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Oxidatively Induced α-Hydrogen Abstraction. A Mild Protocol to Generate Terminal Titanium Alkylidenes Containing a *β*-Hydrogen

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One-electron oxidation of the Ti(III) bis-isobutyl complexes (nacnac)Ti($CH_2{}^iPr$)$_2$ (**1**) (nacnac$^-$ = [ArNC(^{t}Bu)]$_2$CH, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) and (PNP)Ti($CH_2{}^iPr$)$_2$ (**4**) (PNP$^-$ = N[2-P(CHMe$_2$)$_2$-4-methylphenyl]$_2$) with AgOTf promotes exclusive α-hydrogen abstraction to provide the first structurally characterized examples of terminal group 4 alkylidenes bearing a *β*-hydrogen, namely, (nacnac)Ti=CH^{i}Pr(OTf) (**2**) and (PNP)Ti=CH^{i}Pr(OTf) (**5**). These complexes have been prepared and characterized by means of multinuclear NMR spectroscopy as well as single-crystal X-ray diffraction analysis. In the case of the nacnac framework, the reactive Ti=CH^{i}Pr motif can readily engage in an intramolecular Wittig-like rearrangement. However, the isobutylidene motif can be stabilized when supported by a more robust ancillary ligand such as PNP, which is demonstrated by the thermal resistance of **5** and the preparation of a rare example of a stable alkylidene methyl complex (PNP)Ti=CH^{i}Pr(Me) (**6**).

Introduction

Alkyl lithiums or Grignards containing *β*-hydrogens are often sought as efficient reducing reagents in the organotransition metal chemistry of group 4.[1,2] Prototypical among these nucleophiles are the ^{t}Bu, ^{n}Bu, and ^{i}Bu class of alkyls. For example, “in situ Ti(II)” coupling reagents can be generated in the presence of nucleophiles such as ^{i}PrLi, ^{n}BuLi, ^{i}BuLi, or the corresponding Grignard reagents.[1−4] However, in some cases the transient Ti(II) species, generated from a Ti(IV) reduction using an alkyl reagent such as an isobutyl, can sometimes be trapped with an inert substrate such as N_2.[5] One credible reason for these alkyls being so unstable on the metal could originate from energetically favorable decomposition pathways such as *β*-hydrogen elimination or *β*-hydrogen abstraction reactions. Consequently, common reagents such as TiCl$_4$(THF)$_2$ can be readily converted to “TiCl$_2$(THF)$_x$”, 1-butene, and butane with 2 equiv of ^{n}BuLi.[6] As a result, promoting α-hydrogen abstraction as opposed to *β*-hydrogen elimination or abstraction is a rare phenomenon in organometallic chemistry, unless *β*-hydrogen-free alkyl groups are invoked.[7] Therefore, the above arguments might explain why most terminal alkylidenes of group 4[5,8−15] are restricted only to alkyl groups lacking *β*-hydrogens.[7,16,17] In principle, if an alkylidene with *β*-hydrogens were to be assembled, rearrangement of an alkylidene to an olefin would also be a competitive pathway given the intrinsic instability of *β*-hydrogens with respect to the bound olefin. The latter rearrangement has been recognized as a potentially damaging side-reaction within the alkene metathesis cycle.[18] Despite these restrictions, the microscopic reverse, olefin to alkylidene, has been observed with low-valent second- and third-row transition

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metal centers.[19] In fact, Schrock has observed the base-induced rearrangement of tantalum−olefin complexes to the thermodynamically more favored β-hydrogen-containing alkylidenes.[19f] The energetic favorability of the latter alkylidene was attributed to a strong α-agostic interaction with the metal center.

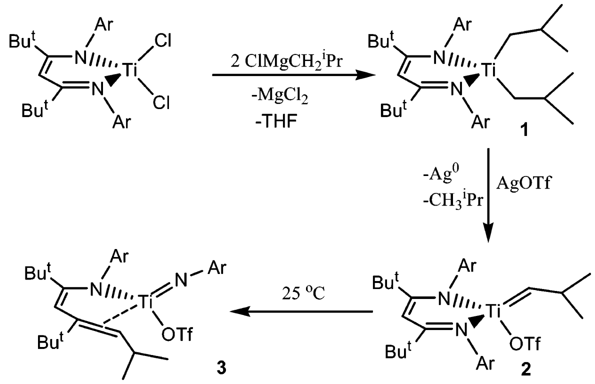
In lieu of these limitations, one alternate option to promoting α-hydrogen abstraction under mild conditions is an oxidatively induced α-hydrogen abstraction.[13] The latter process is facile at low temperatures and does not depend on external stimulants such as heat, light, or base to promote the α-hydrogen abstraction step.[20] In addition, the protocol avoids the use of powerful electrophiles (e.g., AlR$_3$), hence resulting in a terminal, Lewis acid-free, and low-coordinate alkylidene complex.[21]

In this article, we wish to report that one-electron oxidation of titanium complexes bearing alkyl groups with β-hydrogens promotes, exclusively, α-hydrogen abstraction to afford the first structural examples of terminal titanium alkylidenes with a β-hydrogen.[17] Synthesis, characterization, and single-crystal structural studies of this new class of terminal alkylidene, specifically isobutylidenes, are presented and discussed. Depending on the supporting ancillary ligand, the titanium isobutylidene functionality is sufficiently stable for further reaction chemistry.

