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Article

Reactivity at the β-Diketiminate Ligand Nacnac$^-$ on Titanium(IV) (Nacnac$^-$ = [Ar]NC(CH_3)CHC(CH_3)N[Ar], Ar = 2,6-[CH(CH_3)$_2$]$_2$$C_6H_3$). Diimine-alkoxo and Bis-anilido Ligands Stemming from the Nacnac$^-$ Skeleton

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The reaction of ketene $OCCPh_2$ with the four-coordinate titanium(IV) imide (L_1)Ti=NAr(OTf) (L_1^- = [Ar]NC(CH_3)CHC(CH_3)N[Ar], Ar = 2,6-[CH(CH_3)$_2$]$_2$$C_6H_3$) affords the tripodal dimine-alkoxo complex (L_2)Ti=NAr(OTf) (L_2^- = [Ar]NC(CH_3)CHC(O)=CPh_2C(CH_3)N[Ar]). Complex (L_2)Ti=NAr(OTf) forms from electrophilic attack of the β-carbon of the ketene on the γ-carbon of the Nacnac$^-$ $NCC_\gamma CN$ ring. On the contrary, nucleophiles such as LiR (R^- = Me, $CH_2{}^tBu$, and CH_2SiMe_3) deprotonate cleanly in OEt_2 the methyl group of the β-carbon on the former Nacnac$^-$ backbone to yield the etherate complex (L_3)Ti=NAr(OEt_2), a complex that is now supported by a chelate bis-anilido ligand (L_3^{2-} = [Ar]NC(CH_3)CHC(CH_2)N[Ar]). In the absence of electrophiles or nucleophiles, the robust (L_1)Ti=NAr(OTf) template was found to form simple adducts with Lewis bases such as CN^tBu or $NCCH_2$(2,4,6-$Me_3C_6H_2$). Complexes (L_2)Ti=NAr(OTf), (L_3)Ti=NAr(OEt_2), and the adducts (L_1)Ti=NAr(OTf)(XY) [XY = CN^tBu and $NCCH_2$(2,4,6-$Me_3C_6H_2$)] were structurally characterized by single-crystal X-ray diffraction studies.

Introduction

Although β-diketimines (often referred to as NacnacH) were prepared over 30 years ago,[1] the coordination chemistry developed from such a simple class of molecules is just currently undergoing a dramatic renaissance.[2,3] Several features make this class of ligands attractive. First and foremost, general syntheses of Schiff bases are often achieved easily by condensation reactions stemming from commercially available starting materials such as the amine and the corresponding dione.[3−6] This feature allows the ligands to be prepared, conveniently, in multigram scales. More novel methods for preparing β-diketimines (symmetric and asymmetric forms) have been described in depth in a current review.[3] Second, β-diketimines are easy to modify at the α-nitrogens,[3,6−10] the β-carbons,[6] and the γ-carbon positions (Figure 1).[8,11−13] Variation of these substituents provides an

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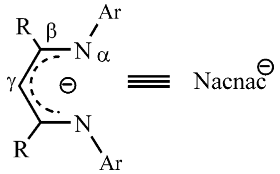

Figure 1. Representation of α-, *β*-, and *γ*-positions in the *β*-diketiminate ligand. The R group is Me or ^{t}Bu, and Ar represents a substituted or unsubstituted aryl group.

opportunity to examine both the electronic and the steric effects governing these class of ligands.

One of the most important aspects associated with the Nacnac$^-$ ligand is its ability to support reactive metal fragments.[3,8,14−18] Hence, the robust nature of Nacnac$^-$ has prompted the use of such ligands in catalysis,[17,19−22] and Nacnac-based complexes are just now becoming common targets for carrying out catalytic transformations such as olefin polymerization,[5,17,21,22] ring-opening polymerization, and copolymerization reactions.[19,20]

Although regarded as robust, the supporting *β*-diketiminate ligand in a complex can occasionally become involved in the reaction. Thus, *β*-diketiminates can potentially be "non-innocent" ligands in the context of organometallic chemistry. One common degradation of Nacnac$^-$ is C−H abstraction in the aryl groups on the α-nitrogens, leading to metalation or metal hydride formation.[3,5h,17b,23] Other, more unusual reactions of the ligand include electrophilic activation of the *γ*-carbon[3,7,8,13,24] and deprotonation of the methyl group attached to the *β*-carbon in the NCCCN ring.[3,25] More recently, cross-metathesis of the imine functionality of Nacnac$^-$ with a neopentylidene[18] or phosphinidene[26] unit has also been reported (imine−alkylidene cross-metathesis, or a Wittig/Staudinger-like reaction).[18] Inspired by the work of the groups of Budzelaar,[6] Jordan,[13] Lappert,[24] Roesky,[25] and Theopold[5d,21a,21d,21e] in the chemistry of electrophilic Nacnac-based complexes of the p-, d-, and f-block elements, we sought reactivity of Nacnac$^-$ with electrophiles and nucleophiles when this ligand is coordinated to titanium(IV).

Herein, we report the preliminary reactivity of the four-coordinate imide complex $(L_1)Ti{=}NAr(OTf)$ ($L_1^- = [Ar]NC(CH_3)CHC(CH_3)N[Ar]$, $Ar = 2{,}6\text{-}[CH(CH_3)_2]_2C_6H_3$) with unsaturated organic substrates. Our interest in exploring the chemistry of the $Ti{=}NAr$ fragment has led unexpectedly to two new class of ligands defined as L_2 and L_3 ($L_2^- = [Ar]NC(CH_3)CHC(O){=}CPh_2C(CH_3)N[Ar]$, $L_3^{2-} = [Ar]NC(CH_3)CHC(CH_2)N[Ar]$), both of which are derived from the titanium−Nacnac template "(Nacnac)Ti". When Nacnac$^-$ is coordinated to titanium(IV), two modifications of the ligand are accomplished readily. One modification occurs by electrophilic activation of the *γ*-carbon of the NCCCN ring with diphenylketene, whereas the other takes place from the deprotonation of the methyl group attached to the *β*-carbon of the Nacnac$^-$ ring with nucleophiles (e.g., alkyllithiums). These transformations occur cleanly and yield novel titanium complexes containing a tripodal diimine-alkoxo and a chelate bis-anilido ligand, respectively.

