH₃, 3H), 1.88 (s, Ti-FeBuCCMe(CH)H, 1H), 1.48 (s, CH₃, 3H), 1.39 (d, CHMe₂, 6H), 1.21 (s, Bu, 9H), 1.08 (d, CHMe₂, 6H), 1.01 (d, CHMe₂, 6H), 0.93 (d, CHMe₂, 6H).

For 7-Br: ^1H NMR (23 °C, 399.8 MHz, CD₂Cl₂): δ 7.50 – 6.79 (m, C₆H₅, 6H), 5.60 (s, C(Me)C(Me)(CH), 1H), 2.72 (septet, CHMe₂, 2H), 2.49 (s, CH₃, 6H), 2.08 (s, CH₃, 6H), 1.18 (d, CHMe₂, 6H), 0.53 (d, CHMe₂, 6H), 0.58 (s, CH₃, 6H).

Synthesis of [FeBu-C=C(Me)C(Me)(N)[Ar]]Ti=NR-(η³-B₃H₄), 5-Br₃, and Ti(2,6-(CMe₂)(CHMe₂)C₆H₃)(N=C(Me)-CH(Me)-C(Me)(N)[2,6-(CMe₂)(CHMe₂)C₆H₃](η³-B₃H₄)], 7-Br₄. In a vial was dissolved in 10 mL of hexane 3-BrH [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 a few red crystals of 5-Br₃. The precipitate was collected, recrystallized from toluene with LiBH₄ in Et₂O. In a vial was dissolved [165 mg, 0.16 mmol] in 10 mL of Et₂O and the solution cooled to 78 °C. The precipitate was collected via filtration, washed with cold Et₂O, and dried under reduced pressure. The orange powder was crystallized form dichloromethane – Et₂O at ~35 °C to afford in two crops orange crystals of 9 [84 mg, 0.06 mmol, 82% yield]. Some assignments of ^1H and ^13C NMR resonances were determined by HMBC experiments. ^1H NMR (23 °C, 399.8 MHz, CD₂Cl₂): δ 7.23 – 7.05 (m, C₆H₅, 12H), 4.79 (s, C(Me)C(CH)=O=FeBuC(Me), 2H), 4.71 (s, C(Me)C(CH)=O=FeBuC(Me), 2H), 2.52 (overlapping septets, CHMe₂, 8H), 2.05 (s, C(Me)(CH)=O=FeBuC(Me), 6H), 2.00 (s, C(Me)(CH)=O=FeBuC(Me), 6H), 1.19 (s, C(Me)(CH)=O=FeBuC(Me), 18H), 1.17 (br, CHMe₂, 12H), 1.07 (br, CHMe₂, 12H), 0.97 (br, CHMe₂, 12H), 0.89 (br, CHMe₂, 12H).

Synthesis of [(Nac-CH₃)₂(μ-O)(μ-OTf)]₂ (8) with OC₃Ph₃. Synthesis of [(L₆)Ti₂(μ-O)(μ-OTf)](OTf) (9). In a vial was dissolved 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. 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 clear 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 CH₂Cl₂, concentrated, and cooled to ~35 °C to yield orange blocks of 10 [47 mg, 0.0284 mmol, 73% yield]. ^1H NMR (25 °C, 399.8 MHz, CD₂Cl₂): δ 6.85 – 7.31 (br, aryl, 3H), 4.78 (s, C(Me)C(CH)=O=FeBuC(Me), 2H), 2.26 – 2.53 (br, CHMe₂, 8H), 1.73 (s, C(Me)C(CH)=O=FeBuC(Me), 6H), 1.66 (s, C(Me)C(CH)=O=FeBuC(Me), 6H), 0.66 – 1.09 (br, CHMe₂, 48H).

^13C NMR (25 °C, 100.6 MHz, CD₂Cl₂): 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, 124.3, 23.73 (CH₃), 23.56 (CH₃), 24.25 (CH₃), 24.77 (CH₃), 23.66 (CH₃). ^3P NMR (23 °C, 282.3 MHz, CD₂Cl₂): δ –75.71 (s, OSO₂CF₃). Anal. Calcd for C₃H₃NO₃PSF₂Ti₃: C, 59.33; H, 7.05; N, 3.84. Found: C, 59.26; H, 7.23; N, 3.94.