Results and Discussion

Recently, our group reported that (nacnac)Ti(CH$_2{}^t$Bu)$_2$ (nacnac$^-$ = [ArNC(^{t}Bu)]$_2$CH, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$), when oxidized by one electron, afforded alkylidene species of the type (nacnac)Ti=CH^{t}Bu(X) (X$^-$ = OTf, I) in excellent yields. The anion present in the oxidant determines the nature of X.[13b] However, the alkyl groups must be sterically imposing in order to promote the α-hydrogen abstraction since complexes such as (nacnac)Ti(CH$_3$)$_2$ (nacnac$^-$ = [ArNC(^{t}Bu)]$_2$CH, Ar = 2,6-^{i}Pr$_6$H$_2$), when oxidized by AgOTf, do not afford the corresponding methylidene (nacnac)Ti=CH$_2$(OTf), but the five-coordinate titanium complex (nacnac)Ti(CH$_3$)$_2$(OTf).[13b] For this reason we turned our attention to bulky alkylating groups that contain β-hydrogens. Unfortunately, attempts to alkylate (nacnac)TiCl$_2$[13b] with 2 equiv of RMgCl (R = ^{i}Pr or ^{t}Bu) proved difficult, presumably due to excess crowding imposed by the alkyl groups. Contrary to sterics, efforts to incorporate the less crowded ^{n}Bu group onto Ti(III) were also unsuccessful for reasons that we currently do not understand. The latter result was also surprising, since Budzelaar and co-workers have reported exceedingly stable bis ^{n}Bu complexes of Ti(III) supported by the less crowded β-diketiminate ligand [ArNC(Me)]$_2$CH (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$).[22] In view of that, we concentrated our attention toward the isobutyl group, which has a bulk size comparable to the neopentyl fragment, yet possesses both α- and β-hydrogens.

Scheme 1. Synthesis of Complexes 1−3



Accordingly, when a pentane solution of (nacnac)TiCl$_2$[13b] is treated with 2 equiv of ^{i}BuMgCl at −35 °C, the bis-alkyl titanium(III) complex (nacnac)Ti(^{i}Bu)$_2$ (**1**) is readily obtained in 79% yield upon workup of the reaction mixture (Scheme 1). While solution magnetic measurements of **1** are consistent with a d^1 paramagnetic species ($\mu_{\text{eff}} = 1.95\ \mu_{\text{B}}$), the molecular structure displays the expected connectivity for a four-coordinate Ti(III) bis-alkyl (Ti−C$_\alpha$, 2.117(3) and 2.146(3) Å, Figure 1) complex in a tetrahedral environment.[23,24] Although most nonperipheral hydrogen atoms from the alkyl groups were located and refined isotropically, no α- or β-hydrogen agostic interactions were evident from the crystal structure (Figure 1). Complex **1** is thermally stable in solution, but one-electron oxidation with AgOTf in pentane at −35 °C promotes *only α-hydrogen abstraction* concomitant with Ag^0 and isobutane formation to afford a rare example of the isobutylidene[23,26] complex (nacnac)Ti=CH^{i}Pr(OTf) (**2**) as dark red blocks in 73% yield (Scheme 1). Diagnostic features for **2** include four diasteriotopic methyl groups for the nacnac-isopropyls and one ^{t}Bu environment for the nacnac$^-$ backbone. A C$_\alpha$ resonance centered at δ 258.9 ppm with a $J_{\text{C−H}}$ coupling constant of 86 Hz is representative of **2** having a terminal alkylidene functionality.[7,13] The $J_{\text{C−H}}$ coupling from the ^{13}C NMR spectral data

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[24] Crystallographic details for (nacnac)Ti(CH$_2{}^i$Pr)$_2$ (**1**): A green crystal of approximate dimensions 0.35 × 0.35 × 0.35 mm^3 was selected and mounted on a glass fiber. A total of 183 625 reflections ($-39 \le h \le 39$, $-17 \le k < 17$, $-35 \le l \le 35$) were collected at T = 123(2) K in the range 2.76−30.01°, of which 17 852 were unique (R_{int} = 0.0517), Mo Kα radiation (λ = 0.71073 Å). A direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. There is a disorder in some of the peripheral groups of one of the two independent molecules in the asymmetric unit. All hydrogen atoms not associated with the disordered atoms were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement. All hydrogen atoms associated with the disorder were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. All non-hydrogen atoms were refined with anisotropic displacement parameters. The residual peak and hole electron densities were 0.601 and −0.296 e A^{-3}. The absorption coefficient was 0.240 mm^{-1}. The least squares refinement converged normally with residuals of $R(F)$ = 0.0387, $wR(F^2)$ = 0.1123 and a GoF = 1.012 ($I > 2\sigma(I)$). C$_{43}$H$_{71}$N$_2$Ti, space group $P2(1)/c$, monoclinic, a = 28.380(1) Å, b = 12.6335(7) Å, c = 24.976(1) Å, β = 114.676(1)°, V = 8137.0(7) Å^3, Z = 8, D_{calcd} = 1.084 mg/m^3, F(000) = 2920.

[25] To our knowledge only one example of a terminal isobutylidene complex has been reported. Hansen, S. M.; Volland, M. A. O.; Rominger, F.; Eisentrager, F.; Hofmann, P. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1273−1276.

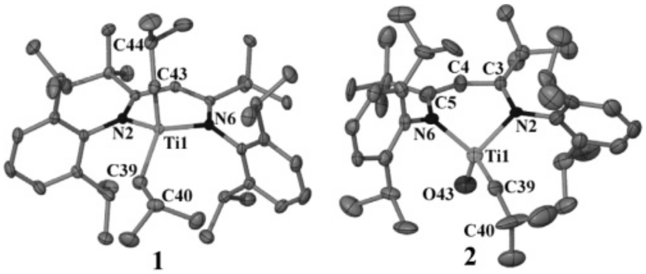

Figure 1. Molecular structures of **1** and **2.** All H atoms and solvent molecules have been omitted for clarity. The SO_2CF_3 group of **2** has also been removed. For **1**: Ti(1)−C(43), 2.146(3); Ti(1)−C(39), 2.117(3); Ti(1)−N(2), 2.0154(9); Ti(1)−N(6), 2.020(1); Ti(1)−C(43)−C(44), 127.69(9); N(2)−Ti(1)−N(6), 96.76(4); Ti(1)−C(39)−C(40), 131.2(1); C(43)−Ti(1)−C(39), 104.40(5); N(2)−Ti(1)−C(39),; N(2)−Ti(1)−C(43),; N(6)−Ti(1)−C(39),; N(6)−Ti(1)−C(43),. For **2**: Ti(1)−C(39), 1.86(1); Ti(1)−N(2), 2.054(8); Ti(1)−N(6), 2.023(8); Ti(1)−O(43), 2.007(7); Ti(1)−C(39)−C(40), 167(1); N(2)−Ti(1)−N(6), 95.6(3); C(39)−Ti(1)−O(43), 110.1(4); N(2)−Ti(1)−C(39), 105.3(4); N(2)−Ti(1)−O(43), 110.8(3); N(6)−Ti(1)−C(39), 116.2(5); N(6)−Ti(1)−O(43), 117.1(3).

suggests a strong α-hydrogen agostic interaction taking place with the metal center.[5,7] Most notably, the ^1H NMR spectrum of **2** reveals a doublet of septets for the isobutylidene β-hydrogen, while the α-hydrogen on the alkylidene resolves as a doublet. As a result, all NMR spectroscopic data are consistent with complex **2** retaining C_s symmetry in solution and containing a distorted, terminal alkylidene functionality possessing α- and β-hydrogens.