Experimental Section

General Considerations. Unless otherwise stated, all operations were performed in an M. Braun Lab Master double drybox under

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an atmosphere of purified nitrogen or using high-vacuum standard Schlenk techniques under an argon atmosphere.[27] 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.[28] Diethyl ether and CH_2Cl_2 were dried by passage through two columns of activated alumina.[28] THF was distilled, under nitrogen, from purple sodium benzophenone ketyl and stored over sodium metal. Distilled THF was transferred under vacuum into bombs before being pumped into the drybox. C_6D_6 and CD_2Cl_2 were purchased from Cambridge Isotope Laboratory (CIL), degassed, and dried over 4 Å molecular sieves and CaH_2, respectively. CD_2Cl_2 was vacuum transferred from the CaF_2 mixture and stored in a reaction vessel under N_2. Celite, alumina, and 4-Å molecular sieves were activated under vacuum overnight at 200 °C. Li(Nacnac)[4] (Nacnac$^-$ = [Ar]-NC(Me)CHC(Me)N[Ar], Ar = 2,6-$(CHMe_2)_2C_6H_3$), (Nacnac)$TiCl_2$(THF),[6,18a] (Nacnac)Ti=NAr(OTf),[18b] and OC_2Ph_2[29] were prepared according to the literature procedures. Solid Li^{t}Bu was collected by cooling a saturated pentane solution to −78 °C followed by rapid filtration. LiNHAr was prepared by deprotonation of freshly distilled aniline at −35 °C with *n*-BuLi in hexanes. The white solid was collected via filtration, washed with pentane, and dried under reduced pressure. All other chemicals were used as received. Solution infrared spectra (CaF_2 plates) were measured using a Nicolet 510P FTIR spectrometer. CHN analysis was performed by Desert Analytics, Tucson, AZ. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Varian 400- or 300-MHz NMR spectrometers. ^{1}H and ^{13}C NMR chemical shifts are reported with reference to solvent resonances (residual C_6D_5H in C_6D_6, 7.16 and 128.0 ppm; residual $CHDCl_2$ in CD_2Cl_2, 5.32 ppm 53.8 ppm). ^{19}F NMR chemical shifts are reported with respect to external $HOCOCF_3$ (−78.5 ppm). X-ray diffraction data were collected on a SMART6000 (Bruker) system under a stream of N_2(g) at low temperatures.

Synthesis of (L$_1$)Ti=NAr(OTf)(CN^{t}Bu). In 10 mL of pentane was suspended (L$_1$)Ti=NAr(OTf) (97 mg, 0.12 mmol), and the solution was cooled to −35 °C. To the cold solution was added a cold pentane solution (5 mL) containing CN^{t}Bu (10.21 mg, 0.12 mmol). After being stirred for 1 h, the solution was filtered, concentrated, and cooled overnight at −35 °C to afford in two crops yellow-brown crystals of (L$_1$)Ti=NAr(OTf)(CN^{t}Bu) (86.4 mg, 0.099 mmol, 82% yield). ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.30−6.50 (m, C_6H_3, 9H), 5.47 (s, C(Me)C*H*C(Me), 1H), 4.34 (septet, C*H*Me$_2$, 1H), 4.01 (septet, C*H*Me$_2$, 1H), 3.75 (septet, C*H*Me$_2$, 1H), 3.67 (septet, C*H*Me$_2$, 1H), 2.62 (septet, C*H*Me$_2$, 1H), 2.51 (septet, C*H*Me$_2$, 1H), 1.77 [s, C(*Me*)CHC(Me), 3H], 1.66 [s, C(Me)CHC(*Me*), 3H], 1.50 (d, CH*Me*$_2$, 3H), 1.35 (overlapping d, CH*Me*$_2$, 6H), 1.30−1.17 (overlapping d, CH*Me*$_2$, 15H), 1.14 (d, CH*Me*$_2$, 3H), 1.08 (d, CH*Me*$_2$, 3H), 1.04 (d, CH*Me*$_2$, 3H), 1.00 (d, CH*Me*$_2$, 3H), 0.98 (s, *Me*$_3$CNC, 9H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 168.2 [*C*(Me)CHC(Me)], 166.3 [C(Me)CH*C*(Me)], 159.5 (*C*N^{t}Bu), 144.4 (aryl), 144.1 (aryl), 143.5 (aryl), 143.2 (aryl), 142.4 (aryl), 141.7 (aryl), 128.1 (aryl), 127.9 (aryl), 127.0 (aryl), 127.0 (aryl), 125.1 (aryl), 124.9 (aryl), 124.4 (aryl), 124.2 (aryl), 124.1 (aryl), 122.8 (aryl), 122.2 (aryl), 101.7 [C(Me)*C*HC(Me), 1H], 57.33 (CN*C*Me$_3$), 29.24 (*C*HMe$_2$), 29.06 (CNC*Me*$_3$), 28.02 (*C*HMe$_2$), 27.82 (*C*HMe$_2$), 27.79 (*C*HMe$_2$), 27.67 (*C*HMe$_2$), 26.26 (CH*Me*$_2$), 26.01 (CH*Me*$_2$), 25.89 (CH*Me*$_2$), 25.51 (CH*Me*$_2$), 25.25 (CH*Me*$_2$), 25.19 (CH*Me*$_2$), 24.94 (CH*Me*$_2$), 24.80 (CH*Me*$_2$), 24.73 (CH*Me*$_2$), 24.64 (CH*Me*$_2$), 24.38 (CH*Me*$_2$), 24.24 (CH*Me*$_2$), 23.67 (CH*Me*$_2$). ^{19}F NMR (23 °C, 282.3 MHz, C_6D_6): δ −77.19 (OSO$_2$C*F*$_3$). IR (CaF_2, C_6H_6): 3098 (m), 3071 (s), 3029 (s), 2967 (s), 2868 (m), 2213 (m, $\nu_{C\equiv N}$), 1818 (w), 1529 (s), 1483 (s), 1464 (m), 1437 (m), 1378 (s), 1341 (s), 1315 (s), 1274 (m), 1255 (m), 1236 (m), 1200 (s), 1103 (w), 1039 (s), 1003 (s) cm^{-1}. Anal. Calcd for $C_{47}H_{67}N_4O_3F_3STi$: C, 64.66; H, 7.34; N, 6.42. Found: C, 65.00; H, 7.73; N, 6.31.