Treatment of [(NacNa)(Ti=μ-O)(μ-OTf)] (8) with OC₃Ph₃. Synthesis of [(L₆)Ti₂(μ-O)(μ-OTf)](OTf) (10). In a vial was dissolved 9 [50 mg, 0.040 mmol] and the solution cooled to ~35 °C to yield orange blocks of 10 [47 mg, 0.0284 mmol, 73% yield]. ^1H NMR (23 °C, 400 MHz, CD₂Cl₂): δ 6.85 – 7.31 (br, aryl, 3H), 4.78 (s, C(Me)C(CH)=O=FeBuC(Me), 2H), 2.26 – 2.53 (br, CHMe₂, 8H), 1.73 (s, C(Me)C(CH)=O=FeBuC(Me), 6H), 1.66 (s, C(Me)C(CH)=O=FeBuC(Me), 6H), 0.66 – 1.09 (br, CHMe₂, 48H).

^13C NMR (25 °C, 100.6 MHz, CD₂Cl₂): 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, 124.3, 23.73 (CH₃), 23.56 (CH₃), 24.25 (CH₃), 24.77 (CH₃), 23.66 (CH₃). ^3P NMR (23 °C, 282.3 MHz, CD₂Cl₂): δ –75.71 (s, OSO₂CF₃). Anal. Calcd for C₃H₃NO₃PSSF₂Ti₃: C, 64.73; H, 6.23; N, 3.40. Found: C, 63.74; H, 6.29; N, 3.55.

Treatment of 3-OTf with CO₂. Synthesis of [(L₆)Ti₂(μ-O)(μ-OTf)](OTf) (9). In a vial was dissolved in 10 mL of Et₂O 3-OTf [100 mg, 0.15 mmol] and the solution cooled to ~78 °C. To the cold and degassed solution was syringed CO₂ 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 Et₂O, and dried under reduced pressure. The orange powder was crystallized form dichloromethane – Et₂O at ~35 °C to afford in two crops orange crystals of 9 [84 mg, 0.06 mmol, 82% yield]. Some assignments of ^1H and ^13C NMR resonances were determined by HMBC experiments. ^1H NMR (23 °C, 399.8 MHz, CD₂Cl₂): δ 7.17 – 6.91 (m, aryI,

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Treatment of 3-OTf with NCCHMe₂ Synthesis of (Nacnac)Ti=NC(CF₂Bu)CH₃)(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 NCCHMe₂ [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 solids was collected by filtration and washed with cold pentane. Recrystallization from Et₂O at −35 °C afforded in two crops red crystals of [12] [92 mg, 0.11 mmol, 73% yield]. ³¹C NMR (23 °C, 125.8 MHz, CDCl₃): δ 7.06−7.19 (m, C₆H₅, 6H), 6.87 (s, C₆H₅, 2H), 4.96 (s, C₆H₅CH(CMe), 1H), 3.41 (s, NC/CBuCH₂C₆H₅Me, 1H), 3.2−3.1 (overlapping septets, C₆H₅Me₂, 2H), 2.94 (s, NC/CBuCH₂C₆H₅Me, 1H), 2.04 (s, p-MeC₆H₄, 3H), 2.77 (s, p-MeC₆H₄, 6H), 1.73 (s, C₆H₅Me, 1H), 1.57 (s, C₆H₅CH(CMe), 1H), 1.39 (d, C₆H₅CH₃, 6H), 1.33 (d, C₆H₅CH₃, 6H), 0.93 (s, C₆H₅CH₃Me, 9H), 0.91 (d, C₆H₅CH₃Me, 6H). ¹H NMR (23 °C, 125.8 MHz, CDCl₃): δ 7.06−7.22 (m, C₆H₅, 6H), 7.11 (m, C₆H₅, 2H), 4.92 (s, C₆H₅CH(CMe), 1H), 3.34 (septet, C₆H₅CH₂, 3H), 2.33 (septet, C₆H₅CH₂, 3H), 1.32 (septet, C₆H₅CH₂, 3H), 1.29 (septet, C₆H₅CH₂, 3H), 1.23 (d, C₆H₅CH₂, 3H), 1.19 (d, C₆H₅CH₂, 3H), 0.788 (s, NC/CBuMe, 6H). ¹³C NMR (25 °C, 125.8 MHz, CDCl₃): δ 167.1 (C₆H₅CH(CMe)), 147.3 (aryl), 143.7 (aryl), 143.1 (aryl), 142.4 (aryl), 128.8 (aryl), 128.2 (aryl), 126.7 (aryl), 126.8 (aryl), 124.9 (aryl), 123.9 (aryl), 121.1 (C₆H₅CH(CMe)), 85.46 (C₆H₅Me₂), 28.01 (CH₃), 28.51 (CH₃), 25.32 (CH₃), 24.88 (CH₃), 24.41 (CH₃), 24.31 (CH₃), 23.95 (CH₃). ¹⁹F NMR (23 °C, 282.3 MHz, CDCl₃): δ −79.00 (s, OSO₂CF₃). Anal. Caled for C₃₆H₃₂F₈O₅Ti: C, 65.58; H, 6.99; N, 6.38. Found: C, 65.28; H, 7.11; N, 6.29.