Large red-brown crystals of **2** were grown from pentane at −35 °C, and the single-crystal molecular structure confirmed a four-coordinate titanium complex having C_s symmetry and a short Ti═C bond length (Ti(1)−C(39) = 1.87(1) Å, Figure 1).[23,26] It should be emphasized that the data quality for the crystal is poor, presumably due to decomposition of the crystal prior to transferring it to the cold stream of N_2.[26] Despite this, the molecular structure unarguably depicts an alkylidene isopropyl group that lies along the σ-plane bisecting N−Ti−N and is oriented along the same side with respect to the triflato ligand. The obtuse Ti(1)−C(39)−C(40) angle of 167(1)° provides strong crystallographic credence for an α-agostic interaction taking place with the four-coordinate Ti(IV) center. No β-hydrogen agostic interaction was evident from the orientation of the β-H in the molecular structure of complex **2**.

Although isolable at cold temperatures (−35 °C) under an inert atmosphere, complex **2** is a kinetic product since solutions cleanly decompose over 24 h at 25 °C to afford (η^2-H^{i}PrC═C(^{t}Bu)CHC(^{t}Bu)N[Ar])Ti═NAr(OTf) (**3**), a compound resulting from an intramolecular Wittig-like rearrangement.[13,27] Despite complex **2** having ^{t}Bu groups to block the intramolecular [2+2]-cycloaddition,[13a,b] the alkylidene functionality is apparently far less crowded and hitherto more prone to the intramolecular group-transfer process (Scheme 1). Complex **3** was characterized by a combination of ^1H and ^{13}C NMR spectroscopy as well single-crystal X-ray diffraction analysis (Figure 2).[23,27] Salient metrical parameters for the olefin imide moieties in complex **3** are depicted with the molecular structure in Figure 2. Complex **3** is a close analogue of other titanium imide complexes reported by our group, namely, the Wittig-rearranged complexes (η^2-H^{t}BuC═C(^{t}Bu)CHC(^{t}Bu)N[Ar])Ti═NAr(X) (X^- = OTf, Cl, Br, I, BH_4, CH_2SiMe_3).[13a−c]

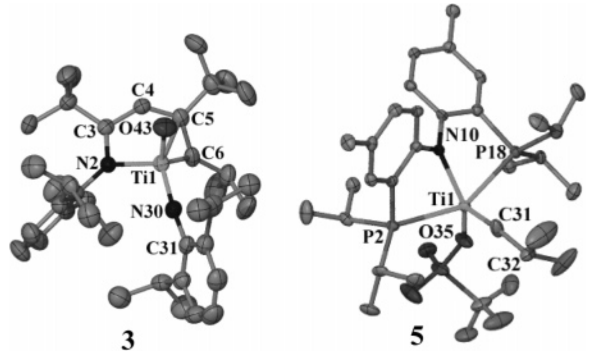

Figure 2. Molecular structures of **3** and **5**. All H atoms and solvent molecules have been omitted for clarity. The SO_2CF_3 group of **3** has also been removed. For **3**: Ti(1)−C(6), 2.203(6); Ti(1)−N(2), 2.005(2); Ti(1)−N(30), 1.714(2); Ti(1)−C(3), 2.588(5); Ti(1)−O(43), 2.009(2); N(2)−C(3), 1.340(6); C(6)−C(5), 1.394(2); C(5)−C(4), 1.415(2); C(4)−C(3), 1.425(2); Ti(1)−N(30)−C(31), 173.2(1); O(43)−Ti(1)−N(30), 106.41(5); N(2)−Ti(1)−N(30), 109.98(5); C(6)−Ti(1)−N(30), 105.35(6). For **5**: Ti(1)−C(31), 1.858(5); Ti(1)−N(10), 2.036(4); Ti(1)−O(35), 1.986(3); Ti(1)−P(2), 2.579(4); Ti(1)−P(18), 2.596(4); P(18)−Ti(1)−P(2), 151.13(5); N(10)−Ti(1)−C(31), 113.2(2); Ti(1)−C(31)−C(32), 162.1(5); N(10)−Ti(1)−P(2), 76.80(11); N(10)−Ti(1)−P(18), 75.62(11); O(35)−Ti(1)−C(31), 113.3(2).

To prepare more kinetically stable alkylidene complexes of titanium, we resorted to the robust pincer framework N[2-P(CHMe$_2$)$_2$-4-methylphenyl]$_2^-$ (PNP) previously reported by Ozerov and co-workers.[14] Following a protocol analogous to that of **1**, the d^1 complex (PNP)Ti(^{i}Bu)$_2$[23] (**4**) was prepared, and subsequent oxidation with AgOTf afforded the five-coordinate isobutylidene (PNP)Ti═CH^{i}Pr(OTf) (**5**) in 73% yield (Scheme 2).[28] The alkylidene motif in **5** displays spectroscopic features similar to **2** in both the ^1H and ^{13}C NMR spectra (^{13}C NMR, Ti═*C* = 296.9 ppm; ^1H NMR, Ti═C*H* = 8.46 ppm, Ti═CHC*H*Me$_2$ = 2.55 ppm). In addition, the ^{31}P NMR spectrum