Synthesis of (L$_1$)Ti=NAr(OTf)(NCH$_2$Mes). In 5 mL of pentane was suspended (L$_1$)Ti=NAr(OTf) (77 mg, 0.097 mmol), and the solution was cooled to −35 °C. To the cold solution was added a cold pentane solution (5 mL) containing mesitylacetonitrile (15.5 mg, 0.097 mmol). After 5 min, a yellow-brown precipitate began to form, and the reaction mixture was allowed to stir for an additional 40 min. The solid was collected by filtration and washed with cold pentane. Recrystallization from Et_2O at −35 °C afforded two crops of brown crystals of (L$_1$)Ti=NAr(OTf)(NCCH$_2$Mes) (64.6 mg, 0.068 mmol, 70% yield). ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.3−6.5 (m, C_6H_3, 9H), 6.61 (s, C$_6$*H*$_2$, 2H), 5.48 [s, C(Me)C*H*C(Me), 1H], 4.32 (septet, C*H*Me$_2$, 1H), 4.07 (septet, C*H*Me$_2$, 1H), 3.82 (septet, C*H*Me$_2$, 1H), 3.61 (septet, C*H*Me$_2$, 1H), 3.31 (dd, NCC*H*$_2$Mes, 2H), 2.61 (septet, C*H*Me$_2$, 1H), 2.45 (septet, C*H*Me$_2$, 1H), 2.09 (s, *p-Me*$_3$C$_6$H$_2$, 3H), 2.01 (s, o-*Me*$_3$C$_6$H$_2$, 6H), 1.78 (s, C(*Me*)CHC(Me), 3H), 1.71 [s, C(Me)CHC(*Me*), 3H], 1.46 (d, CH*Me*$_2$, 3H), 1.39 (d, CH*Me*$_2$, 3H), 1.30−1.18 (overlapping d, CH*Me*$_2$,18H), 1.15 (d, CH*Me*$_2$, 3H), 1.07 (d, CH*Me*$_2$, 6H), 0.96 (d, CH*Me*$_2$, 3H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 168.0 [*C*(Me)CHC(Me)], 166.7 [C(Me)CH*C*(Me)], 159.8 (N*C*CH$_2$), 147.6 (aryl), 146.5 (aryl), 145.0 (aryl), 143.4 (aryl), 142.4 (aryl), 141.9 (aryl), 141.4 (aryl), 140.4 (aryl), 138.0 (aryl), 137.1 (aryl), 129.4 (aryl), 128.1 (aryl), 127.9 (aryl), 127.5 (aryl), 127.4 (aryl), 127.2 (aryl), 127.0 (aryl), 126.6 (aryl), 124.8 (aryl), 124.5 (aryl), 124.2 (aryl), 124.2 (aryl), 123.0 (aryl), 122.8 (aryl), 122.3 (aryl), 122.1 (aryl), 29.18, 27.94 27.79, 27.73, 26.03, 25.89, 25.77, 25.47, 25.20, 24.97, 24.91, 24.78 (*Me*), 24.21 (*Me*), 24.10 (*Me*), 23.54 (*Me*), 23.32 (*Me*), 20.87 (*Me*), 20.40 (*Me*), 18.48 (*Me*). ^{19}F NMR (23 °C, 282.3 MHz, C_6D_6): δ −78.16 (OSO$_2$C*F*$_3$). IR (CaF_2, C_6H_6): 3077 (s), 3029 (s), 3023 (w), 2965 (w), 1960 (m, $\nu_{C\equiv N}$), 1815 (m), 1586 (w), 1529 (w), 1474 (s), 1351 (w), 1227 (w), 1199 (w), 1007 (s) cm^{-1}. Anal. Calcd for $C_{53}H_{71}N_4O_3F_3STi$: C, 67.07; H, 7.54; N, 5.90. Found: C, 67.39; H, 7.82; N, 5.89.

Synthesis of (L$_2$)Ti=NAr(OTf). In 5 mL of Et_2O was dissolved (L$_1$)Ti=NAr(OTf) (60.8 mg, 0.08 mmol), and the solution was cooled to −35 °C. To the cold solution was added an equally cold Et_2O solution (5 mL) containing OC_2Ph_2 (17 mg, 0.09 mmol). After 10 min, a yellow-brown precipitate began to form, and the reaction mixture was allowed to stir for an additional 40 min. The solid was collected by filtration and washed with cold pentane. Recrystallization from THF layered with pentane at −35 °C afforded two crops of brown crystals of (L$_2$)Ti=NAr(OTf) (65.26 mg, 0.07 mmol, 87% yield). ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.86 [d, (C$_6$*H*$_5$)$_2$C=C−O, 2H], 7.30−6.60 (m, C$_6$*H*$_3$ and C$_6$*H*$_5$, 17H), 4.64 [s, C(Me)C*H*C(Me), 1H], 4.60 (septet, C*H*Me$_2$, 1H), 3.81 (septet, C*H*Me$_2$, 1H), 3.00 (septet, C*H*Me$_2$, 1H), 2.90 (septet, C*H*Me$_2$, 1H), 2.77 (septet, C*H*Me$_2$, 1H), 2.38 (septet, C*H*Me$_2$, 1H), 1.70 (d, CH*Me*$_2$, 3H), 1.63 (d, CH*Me*$_2$, 3H), 1.52 (d, CH*Me*$_2$, 3H), 1.49 (d, CH*Me*$_2$, 3H), 1.43 [s, C(*Me*)CHC(Me), 3H], 1.20 (d, CH*Me*$_2$, 3H), 1.16 (d, CH*Me*$_2$, 3H), 1.13 [s, C(Me)CHC(*Me*), 3H], 1.08 (d, CH*Me*$_2$, 3H), 1.05 (d, CH*Me*$_2$, 3H), 0.97 (d, CH*Me*$_2$, 3H), 0.82 (d, CH*Me*$_2$, 3H), 0.67 (d, CH*Me*$_2$, 3H), 0.39 (d, CH*Me*$_2$, 3H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 179.5 [*C*(Me)CHC(Me)], 171.5

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(27) 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, DC, 1987; pp 79−98.