Treatment of 3-OTf with N₃(1-adamantyl). Synthesis of (Nacnac)Ti=N(C₆H₄Bu)(C₆H₅Me)(OTf) (15). 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 N₃Ad [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 three yellow crystals of [15] [100 mg, 0.12 mmol, 82% yield]. For 15: ¹³C NMR (23 °C, 125.8 MHz, CDCl₃): δ 7.2−7.11 (m, C₆H₅, 6H), 4.92 (s, C₆H₅CH(CMe), 1H), 3.34 (septet, C₆H₅CH₂, 3H), 2.33 (septet, C₆H₅CH₂, 3H), 1.32 (septet, C₆H₅CH₂, 3H), 1.29 (septet, C₆H₅CH₂, 3H), 1.23 (d, C₆H₅CH₂, 3H), 1.19 (d, C₆H₅CH₂, 3H), 0.788 (s, NC/CBuMe, 6H). ¹³C NMR (25 °C, 125.8 MHz, CDCl₃): δ 168.9 (C₆H₅CH(CMe)), 167.7 (C₆H₅CH(CMe)), 145.4 (C₆H₅), 145.2 (C₆H₅), 142.5 (C₆H₅), 142.4 (C₆H₅), 140.9 (C₆H₅), 140.7 (C₆H₅), 127.5 (C₆H₅), 127.5 (C₆H₅), 124.8 (C₆H₅), 124.7 (C₆H₅), 124.1 (C₆H₅), 123.9 (C₆H₅), 100.8 (C₆H₅CH(CMe)), 93.49 (C₆H₅BuAd), 41.47 (Ad), 41.35 (Ad), 38.46 (N₃CHMe₂Ad), 37.25 (Ad), 30.35 (Ad), 30.15 (CH₃Bu), 29.46 (28.95 (NCCHMe₃Ad), 28.91 (C₆H₅Me₂), 28.71 (C₆H₅Bu), 25.85 (CH₃), 25.74 (CH₃), 24.95 (CH₃), 24.74 (CH₃), 24.62 (CH₃), 24.54 (CH₃), 24.51 (CH₃), 24.47 (CH₃), 24.18 (CH₃), 23.62. ¹⁹F NMR (23 °C, 282.3 MHz, CDCl₃): δ −78.05 (s, OSO₂CF₃). Anal. Caled for C₃₆H₃₂O₈F₈S₉Ti: C, 63.38; H, 7.40; N, 5.41. Found: C, 64.80; H, 7.98; N, 5.03.