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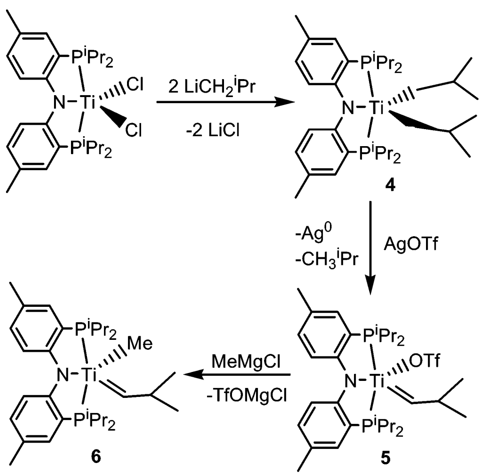
[26] Crystallographic details for (nacnac)Ti═CH^{i}Pr(OTf) (**2**): An orange-brown plate of approximate dimensions 0.20 × 0.20 × 0.05 mm^3 was selected and mounted on a glass fiber. A total of 19 325 reflections ($-12 \le h \le 9$, $-20 \le k \le 21$, $-21 \le l \le 22$) were collected at T = 125(2) K in the range 2.32−22.32°, of which 1536 were unique (R_{int} = 0.3258), Mo Kα radiation (λ = 0.71073 Å). A direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. 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 residual peak and hole electron densities were 0.476 and −0.273 e A^{-3}. The largest residuals were in the vicinity of the triflate group. The absorption coefficient was 0.309 mm^{-1}. The least squares refinement converged normally with residuals of $R(F)$ = 0.0570, $wR(F^2)$ = 0.1416 and a GoF = 0.641 ($I > 2\sigma(I)$). $C_{40}H_{60}F_3N_2O_3STi$, space group $P2(1)2(1)2(1)$, orthorhombic, a = 10.912(9) Å, b = 18.99(1) Å, c = 19.84(1) Å, $\alpha = \beta = \gamma$ = 90°, V = 4112(6) Å^3, Z = 4, D_{calcd} = 1.218 mg/m^3, $F(000)$ = 1612.

[27] Crystallographic details for (η^2-H^{i}PrC═C(^{t}Bu)CHC(^{t}Bu)N[Ar])Ti═NAr(OTf) (**3**): A brown-red prism of approximate dimensions 0.35 × 0.35 × 0.30 mm^3 was selected and mounted on a glass fiber. A total of 52 328 reflections ($-19 \le h \le 19$, $-26 \le k \le 26$, $-23 < l \le 23$) were collected at T = 128(2) K in the range 2.49−26.46°, of which 5200 were unique (R_{int} = 0.1027), Mo Kα radiation (λ = 0.71073 Å). A direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. There is a slight disorder in one of the ^{i}Pr groups. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms not associated with the disorder were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement, and the remaining hydrogen atoms were placed in idealized positions and refined as riding atoms with relative isotropic displacement parameters. The residual peak and hole electron densities were 1.025 and −0.473 e A^{-3}. The absorption coefficient was 0.439 mm^{-1}. The least squares refinement converged normally with residuals of $R(F)$ = 0.0545, $wR(F^2)$ = 0.1569 and a GoF = 0.851 ($I > 2\sigma(I)$). $C_{45}H_{73}F_3N_2O_3STi$, space group $P2(1)/c$, monoclinic, a = 15.245(1) Å, b = 20.245(2) Å, c = 17.852(2) Å, β = 115.068(3)°, V = 4991(1) Å^3, Z = 4, D_{calcd} = 1.101 mg/m^3, $F(000)$ = 1784.

Scheme 2. Synthesis of Complexes 4−6



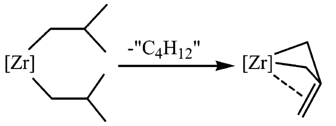
manifests two sets of doublets with a low J_{P-P} coupling constant (54 Hz), which is in accord with the phosphines being significantly slanted from a *trans* geometry.

Single-crystal X-ray diffraction analysis of **5**[28] depicts the expected connectivity with a short Ti═C (1.858(5) Å) bond and an obtuse Ti═C−C angle of 162.1(5)° (Figure 2). The orientation of the ^{i}Pr group places the β-hydrogen away from the metal and orthogonal to the α-hydrogen, the latter of which is interacting with the metal via an α-hydrogen agostic interaction (J_{C-H} = 98 Hz).

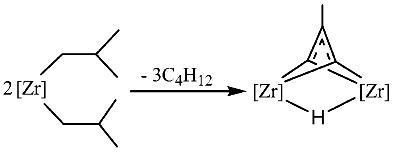
Unlike **2**, complex **5** is kinetically stable under N_2 both as a solid and in solution despite possessing a terminal and nucleophilic alkylidene with a β-hydrogen. In fact, thermolysis of **5** in C_6D_6 (3 days, 80 °C) does not result in any observable decomposition when assayed by ^{1}H and ^{31}P NMR spectroscopy. As a result, the OTf$^-$ functionality in **5** can be readily displaced via treatment with MeMgCl in pentane to afford a rare example of a titanium alkylidene methyl complex, (PNP)Ti═CH^{i}Pr(CH$_3$) (**6**) (82% yield, Scheme 2).[13c,23] Complex **6** is also remarkably stable both in solution and as a solid. However, thermolysis of **6** (C_6D_6, 80 °C) leads to a myriad of products, which we have not identified. The downfield α-C alkylidene resonance (279.4 ppm) and the downfield doublet observed for the isobutylidene hydrogen (8.38 ppm) of **6** are a clear manifestation of a terminal isobutlyidene motif being present. A doublet of septets and a set of diastereotopic doublets resulting from the methine and methyl groups of the isobutylidene isopropyl, respectively, illustrate that the isobutylidene fragment remains intact upon alkylation. In addition, the ^{1}H NMR spectrum of **5** displays a triplet at 0.80 ppm for the titanium-methyl group (J_{H-P} = 2.8 Hz) and a broad resonance in the ^{13}C NMR at 50.0 ppm, which resolves into a quartet in the ^{1}H-coupled ^{13}C (J_{C-H} = 113 Hz). Both ^{1}H and ^{31}P NMR spectra are consistent with complex **6** retaining C_1 symmetry in solution.