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

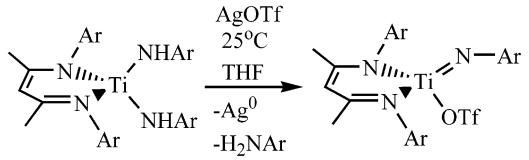
(29) Taylor, E. C.; McKillop, A.; Hawks, G. H. *Org. Synth.* **1988**, *50*, 549.

[C(Me)CH*C*(Me)], 158.2 (Ph$_2$C=*C*O), 150.1 (aryl), 149.3 (aryl), 146.3 (aryl), 143.7 (aryl), 142.5 (aryl), 142.1 (aryl), 141.3 (aryl), 141.2 (aryl), 140.9 (aryl), 140.1 (aryl), 139.4 (aryl), 131.6 (aryl), 129.9 (aryl), 129.1 (aryl), 128.5 (aryl), 127.6 (aryl), 127.4 (aryl), 127.2 (aryl), 126.2 (aryl), 126.0 (aryl), 125.0 (aryl), 124.5 (aryl), 124.2 (aryl), 123.3 (aryl), 122.4 (aryl), 122.1 (aryl), 116.1 (Ph$_2$*C*=CO), 63.63 [C(Me)*C*HC(Me), J_{C-H} = 134 Hz], 29.22 (*C*HMe$_2$), 28.84 (*C*HMe$_2$), 28.55 (*C*HMe$_2$), 28.49 (*C*HMe$_2$), 27.87 (*C*HMe$_2$), 27.56 (*C*HMe$_2$), 26.09 (*Me*), 25.62 (*Me*), 25.47 (*Me*), 25.29 (*Me*), 25.98 (*Me*), 24.95 (*Me*), 24.91 (*Me*), 24.74 (*Me*), 24.68 (*Me*), 24.03 (*Me*), 23.86 (*Me*), 23.76 (*Me*), 22.75 (*Me*). ^{19}F NMR (23 °C, 282.3 MHz, C_6D_6): δ −75.20 (OSO$_2$C*F*$_3$). IR (CaF_2, C_6H_6): 3071 (s), 3040 (s), 3029 (s), 2965 (s), 2869 (s), 1642 (m), 1585 (m), 1492 (w), 1474 (m), 1464 (m), 1442 (m), 1351 (s), 1324 (w), 1275 (w), 1227 (s), 1199 (s), 1136 (m), 1069 (m), 1039 (s), 1034 (s), 1007 (s), 963 (m), 912 (m) cm^{-1}. Anal. Calcd for $C_{56}H_{68}N_3O_4F_3STi$: C, 68.34; H, 6.96; N, 4.27. Found: C, 68.54; H, 7.12; N, 4.55.

Synthesis of (L$_3$)Ti=NAr(OEt$_2$). In 10 mL of Et_2O was dissolved (L$_1$)Ti=NAr(OTf) (190 mg, 0.24 mmol), and the solution was cooled to −35 °C. To the cold solution was added a cold Et_2O solution (5 mL) of LiCH$_2$^{t}Bu (20.64 mg, 0.26 mmol) (alternatively, 1.1 equiv of LiMe and LiCH$_2$SiMe$_3$ can be used). After being stirred for 30 min, the solution was filtered and dried under reduced pressure. The yellow powder was extracted with pentane, filtered, concentrated, and cooled to −35 °C to afford two crops of yellow crystals of (L$_3$)Ti=NAr(OEt$_2$) (138.2 mg, 0.19 mmol, 80% yield). ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.30−6.60 (m, C$_6$*H*$_3$, 9H), 5.14 [s, C(Me)C*H*C(CH$_2$), 1H], 4.70 [m, O(C*H*$_2$CH$_3$)$_2$, 2H], 4.00 (septet, C*H*Me$_2$, 1H), 3.91 [m, O(C*H*$_2$CH$_3$)$_2$, 2H], 3.79 (septet, C*H*Me$_2$, 1H), 3.61 [s, C(Me)CHC(C*H*$_2$), 1H], 3.49 (septet, C*H*Me$_2$, 2H), 3.33 [s, C(Me)CHC(C*H*$_2$), 1H], 3.29 (d, CH*Me*$_2$, 2H), 1.53 [s, C(*Me*)CHC(CH$_2$), 3H], 1.50 (d, CH*Me*$_2$, 3H), 1.46 (d, CH*Me*$_2$, 3H), 1.44 (d, CH*Me*$_2$, 3H), 1.43 (d, CH*Me*$_2$, 3H), 1.36 (d, CH*Me*$_2$, 3H), 1.30 (d, CH*Me*$_2$, 3H), 1.19 (d, CH*Me*$_2$, 3H), 1.06 (d, CH*Me*$_2$, 3H), 0.99 (d, CH*Me*$_2$, 6H), 0.81 [t, O(CH$_2$C*H*$_3$)$_2$, 6H], 0.74 (d, CH*Me*$_2$, 6H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 157.5 [*C*(Me)CHC(CH$_2$)], 152.8 (aryl), 148.2 (aryl), 147.8 (aryl), 144.8 (aryl), 144.2 (aryl), 143.3 (aryl), 142.7 (aryl), 142.6 (aryl), 141.9 (aryl), 125.8 (aryl), 125.6 (aryl), 124.8 (aryl), 124.2 (aryl), 123.9 (aryl), 123.6 (aryl), 122.2 (aryl), 121.2 (aryl), 100.4 [C(Me)*C*HC(CH$_2$), J_{C-H} = 156 Hz], 86.28 [C(Me)CHC(*C*H$_2$), J_{C-H} = 157 Hz], 70.48 [O(*C*H$_2$CH$_3$)$_2$], 28.66 (*C*HMe$_2$), 28.53 (*C*HMe$_2$), 28.31 (*C*HMe$_2$), 28.16 (*C*HMe$_2$), 27.81 (*C*HMe$_2$), 26.52 (*Me*), 25.67 (*Me*), 25.50 (*Me*), 25.17 (*Me*), 25.14 (*Me*), 25.11 (*Me*), 25.04 (*Me*), 24.44 (*Me*), 24.05 (*Me*), 23.75 (*Me*), 23.69 (*Me*), 13.12 (O(CH$_2$*C*H$_3$)$_2$). IR (CaF_2, C_6H_6): 3098 (s), 3071 (s), 3029 (s), 2962 (s), 2927 (s), 2867 (s), 1814 (w), 1597 (m), 1495 (m), 1463 (s), 1438 (s), 1420 (s), 1359 (s), 1325 (s), 1277 (s), 1254 (s), 1240 (m), 1202 (s), 1109 (m), 1039 (s), 1000 (s), 974 (m) cm^{-1}. Anal. Calcd for $C_{45}H_{67}N_3OTi$: C, 75.70; H, 9.46; N, 5.89. Found: C, 75.96; H, 9.84; N, 6.25.