Treatment of 3-OTf with HNCPh₂. Synthesis of (Nacnac)Ti=NXCPh₂(N=C₆H₅Bu)(OTf) (16). In a vial was dissolved 3-OTf [50 mg, 0.07 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 PhCNH [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 two light green crystals of [16] [46 mg, 0.05 mmol, 73% yield]. ¹³C NMR (23 °C, 125.8 MHz, CDCl₃): δ 7.15−6.86 (m, aryl, 16H), 4.92 (s, C₆H₅CH(CMe), 1H), 3.97 (septet, C₆H₅CH₂, 2H), 2.78 (septet, C₆H₅CH₂, 2H), 1.88 (s, C₆H₅CH₂, 2H), 1.51 (s, C₆H₅CH(CMe)), 1.30 (d, C₆H₅CH₃, 6H), 1.25 (d, C₆H₅CH₃, 6H), 1.19 (d, C₆H₅CH₃, 6H), 0.80 (d, C₆H₅CH₃, 6H), 0.46 (s, C₆H₅CH₃, 9H). ¹⁹F NMR (25 °C, 282.3 MHz, CDCl₃): δ 168.0 (C₆H₅CH(CMe), 146.9 (aryl), 145.1 (aryl), 142.6 (aryl), 140.7 (aryl), 128.6 (aryl), 127.5 (aryl), 126.1 (aryl), 124.8 (aryl), 124.1 (aryl), 93.57 (C₆H₅CH(CMe), Jₐ-C = 162), 88.76 (NCPh₂), 53.12 (CH₃Bu), Jₐ-C = 127), 31.81 (CH₃CMe₃), 31.14 (CH₃CMe₃), 29.83 (C₆H₅Me₂), 29.85 (C₆H₅Bu), 25.24 (CH₃), 24.44 (CH₃), 24.38 (CH₃), 24.26 (CH₃), 23.89 (CH₃). ¹³C NMR (25 °C, 282.3 MHz, CDCl₃): δ −77.80 (s, OSO₂CF₃). Anal. Caled
for C6H4NO3F3Sti: C, 66.57; H, 7.22; N, 4.85. Found: C, 65.24; H, 7.91; N, 5.44.

**Synthesis of (Nacnac)TiCl2 (17).** In a reaction vessel was suspended TiCl4 [1 g, 6.5 mmol] in Et2O (100 mL), and to the solution was added an Et2O solution (20 mL) containing Li(Nacnac)2 [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]. 1H NMR (23 °C, 399.8 MHz, C6D6): δ 7.26 (1/2 = 13 Hz), 7.11 (1/2 = 45 Hz), 5.57 (1/2 = 125 Hz), 2.98 (1/2 = 163 Hz), −0.06 (1/2 = 241 Hz). Anal. Calcd for C61H54N3O3F3Ti: C, 66.57; H, 7.22; N, 4.85. Found: C, 66.19; H, 8.63; N, 4.40.

**Synthesis of (Acac)ti(C2H5)3 (18).** In a reaction vessel was dissolved 17 [662 mg, 1.07 mmol] in 30 mL of Et2O and the solution cooled to −35 °C. To the cold solution was added a cold Et2O solution (10 mL) of LiCH2Bu [175 mg, 2.24 mmol]. After stirring for 30 min the solution was filtered and dried under reduced pressure. The brown powder was extracted with hexane and filtered, and the filtrate was again filtered and cooled to −35 °C to afford in two crops green crystals of 18 [526 mg, 0.76 mmol, 71% yield]. 1H NMR (23 °C, 399.8 MHz, C6D6): δ 7.26 (1/2 = 13 Hz), 7.11 (1/2 = 45 Hz), 5.57 (1/2 = 125 Hz), 2.98 (1/2 = 163 Hz), −0.06 (1/2 = 241 Hz). Anal. Calcd for C67H74N3O3F3Ti: C, 68.95; H, 7.30; N, 4.52. Found: C, 68.94; H, 7.29; N, 4.51.

**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, TMSO, as an internal standard in 675 mg of C6D6) 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 methadone product 3-I occurred. No side products were observed, as evidenced by 1H NMR spectroscopy. The NMR probe temperature was monitored using a thermocouple and a digital temperature controller. The TMSO resonance was integrated to 1000, and the decay of the hydrogen resonance for the γ-carbon of the Nacna 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 ± 0.5 s−1) performed at 57.0 °C. Activation parameters were performed in triplicate for each temperature run (ΔH* = 21.3 ± 0.2 kcal/mol, ΔS* = −8 ± 3 cal/mol K). Solvent dependence tests were determined by performing the above experiments with different solvents.