Conclusions

In summary, we have prepared and structurally characterized two unique examples of group 4 terminal alkylidene complexes containing a β-hydrogen. The following work presented here demonstrates that isobutyl groups bound to titanium can selectively undergo α-hydrogen abstraction over the more common β-hydrogen elimination and α-hydrogen abstraction themes, when promoted by a one-electron oxidation step. We also fail to observe other rare but reported rearrangements involving the decomposition of d^0 complexes bearing two isobutyl ligands. For example, γ-H abstraction processes have been shown to ultimately generate σ^2,π-butadiene Zr derivatives (eq 1),[29] while multiple intra- and intermolecular C−H bond activation steps can produce a μ-[σ^2,η^3-C$_4$H$_5$] ligand bridged between two Zr centers (eq 2).[30] On the basis of our work, M═CHR functionalities of the early-transition metal series are no longer restricted to R groups where β-hydrogens are excluded. We are currently exploring what other β-hydrogen alkylidene fragments can be incorporated onto titanium and whether systems similar to **5** and **6** can undergo reductive elimination of the alkylidene to the olefin.



(1)



(2)

Experimental Section

General Considerations. Unless otherwise stated, all operations were performed in an M.Braun Lab Master double-drybox under an atmosphere of purified nitrogen or using high-vacuum standard Schlenk techniques under an argon atmosphere.[31] Anhydrous n-hexane, pentane, toluene, and benzene were purchased from Aldrich in sure-sealed reservoirs (18 L) and dried by passage through two columns of activated alumina and a Q-5 column.[32] Diethyl ether was dried by passage through a column of activated alumina.[32] THF was distilled, under nitrogen, from purple sodium benzophenone ketyl and stored under sodium metal. Distilled THF was transferred under vacuum into bombs before being pumped into a drybox. C_6D_6 and C_7D_8 were purchased from Cambridge Isotope Laboratory (CIL), degassed, and vacuum transferred to 4 Å molecular sieves. THF-d_8 was purchased from CIL and used as received. Celite, alumina, and 4 Å molecular sieves were activated under vacuum overnight at 200 °C. Li(nacnac)[22] (nacnac$^-$ = [ArNC(^{t}Bu)]$_2$CH, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$), (nacnac)TiCl$_2$,[13b] and Li(PNP) (PNP = N[2-P(CHMe$_2$)$_2$-4-methylphenyl]$_2$$^-$)[14] were prepared according to the literature. All other chemical were used as received. CHN analyses were performed by Desert Analytics, Tucson, AZ. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on Varian 400 or 300 MHz NMR spectrometers. ^{1}H and ^{13}C NMR are reported with

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[28] Crystallographic details for (PNP)Ti═CH^{i}Pr(OTf) (**5**): A dark red crystal of approximate dimensions 0.25 × 0.25 × 0.20 mm^3 was selected and mounted on a glass fiber. A total of 22 328 reflections ($-12 \le h \le 10$, $-25 \le k < 25$, $-19 \le l \le 23$) were collected at T = 128(2) K in the range 2.11−27.55°, of which 9642 were unique (R_{int} = 0.0508), Mo Kα radiation (λ = 0.71073 Å). A direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. All non-hydrogen atoms were refined with anisotropic displacement parameters. The residual peak and hole electron densities were 1.025 and −0.473 e A^{-3}. The absorption coefficient was 0.439 mm^{-1}. The least squares refinement converged normally with residuals of $R(F)$ = 0.0576, $wR(F^2)$ = 0.1249 and a GoF = 0.869 ($I > 2\sigma(I)$). C$_{31}$H$_{48}$F$_3$NO$_3$P$_2$STi, space group P2(1), monoclinic, a = 9.9065(9) Å, b = 20.034(7) Å, c = 18.234(7) Å, β = 103.196(3)°, V = 3523.4(5) Å^3, Z = 4, D_{calcd} = 1.285 mg/m^3, F(000) = 1440.

[29] Keaton, R. J.; Koterwas, L. A.; Fettinger, J. C.; Sita, L. R. *J. Am. Chem. Soc.* **2002**, *124*, 5932−5933.

[30] Keaton, R. J.; Sita, L. R. *Organometallics* **2002**, *21*, 4315−4317.

[31] 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.

[32] Pangborn; A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.

reference to solvent resonances (residual C_6D_5H in C_6D_6, 7.16 and 128.0 ppm). ^{19}F NMR chemical shifts are reported with respect to external $HOCOCF_3$ (−78.5 ppm). ^{31}P NMR chemical shifts are reported with respect to external H_3PO_4 (aqueous solution, δ 0.0 ppm). Solution magnetization measurements were determined by the method of Evans.[33] X-ray diffraction data were collected on a SMART6000 (Bruker) system under a stream of N_2 (g) at low temperatures.[34,35]

Preparation of (nacnac)Ti(^{i}Bu)$_2$ (1). To a stirring pentane suspension of (nacnac)$TiCl_2$ [462 mg, 0.74 mmol] at −35 °C was added dropwise a solution of ClMg^{i}Bu$_2$ [2 M in ether, 0.76 mL, 1.53 mmol]. The solution was allowed to warm to room temperature and was stirred for 20 min. The solution was filtered, and the resulting green solution was reduced in volume in vacuo and cooled to −35 °C for 24 h to afford green crystals of **1** [392 mg, 0.59 mmol, 79% yield].

For **1**: ^{1}H NMR (C_6D_6, 300.1 MHz, 25 °C): δ 7.66 ($\Delta\nu_{1/2}$ = 224 Hz), 5.59 ($\Delta\nu_{1/2}$ = 41 Hz), 4.27 ($\Delta\nu_{1/2}$ = 51 Hz), 3.73 ($\Delta\nu_{1/2}$ = 126 Hz), 3.31 ($\Delta\nu_{1/2}$ = 358 Hz), 3.01 ($\Delta\nu_{1/2}$ = 55 Hz), 0.58 ($\Delta\nu_{1/2}$ = 120 Hz). Evans magnetic moment (C_6D_6, 298 K): μ_{eff} = 1.95 μ_B. Anal. Calcd for $C_{43}H_{71}N_2Ti$: C, 77.79; H, 10.78; N, 4.22. Found: C, 77.79; H, 10.64; N, 3.99.