X-ray Crystallography. Inert-atmosphere techniques were used to place the crystal onto the tip of a diameter glass capillary (0.06−0.20 mm) mounted on a SMART6000 (Bruker) at 113(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 3 s and a detector distance of 5.0 cm. A randomly oriented region of a sphere in reciprocal space was surveyed. Three sections of 606 frames were collected with 0.30° steps in ω at different ϕ settings with the detector set at −43° in 2θ. Final cell constants were calculated from the *xyz* centroids of strong reflections from the actual data collection after integration (SAINT).[30] The structure was solved using SHELXS-97 and refined with SHELXL-97.[31] 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 that located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were refined with isotropic displacement parameters (unless otherwise specified).

Scheme 1. Synthetic Route to the Four-Coordinate Titanium Imide Complex (L$_1$)Ti=NAr(OTf) by Oxidatively Induced α-Hydrogen Abstraction.



(L$_1$)Ti=NAr(OTf)

(L$_1$)Ti=NAr(OTf)(CN^{t}Bu). Single crystals were grown at −35 °C from a saturated pentane solution. Intensity statistics and systematic absences suggested the centrosymmetric space group C_c, and subsequent solution and refinement confirmed this choice. 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.

(L$_1$)Ti=NAr(OTf)(NCCH$_2$Mes). Single crystals were grown at −35 °C from a saturated pentane solution. Intensity statistics and systematic absences suggested the centrosymmetric space group $P2_1/n$, and subsequent solution and refinement confirmed this choice. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement.

(L$_2$)Ti=NAr(OTf)·2THF. Single crystals were grown at −35 °C from a saturated THF solution layered with pentane. Intensity statistics and systematic absences suggested the centrosymmetric space group *P*-1. In addition to the titanium complex, two THF solvent molecules are present. One is well-defined, and the other is disordered. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms with the exception of those associated with one disordered THF were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement.

(L$_3$)Ti=NAr(OEt$_2$). Single crystals were grown at −35 °C from a saturated pentane solution. Intensity statistics and systematic absences suggested the centrosymmetric space group *P*-1 and subsequent solution and refinement confirmed this choice. 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.

Results and Discussion

When an ether-based solution of the four-coordinate titanium imide complex (L$_1$)Ti=NAr(OTf)[18b] (prepared according to Scheme 1) is treated with Lewis bases such as XY (XY = CN^{t}Bu or NCCH$_2$Mes), the adduct (L$_1$)Ti=NAr(OTf)(XY) (XY = CN^{t}Bu, 82%; XY = NCCH$_2$Mes, Mes

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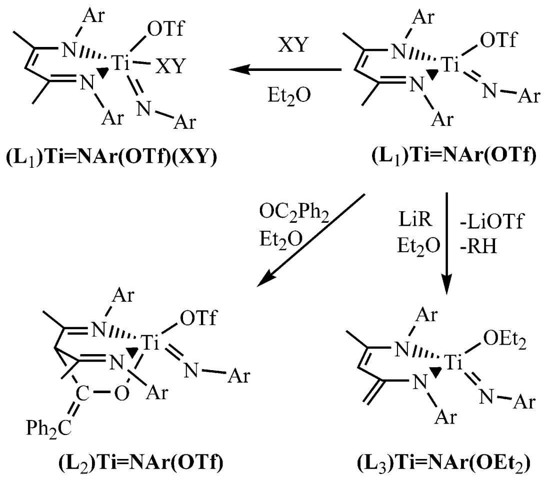
[30] *SAINT 6.1*; Bruker Analytical X-ray Systems: Madison, WI.

[31] *SHELXTL-Plus V5.10*; Bruker Analytical X-ray Systems: Madison, WI.

Table 1. Crystallographic Data for Complexes $(L_1)Ti{=}NAr(OTf)(CN^tBu)$, $(L_1)Ti{=}NAr(OTf)(NCCH_2Mes)$, $(L_2)Ti{=}NAr(OTf)$, and $(L_3)Ti{=}NAr(OEt_2)$