**Crystal Structure Determinations. Data Collection and Refinement.** Inert atmosphere techniques were used to place the crystal onto the tip of a diameter glass capillary (0.03–0.2 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-
Four-coordinate titanium alkylidene complexes were calculated from the xyz mounting process and in some cases during the data collection. and moisture and often suffer from degradation during the Four-coordinate titanium alkylidene complexes Organometallics, Vol. 24, No. 8, 2005 interpretation exclusively in terms of discrete chemical moieties. We do so that they superficially appear more attractive. The structure was solved using SHELXS-97 and refined with SHELXL-97. 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. All hydrogen atoms were placed in ideal positions and 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. Most of the crystals examined are exceedingly reactive to O2 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 P21/c, and subsequent solution and refinement confirmed this choice. A large peak (ca. 3 eÅ⁻³) appeared in the difference map near C(34). Initially it was thought that this might be a disorder in the –CF3Bu group, but it was finally recognized that there was a second form of the molecule superimposed in the lattice. Careful examination located two alternate positions for the Ti1 and I33 atoms with relative isotropic displacement parameters.

For 3-BH: Intensity statistics and systematic absences suggested the non-centrosymmetric space group Cmc21, and subsequent solution and refinement confirmed this choice. A disordered hydrogen atom was located in one of the 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 3-CH2Cl: Intensity statistics and systematic absences suggested the centrosymmetric space group P21/m, 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 3-B: Intensity statistics and systematic absences suggested the centrosymmetric space group P1, and subsequent solution and refinement confirmed this choice. A disordered solvent molecule (Et2O) 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 3-Br: Intensity statistics and systematic absences were located in subsequent Fourier maps and refined as isotropic contributors. The final difference Fourier was featureless with the exception of one peak of 1.95 eÅ⁻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 P1, 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: Intensity statistics and systematic absences suggested the centrosymmetric space group Cmc21, and subsequent solution and refinement confirmed this choice. A disordered hydrogen atom was 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-CH2Cl: Intensity statistics and systematic absences suggested the centrosymmetric space group P21/m, 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-Et2O: Intensity statistics and lack of systematic absences suggested the centrosymmetric space group P1, and subsequent solution and refinement confirmed this choice. A disordered solvent molecule (Et2O) 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-C6H15: Intensity statistics and systematic absences suggested the centrosymmetric space group P1, 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 P1, and subsequent solution and refinement confirmed this choice. A disordered was present in the O2SCF ligand. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were located and refined isotropically.

For 15-C6H12: Intensity statistics and systematic absences suggested the noncentrosymmetric space group P212121, 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 Bu group. The disorder was well
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-OTfC₆H₁₄: Intensity statistics and systematic absences suggested the centrosymmetric space group P2₁/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.

Acknowledgment. We thank Indiana University—Bloomington, the Camille and Henry Dreyfus Foundation, the Ford Foundation, and the National Science Foundation (CHE-0348941) for financial support of this research. D.J.M. wishes to thank Prof. K. G. Caulton, Prof. K. Meyer, Dr. Roger Isaacson, Dr. Maren Pink, and Mr. Xile Hu for insightful discussions, and the Indiana University Information Technology Research and Academic Computing Services for access to the high-performance computing system. L.A.W. acknowledges the National Science Foundation for a pre-doctoral fellowship.

Supporting Information Available: Complete crystallographic data for compounds [2][B(C₆F₅)₄], 2-F, 3-I, 3-Br, 3-BH₄, 4, 5-I, 5-BH₄, 7-OTf, 7-BH₄, 9–15, and 17–19 (CIF), and complete geometrical parameters for the optimized geometries of ([2,6-Me₂C₆H₄]NC(H)CHC(H)N[2,6-Me₂C₆H₄])₂Ti(CH₃)₂ and ([2,6-Me₂C₆H₄]NC(H)CHC(H)N[2,6-Me₂C₆H₄])₂Ti=CHMe(Cl) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

OM049400B