Preparation of (nacnac)Ti═CH^{i}Pr(OTf) (2). In a vial was dissolved **1** [197 mg, 0.30 mmol] in pentane (15 mL), and the solution was cooled to −35 °C. To the cold green solution was added solid AgOTf [83.9 mg, 0.33 mmol], and the mixture was stirred for 20 min. The solution changed from green to a dark red color with precipitation of silver. The solution was filtered, reduced in volume in vacuo, and cooled to −35 °C to afford **2** as dark red crystals [168 mg, 0.22 mmol, 73% yield].

For **2**: ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.10−7.00 (m, 6H, Ar-*H*), 5.48 (s, 1H, ArN(^{t}Bu)CC*H*C(^{t}Bu)NAr), 4.27 (d, 1H, Ti═C*H*CHMe$_2$), 3.28 (septet, 2H, C*H*Me$_2$), 3.08 (septet, 2H, C*H*Me$_2$), 2.16 (doublet of septet, 1H, Ti═CHC*H*Me$_2$), 1.80 (d, 6H, CH*Me$_2$*), 1.47 (d, 6H, CH*Me$_2$*), 1.33 (d, 6H, CH*Me$_2$*), 1.25 (d, 6H, CH*Me$_2$*), 1.01 (s, 18H, ArN(^{t}Bu)CCHC(^{t}Bu)NAr), 0.29 (d, 6H, CH*Me$_2$*). ^{13}C NMR (23 °C, 100.6 MHz, C_6D_6): δ 258.9 (Ti═*C*HCHMe$_2$, $J_{\mathrm{C-H}}$ = 86 Hz), 175.8 (ArN(^{t}Bu)*C*CHC(^{t}Bu)NAr), 147.4 (*C*$_6$H$_3$), 143.1 (*C*$_6$H$_3$), 139.0 (*C*$_6$H$_3$), 127.0 (*C*$_6$H$_3$), 124.4 (*C*$_6$H$_3$), 123.9 (*C*$_6$H$_3$), 92.08 (ArN(^{t}Bu)C*C*HC(^{t}Bu)NAr, $J_{\mathrm{C-H}}$ = 154 Hz), 46.52 (Ti═CH*C*HMe$_2$, $J_{\mathrm{C-H}}$ = 128.1 Hz), 44.38 (ArN(*C*Me$_3$)-CCHC(*C*Me$_3$)NAr), 31.88 ((ArN(C*Me*$_3$)CCHC(C*Me*$_3$)NAr), 30.27 (*C*HMe$_2$), 28.87 (*C*HMe$_2$), 26.88 (*Me*), 26.27 (*Me*), 24.47 (*Me*), 24.28 (*Me*), 23.0 (*Me*). ^{19}F NMR (23 °C, 282.3 MHz, C_6D_6): δ −77.75 (s, Ti−O$_3$SC*F*$_3$). Anal. Calcd for $C_{40}H_{61}N_2O_3SF_3Ti$: C, 63.65; H, 8.14; N, 3.71. Found: C, 63.68; H, 8.00; N, 3.64.

Preparation of (η^2-H^{i}PrC═C(^{t}Bu)CHC(^{t}Bu)N[Ar])Ti═NAr(OTf) (3). In a vial was dissolved **2** [75 mg, 0.30 mmol] in pentane (15 mL), and the solution was kept at glovebox temperature for 24 h. The solution was reduced in volume in vacuo and cooled to −35 °C to afford **3** as dark brown crystals [71 mg, 0.094 mmol, 94% yield].

For **3**: ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.04−6.08 (m, 6H, Ar-*H*), 5.67 (s, 1H, H^{i}PrC═C(^{t}Bu)C*H*C(^{t}Bu)N[Ar]), 4.48 (septet, 1H, C*H*Me$_2$), 3.93 (septet, 1H, C*H*Me$_2$), 3.28 (septet, 1H, C*H*Me$_2$), 3.04 (septet, 1H, C*H*Me$_2$), 2.08 (m, 1H, Me$_2$C*H*CH═C(^{t}Bu)-C*H*C(^{t}Bu)N[Ar]), 1.59−1.56 (overlap of doublets, 6H, CH*Me$_2$*), 1.53 (d, 3H, CH*Me$_2$*), 1.40−1.35 (overlap of doublets, 7H, *H*^{i}PrC═C(^{t}Bu)C*H*C(^{t}Bu)N[Ar] and CH*Me$_2$*), 1.29 (s, 9H, H^{i}PrC═C(^{t}Bu)-CHC(^{t}Bu)N[Ar]), 1.10−1.04 (m, 15H, CH*Me$_2$* and H^{i}PrC═C(^{t}Bu)-CHC(^{t}Bu)N[Ar]), 0.88 (overlap of doublets, 6H, CH*Me$_2$*), 0.46 (d, 3H, CH*Me$_2$*). ^{13}C NMR (23 °C, 100.6 MHz, C_6D_6): δ 171.8 (H^{i}PrC═C(^{t}Bu)CH*C*(^{t}Bu)N[Ar]), 161.5 (H*i*PrC═*C*(^{t}Bu)CHC(^{t}Bu)N-[Ar]), 157.7 (*C*$_6$H$_3$), 147.4 (*C*$_6$H$_3$), 146.9 (*C*$_6$H$_3$), 143.0 (*C*$_6$H$_3$), 142.6 (*C*$_6$H$_3$), 138.2 (*C*$_6$H$_3$), 136.0 (H^{i}Pr*C*═C(^{t}Bu)CHC(^{t}Bu)N[Ar], $J_{\mathrm{C-H}}$ = 122 Hz), 127.3 (*C*$_6$H$_3$), 125.6 (*C*$_6$H$_3$), 123.5 (*C*$_6$H$_3$), 122.7 (*C*$_6$H$_3$), 122.6 (*C*$_6$H$_3$), 122.5 (*C*$_6$H$_3$), 90.25 (H^{i}PrC═C(^{t}Bu)*C*HC-(^{t}Bu)N[Ar], $J_{\mathrm{C-H}}$ = 151 Hz), 43.47 (H^{i}PrC═C(CMe$_3$)CHC-(*C*Me$_3$)N[Ar]), 40.47 (H^{i}PrC═C(*C*Me$_3$)CHC(CMe$_3$)N[Ar]), 33.43 (*C*HMe$_2$), 31.41 (H^{i}PrC═C(CMe$_3$)CHC(C*Me*$_3$)N[Ar]), 30.61 (H^{i}Pr-C═C(C*Me*$_3$)CHC(CMe$_3$)N[Ar]), 30.20 (*C*HMe$_2$), 28.90 (*C*HMe$_2$), 28.05 (*C*HMe$_2$), 27.29 (*C*HMe$_2$), 26.79 (*Me*), 26.68 (*Me*), 25.36 (*Me*), 24.62 (two *Me* groups), 24.41 (*Me*), 24.27 (*Me*), 24.10 (*Me*), 23.49 (*Me*), 23.22 (*Me*). ^{19}F NMR (23 °C, 282.3 MHz, C_6D_6): δ −77.30 (s, Ti-O$_3$SC*F*$_3$). Anal. Calcd for $C_{40}H_{61}N_2O_3SF_3Ti$: C, 63.65; H, 8.14; N, 3.71. Found: C, 63.03; H, 7.99; N, 3.65.