parameter	$(L_1)Ti{=}NAr(OTf)(CN^tBu)$	$(L_1)Ti{=}NAr(OTf)(NCCH_2Mes)$	$(L_2)Ti{=}NAr(OTf)\cdot 2THF$	$(L_3)Ti{=}NAr(OEt_2)$
empirical formula	$C_{47}H_{67}F_3N_4O_3STi$	$C_{53}H_{71}F_3N_4O_3STi$	$C_{64}H_{84}F_3N_3O_6STi$	$C_{45}H_{67}N_3OTi$
fw	873.01	949.10	1128.30	713.92
crystal system	monoclinic	monoclinic	triclinic	triclinic
space group	*Cc*	*P*2(1)/*n*	*P*-1	*P*-1
a (Å)	18.9125(15)	11.3530(9)	12.455(3)	9.7831(9)
b (Å)	20.0232(16)	23.7155(17)	14.406(4)	10.1479(9)
c (Å)	12.5736(10)	19.1055(14)	18.099(5)	21.7959(19)
α (°)			81.171(7)	79.492(2)
β (°)	98.115(2)	90.474(2)	72.595(7)	87.819(2)
γ (°)			81.697(7)	80.713(2)
V (Å^3)	4713.8(6)	5143.8(7)	3045.2(14)	2099.6(3)
Z	4	4	2	2
D_{calc} (g·cm^{-3})	1.230	1.226	1.231	1.129
crystal size (mm)	0.35 × 0.28 × 0.18	0.30 × 0.25 × 0.25	0.26 × 0.24 × 0.24	0.28 × 0.28 × 0.12
solvent habit, color	Et_2O, yellow-brown	Et_2O, yellow-brown	THF/pentane, orange	Et_2O, yellow
(*h*, *k*, *l*)	$-24 \le h \le 24$, $-25 \le k \le 26$, $-16 \le l \le 16$	$-14 \le h \le 14$, $-30 \le k \le 30$, $-24 \le l \le 24$	$-16 \le h \le 16$, $-18 \le k \le 18$, $-23 \le l \le 23$	$-12 \le h \le 12$, $-13 \le k \le 13$, $-28 \le l \le 28$
F(000)	1864	2024	1204	776
Θ range	2.32−27.50	1.99−27.52	1.97−27.58	2.31−27.49
linear abs. coeff. (mm^{-1})	0.280	0.263	0.236	0.239
total reflcns collected	44443	57739	67596	34820
independent reflcns	10742	11827	14002	9642
unique reflcns	9927	6156	9398	7848
R_{int}	0.0558	0.1054	0.1646	0.0602
data/parameter	10 742/801	11 827/870	14 002/1029	9642/719
R1, wR2 (for $I > 2\sigma(I)$	0.0304, 0.0742	0.0448, 0.0964	0.0544, 0.1662	0.0398, 0.1095
GoF	1.005	0.813	0.992	1.044
peak/hole (e/Å^{-3})	0.252, −0.199	0.319, −0.328	0.887, −0.443	0.566, −0.278

Scheme 2. Synthetic Routes to $(L_1)Ti{=}NAr(OTf)(XY)$ and the Nacnac− Derivatives $(L_2)Ti{=}NAr(OTf)$ and $(L_3)Ti{=}NAr(OEt_2)$ [XY = CN^tBu or $NCCH_2(2,4,6\text{-}Me_3C_6H_2)$; R− = Me, $CH_2{}^tBu$, or CH_2SiMe_3; Ar = $2,6\text{-}[CH(CH_3)_2]_2C_6H_3$].



= $2,4,6\text{-}Me_3C_6H_2$, 70%) is formed in good yield (Scheme 2). Complex $(L_1)Ti{=}NAr(OTf)(XY)$ displays ^1H and ^{13}C NMR resonances in accordance with a C_1 symmetric molecule. Hence, coordination of the base disrupts the former C_s symmetry observed in the imide precursor, thus rendering both aryl groups on β-diketiminate α-nitrogens and β-methyl groups on the Nacnac$^-$ backbone nonequivalent. Other ^1H and ^{13}C NMR spectroscopic features diagnostic of low symmetry include the observation of four nonequivalent isopropyl groups, each having two diasteriotopic methyls and thus portraying a total of eight doublets. Solution IR spectra of $(L_1)Ti{=}NAr(OTf)(CN^tBu)$ indicates that the $\nu_{C\equiv N}$ stretch (2213 cm^{-1}) shifts significantly to higher wavenumbers from that of the corresponding free base, CN^tBu (2134 cm^{-1}).[32] The shift to higher energies in $(L_1)Ti{=}NAr(OTf)(CN^tBu)$ is characteristic for electrophilic metal centers binding CN^tBu.[33] The solution IR spectrum of complex $(L_1)Ti{=}NAr(OTf)(NCCH_2Mes)$ also displays a $\nu_{N\equiv C}$ stretch centered at 1960 cm^{-1}, characteristic of a bound nitrile.

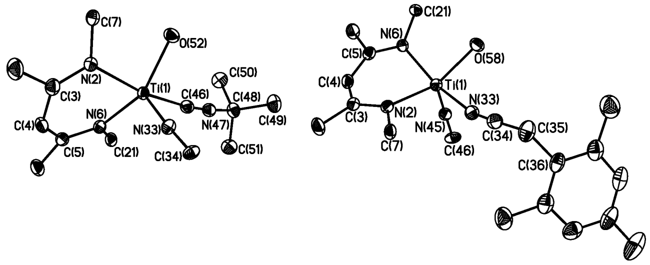


Figure 2. Molecular structure of base adducts $(L_1)Ti{=}NAr(OTf)(CN^tBu)$ (left) and $(L_1)Ti{=}NAr(OTf)(NCCH_2Mes)$ (right) showing atom-labeling scheme with thermal ellipsoids at the 50% probability level. H-atoms and aryl groups on the nitrogens with the exception of the ipso-carbon have been omitted for clarity. O_2SCF_3 groups on the O(52) and O(58) of the triflate ligand have also been excluded.

Single crystals of the adduct $(L_1)Ti{=}NAr(OTf)(XY)$ were grown from pentane at −35 °C. The molecular representation for each complex is depicted in Figure 2. Crystallographic data are displayed in Table 1, and selected metrical parameters are listed in Table 2. Each molecule adopts a pseudo-square-pyramidal geometry with the Lewis base occupying the axial site. Inspection of each structure reveals a chemically unperturbed "(Nacnac)Ti=NAr(OTf)" framework, where coordination of the base only induced geometrical rearrangements in the complex. The $Ti{-}O_{triflate}$, $Ti{-}N_{Nacnac}$, and $Ti{-}N_{imide}$ bond lengths are not deviated considerably from that

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[32] Solution IR (C_6H_6, CaF_2) stretches for free CN^tBu and $NCCH_2(2,4,6\text{-}Me_3C_6H_2)$ are 2134 and 2249 cm^{-1}, respectively.

[33] For an example of an electrophilic Ti(IV) complex having a bound CN^tBu ligand see: Carofiglio, T.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1989**, *28*, 4417.

Table 2. Selected Interatomic Distances (Å) and Angles (°)

$\mathrm{(L_1)Ti{=}NAr(OTf)(CN^{t}Bu)}$							
Ti(1)−N(33)	1.712(3)	Ti(1)−O(52)	2.037(1)	Ti(1)−N(6)	2.086(3)	Ti(1)−N(2)	2.098(3)
Ti(1)−C(46)	2.300(6)	N(6)−C(5)	1.342(2)	C(3)−C(4)	1.402(2)	N(2)−C(3)	1.336(2)
C(4)−C(5)	1.398(2)	C(46)−N(47)	1.143(2)	N(33)−C(34)	1.390(2)	N(6)−C(21)	1.452(2)
N(2)−C(7)	1.458(2)	Ti(1)−C(46)−N(47)	173.2(3)	Ti(1)−N(33)−C(34)	173.2(1)	Ti(1)−N(6)−C(5)	123.5(1)
Ti(1)−N(2)−C(3)	121.84(11)	O(52)−Ti(1)−C(46)	82.02(5)	O(52)−Ti(1)−N(2)	89.11(5)	O(52)−Ti(1)−N(6)	138.99(5)
O(52)−Ti(1)−N(33)	111.32(6)	N(2)−Ti(1)−N(6)	87.64(5)	N(2)−Ti(1)−N(33)	103.42(6)	N(6)−Ti(1)−N(33)	109.19(6)
N(2)−Ti(1)−C(46)	161.03(5)	N(6)−Ti(1)−C(46)	88.14(5)	N(33)−Ti(1)−C(46)	95.44(6)	N(2)−C(3)−C(4)	123.8(5)
C(3)−C(4)−C(5)	128.0(5)	N(6)−C(5)−C(4)	123.1(5)	C(46)−N(47)−C(48)			
$\mathrm{(L_1)Ti{=}NAr(OTf)(NCCH_2Mes)}$							
Ti(1)−N(33)	2.211(9)	Ti(1)−O(58)	2.051(4)	Ti(1)−N(2)	2.090(7)	Ti(1)−N(6)	2.088(7)
N(33)−C(34)	1.138(3)	N(2)−C(3)	1.337(3)	N(6)−C(5)	1.335(3)	C(5)−C(4)	1.393(3)
Ti(1)−N(45)	1.697(7)	N(45)−C(46)	1.402(3)	N(2)−C(7)	1.449(2)	N(6)−C(21)	1.455(2)
Ti(1)−N(45)−C(46)	177.2(6)	Ti(1)−N(6)−C(5)	121.8(4)	Ti−N(2)−C(3)	123.0(4)	N(2)−C(3)−C(4)	123.4(2)
Ti(1)−N(33)−C(34)	167.4(8)	O(58)−Ti(1)−N(33)	80.98(6)	N(33)−Ti(1)−N(2)	88.26(6)	N(33)−Ti(1)−N(6)	156.82(7)
N(33)−Ti(1)−N(45)	98.13(7)	N(6)−C(5)−C(4)	123.6(9)	O(58)−Ti(1)−N(2)	142.24(6)	O(58)−Ti(1)−N(6)	88.66(6)
O(58)−Ti(1)−N(45)	112.15(7)	C(3)−C(4)−C(5)	128.2(2)	C(34)−C(35)−C(36)	113.5(2)	N(45)−Ti(1)−N(6)	104.98(7)
N(45)−Ti−N(2)	105.13(7)	N(6)−Ti(1)−N(2)	87.38(6)				
$\mathrm{(L_2)Ti{=}NAr(OTf)}$							
Ti(1)−N(48)	1.729(2)	Ti(1)−N(6)	2.477(2)	Ti(1)−O(33)	1.930(5)	Ti(1)−N(2)	2.187(9)
Ti(1)−O61	2.262(6)	Ti(1)−O62	2.219(6)	N(48)−C(49)	1.388(3)	N(2)−C(7)	1.465(3)
N(6)−C(21)	1.448(3)	N(2)−C(3)	1.287(3)	N(6)−C(5)	1.290(3)	C(3)−C(4)	1.517(3)
C(5)−C(4)	1.516(3)	O(33)−C(34)	1.332(3)	Ti(1)−S63	2.794(1)	C(34)−C(35)	1.356(3)
O(33)−C(34)−C(35)	124.1(2)	N(48)−Ti(1)−N(2)	100.11(8)	N(2)−Ti(1)−N(6)	82.69(7)	N(48)−Ti(1)−N(6)	177.20(7)
N(48)−Ti(1)−O(33)	101.04(8)	N(2)−Ti(1)−O(33)	84.22(7)	Ti(1)−N(6)−C(5)	114.8(5)	N(6)−Ti(1)−O(33)	79.16(6)
Ti(1)−N(2)−C(3)	118.5(4)	Ti(1)−O(33)−C(34)	128.9(3)	N(6)−C(5)−C(4)	118.1(2)	N(2)−C(3)−C(4)	121.2(9)
O(33)−C(34)−C(4)	114.4(8)	O62−Ti(1)−O61	63.16(6)	Ti(1)−N(48)−C(49)	171.8(5)		
$\mathrm{(L_3)Ti{=}NAr(OEt_2)}$							
Ti(1)−N(33)	1.726(2)	Ti(1)−N(6)	1.966(1)	Ti(1)−O(46)	2.100(1)	Ti(1)−N(2)	1.939(2)
N(2)−C(7)	1.435(7)	N(6)−C(21)	1.442(8)	N(33)−C(34)	1.391(7)	C(3)−C(4)	1.357(2)
N(6)−C(21)	1.442(8)	N(2)−C(3)	1.408(7)	N(6)−C(5)	1.406(7)	C(3)−C19	1.505(2)
C(5)−C(20)	1.348(2)	Ti(1)−N(6)−C(5)	111.55(9)	Ti(1)−N(2)−C(3)	103.19(8)	Ti(1)−N(33)−C(34)	168.9(1)
N(33)−Ti(1)−N(2)	112.83(5)	N(33)−Ti(1)−N(6)	113.40(5)	N(2)−Ti(1)−N(6)	103.10(5)	N(33)−Ti(1)−O(46)	100.26(5)
N(2)−Ti(1)−O(46)	110.77(5)	N(6)−Ti(1)−O(46)	116.89(5)	C(4)−C(3)−C19	119.3(3)	C(4)−C(5)−C(20)	118.0(3)
C(3)−C(4)−C(5)	131.8(3)						