Preparation of (PNP)Ti(CH$_2$CHMe$_2$)$_2$ (4). In a vial was added TiCl$_3$(THF)$_3$ [153 mg, 0.413 mmol] in toluene (5 mL), and the solution was cooled to −35 °C. To the green-blue solution was added a cold (−35 °C) yellow toluene (6 mL) solution of Li(PNP) [171 mg, 0.393 mmol]. The solution changed from blue-green to red then finally to a purple color. The solution was stirred for 1 h and then cooled to −35 °C. To the purple solution was added ClMgCH$_2$CHMe$_2$ [2 M in ether, 423 μL, 0.847 mmol] diluted in toluene (3 mL). The solution changed from purple to brown-red and was stirred for 1 h. The solution was dried in vacuo and was redissolved in pentane. The solution was filtered through a bed of Celite, and the resulting brown solution was reduced in volume in vacuo and cooled to −35 °C to give **4** as a brown powder [141 mg, 0.239 mmol, 58% yield].

For **4**: ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 9.19 ($\nu_{1/2}$ = 50 Hz), 6.56 ($\nu_{1/2}$ = 57 Hz), 5.35 ($\nu_{1/2}$ = 91 Hz), 5.21 ($\nu_{1/2}$ = 90 Hz), 3.89 ($\nu_{1/2}$ = 47 Hz), 2.52 ($\nu_{1/2}$ = 8 Hz), 2.12 ($\nu_{1/2}$ = 5 Hz), 1.97 ($\nu_{1/2}$ = 187 Hz), 0.32 ($\nu_{1/2}$ = 94 Hz), −0.27 ($\nu_{1/2}$ = 54 Hz), −4.83 ($\nu_{1/2}$ = 52 Hz), −5.34 ($\nu_{1/2}$ = 93 Hz), −23.80 ($\nu_{1/2}$ = 369 Hz). μ_{eff} = 1.91 μB (C_6D_6, 298 K, Evans' method). Multiple attempts to obtain satisfactory elemental analysis were unsuccessful.

Preparation of (PNP)Ti═CH^{i}Pr(OTf) (5). In a vial was added **4** [660 mg, 1.117 mmol] in pentane (15 mL), and the solution was cooled to −35 °C. To the solution was added solid AgOTf [301 mg, 1.171 mmol], and the solution was stirred for 1 h. The solution quickly changed from brown to a dark red color with formation of a silver mirror. The solution was filtered, reduced in volume in vacuo, and cooled to −35 °C to give **5** as dark red crystals [556 mg, 0.816 mmol, 73% yield].

For **5**: ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 8.46 (d, 1H, Ti═C*H*CHMe$_2$), 7.11−7.14 (m, 1H, C$_6$*H*$_3$), 6.86−6.96 (m, 3H, C$_6$*H*$_3$), 6.74−6.75 (m, 2H, C$_6$*H*$_3$), 2.51−2.59 (m, 1H, C*H*Me$_2$), 2.27−2.47 (m, 4H, C*H*Me$_2$), 2.15 (s, 3H, C$_6$H$_3$-*Me*), 2.07 (s, 3H, C$_6$H$_3$-*Me*), 1.54 (dd, 3H, CH*Me$_2$*), 1.24−1.39 (m, 9H, CH*Me$_2$*), 1.02−1.15 (m, 6H, CH*Me$_2$*), 0.96 (d, 3H, Ti═CHCH*Me$_2$*), 0.74−0.90 (m, 6H, CH*Me$_2$*), 0.70 (d, 3H, Ti═CHCH*Me$_2$*). ^{13}C NMR (23 °C, 100.6 MHz, C_6D_6): δ 296.9 (Ti═*C*HCHMe$_2$, $J_{\mathrm{C-H}}$ = 98 Hz), 158.8 (d, *C*$_6$H$_3$), 153.3 (d, *C*$_6$H$_3$), 133.4 (*C*$_6$H$_3$), 133.0 (*C*$_6$H$_3$), 132.7 (*C*$_6$H$_3$), 132.0 (*C*$_6$H$_3$), 131.8 (d, *C*$_6$H$_3$), 122.6 (*C*$_6$H$_3$), 121.1 (d, *C*$_6$H$_3$), 120.5 (d, *C*$_6$H$_3$), 118.1 (d, *C*$_6$H$_3$), 115.9 (d, *C*$_6$H$_3$), 47.0 (Ti═CH*C*HMe$_2$), 25.4 (Ti═CHCH*Me$_2$*), 25.2 (d, CHMe$_2$), 24.7 (Ti═CHC*Me$_2$*), 24.0 (d, CHMe$_2$), 22.3 (d, CHMe$_2$), 21.1 (C$_6$H$_3$-*Me*), 21.0 (d, CHMe$_2$), 20.7 (C$_6$H$_3$-*Me*), 20.6 (d, CHMe$_2$), 20.4 (d, CHMe$_2$), 19.5 (d, CHMe$_2$), 18.9 (d, CHMe$_2$), 18.6 (d, CHMe$_2$), 18.1 (d, CHMe$_2$), 17.6 (d, CHMe$_2$), 16.9 (d, CHMe$_2$). ^{31}P NMR (23 °C, 121.5 MHz, C_6D_6): δ 34.3 (d, $J_{\mathrm{P-P}}$ = 54 Hz), 24.8 (d, $J_{\mathrm{P-P}}$ = 54 Hz). ^{19}F NMR (23 °C, 282.3 MHz, C_6D_6): δ −77.0 (s, Ti-O$_3$SCF$_3$). Anal. Calcd for $C_{31}H_{48}NP_2TiO_3F_3S$: C, 54.63; H, 7.10; N, 2.06. Found: C, 54.57; H, 7.28; N, 2.12.

Preparation of (PNP)Ti═CH^{i}Pr(Me) (6). In a vial was added **5** [124 mg, 0.182 mmol] in pentane (4 mL), and the solution was cooled to −35 °C. To the solution was added MeMgCl [3 M in THF, 64 μL, 0.191 mmol] diluted in pentane (4 mL). The solution

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

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

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

changed from dark red to a yellow-brown color. The solution was allowed to stir for 1 h then was dried in vacuo. The solution was redissolved in pentane and filtered. The solution was reduced in volume in vacuo and cooled to −35 °C to give **6** as a yellow-brown powder [81 mg, 0.148 mmol, 82% yield].

For **6**: ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 8.38 (d, 1H, Ti=C*H*CHMe$_2$), 7.23 (dd, 1H, $C_6\mathit{H}_3$), 7.05 (dd, 1H, $C_6\mathit{H}_3$), 6.89−6.96 (m, 3H, $C_6\mathit{H}_3$), 6.83 (d, 1H, C_6H_3), 2.73 (m, 1H, Ti=CHC*H*Me$_2$), 2.30−2.45 (m, 3H, C*H*Me$_2$), 2.17 (s, 3H, C_6H_3-*Me*), 2.144 (s, 3H, C_6H_3-*Me*), 1.90 (sept, 1H, C*H*Me$_2$), 1.31−1.40 (m, 9H, CH*Me*$_2$), 1.23−1.29 (m, 6H, CH*Me*$_2$), 1.10 (d, 3H, Ti=CHCH*Me*$_2$), 1.01−1.08 (m, 6H, CH*Me*$_2$), 0.98 (d, 3H, Ti=CHCH*Me*$_2$), 0.93 (dd, 3H, CH*Me*$_2$), 0.80 (t, J_{P-H} = 2.75 Hz, 3H, Ti-C*H*$_3$). ^{13}C NMR (23 °C, 100.6 MHz, C_6D_6): δ 279.4 (Ti=*C*HCHMe$_2$), 160.0 (dd, *C*$_6$H$_3$), 156.3 (dd, *C*$_6$H$_3$), 133.1 (*C*$_6$H$_3$), 132.8 (d, *C*$_6$H$_3$), 132.7 (*C*$_6$H$_3$), 132.4 (*C*$_6$H$_3$), 128.9 (d, *C*$_6$H$_3$), 126.3 (d, *C*$_6$H$_3$), 120.8 (d, *C*$_6$H$_3$), 119.6 (d, *C*$_6$H$_3$), 118.2 (d, *C*$_6$H$_3$), 116.5 (d, *C*$_6$H$_3$), 50.0 (br, Ti-*C*H$_3$), 44.8 (Ti=CH*C*HMe$_2$), 26.6 (Ti=CHCH*Me*$_2$), 25.8 (Ti=CHCH*Me*$_2$), 25.4 (d, CHMe$_2$), 24.0 (d, CHMe$_2$), 20.9 (d, CHMe$_2$), 20.8 (C_6H_3-*Me*), 20.6 (C_6H_3-*Me*), 20.2 (d, CHMe$_2$), 19.9 (d, CHMe$_2$), 19.8 (d, CHMe$_2$), 19.6 (d, CHMe$_2$), 18.9 (d, CHMe$_2$), 18.6 (d, CHMe$_2$), 18.5 (d, CHMe$_2$), 16.9 (d, CHMe$_2$), 16.7 (d, CHMe$_2$). ^{31}P NMR (23 °C, 121.5 MHz, C_6D_6): δ 32.6 (d, J_{P-P} = 44 Hz), 22.7 (d, J_{P-P} = 44 Hz). Multiple attempts to obtain satisfactory elemental analysis were unsuccessful.

General Parameters for Data Collection and Refinement. Single crystals of **1** (pentane), **2** (hexane), **3** (hexane), and **5** (pentane) were grown at −35 °C. Inert atmosphere techniques were used to place the crystal onto the tip of a glass capillary (0.1 mm diameter) and mounted on a SMART6000 (Bruker) at 112−128(2) K. A preliminary set of cell constants was calculated from reflections obtained from three nearly orthogonal sets of 20−30 frames. The data collection was carried out using graphite-monochromated Mo Kα radiation with a frame time of 10−60 s and a detector distance of 5.0 cm. A randomly oriented region of a sphere in reciprocal space was surveyed. Three sections of 606 frames were collected with 0.30° steps in ω at different ϕ settings with the detector set at −43° in 2θ. Final cell constants were calculated from the *xyz* centroids of strong reflections from the actual data collection after integration (SAINT).[31] The structure was solved using SHELXS-97 and refined with SHELXL-97.[32] A direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares/difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters (unless otherwise mentioned). All hydrogen atoms were refined with isotropic displacement parameters (unless otherwise mentioned).

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Supporting Information Available: CIF files giving complete details for data sets, including tables with atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and structural diagrams, for complexes **1**−**3** and **5**. ^{1}H NMR spectra for **4** and **6**, as well as ^{13}C, ^{31}P, and ^{19}F NMR spectra for **6** are included. This material is available free of charge via the Internet at http://pubs.acs.org.

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