of the base-free precursor (L$_1$)Ti=NAr(OTf).[18b] The isonitrile− and nitrile−titanium bond lengths are merely dative [2.300(6) and 2.211(9) Å), respectively], whereas the N≡C and C≡N bonds are very short [1.143(2) and 1.138(3) Å, respectively] and relatively unperturbed from that of the free Lewis base.[33,34]

Formation of the adducts was somewhat surprising as precedent in the literature concerning the chemistry of four-coordinate titanium imido species suggests that low-coordination environments triggers interesting reactivity.[35,36] In fact, four-coordinate group 4 imido complexes are exceedingly rare,[35,37] presumably because of their inherent reactivity. Complex (L$_1$)Ti=NAr(OTf) fails to react with polar molecules such as CO_2, azides, and N_2CPh_2. Such a result in combination with formation of the adduct (L$_1$)Ti=NAr(OTf)(XY) indicates clearly the robust nature of the (Nacnac)Ti=NAr framework. We also have no evidence to suggest that the bound $^-$OTf ligand in complex (L$_1$)Ti=NAr(OTf)(XY) is dissociating in solution. Lewis bases such as THF or Et_2O do not appear to displace the XY ligands bound to complex (L$_1$)Ti=NAr(OTf).

Our interest in group-transfer reactions stimulated us to investigate the reactivity the Ti=NAr functionality in (L$_1$)Ti=NAr(OTf). Titanium is oxophilic; hence, it was thought that reactions of imido (L$_1$)Ti=NAr(OTf) with unsaturated organic reagents having an O-group could lead to imide group transfer.[36a,38] Treatment of (L$_1$)Ti=NAr(OTf) with OC_2Ph_2 does not attack the Ti=NAr motif inasmuch as a new single product is formed in which the Nacnac$^-$ ligand has undergone electrophilic attack at the γ-carbon of the

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(34) A search in the Structural Database shows crystallized free nitriles to have bond lengths between 1.13 and 1.16 Å: Britton, D. *Cryst. Struct. Commun.* **1979**, *8*, 667. For a bound nitrile to an electrophilic early-transition metal center see: Chen, C.-T.; Doerrer, L. H.; Williams, V. C.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **2000**, 297.

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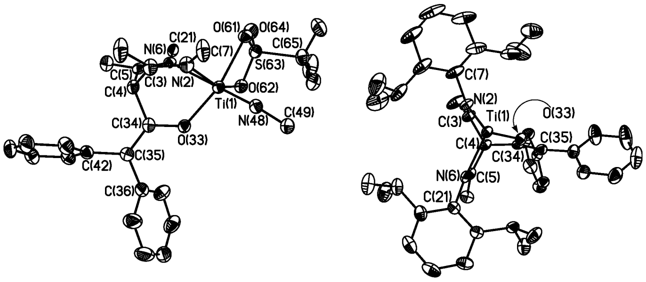

Figure 3. Molecular structure of $(L_2)Ti{=}NAr(OTf)$ showing atom-labeling scheme with thermal ellipsoids at the 50% probability level. H-atoms and the aryl groups on the nitrogen atoms with the exception of the ipso-carbons have been omitted for clarity (left). A perspective view (right) of the ligand down the Ti(1)−C(4) axis is also shown, and the imide and OTf groups on titanium have been omitted for clarity. Two disordered THF molecules present in the asymmetric unit have also been excluded.

NCCCN ring to form $(L_2)Ti{=}NAr(OTf)$ (Scheme 2). It has been demonstrated previously that electrophiles attack the γ-carbon of β-diketiminates, and in some cases, the functionalized ligand can be coordinated to metals.[13,24] Thus, diphenylketene, having an oxygen atom, an electrophilic β-carbon, and a low HOMO−LUMO gap at the C=O bond,[39] makes a suitable reagent for the (Nacnac)Ti frame. A key spectroscopic feature in the formation of $(L_2)Ti{=}NAr(OTf)$ is the dramatic shift in the ^{13}C NMR spectrum of the sp^2 $C_\gamma H$ in the $NCC_\gamma CN$ ring from 94.4 ppm [for complex $(L_1)Ti{=}NAr(OTf)$] to 63.6 ppm [for complex $(L_2)Ti{=}NAr(OTf)$]. This feature is not surprising because such a carbon has undergone rehybridization to an sp^3 CH with J_{C-H} = 134 Hz.[13,40] Both ^1H and ^{13}C NMR spectra are in accordance with complex $(L_2)Ti{=}NAr(OTf)$ retaining C_1 symmetry in solution.

Single crystals suitable for X-ray diffraction were grown from a THF solution layered with pentane at −35 °C, and the molecular structure is depicted in Figure 3. Crystal data and selected metrical parameters are shown in Tables 1 and 2, respectively. Salient features in the crystal structure of $(L_2)Ti{=}NAr(OTf)$ include a short and unperturbed $Ti{=}N_{\{imido\}}$ functionality [Ti(1)−N(48), 1.729(2) Å]. The former Nacnac$^-$ ligand has undergone electrophilic attack at the γ-carbon and is now transformed into a monoanionic tripodal ligand (Figure 3, right side) containing an alkoxo and two imine functionalities with short N=C bonds [N(6)−C(5), 1.290(3) Å; N(2)−C(3), 1.287(3) Å]. The molecule has C_1 symmetry in the solid state, which is also consistent with ^1H and ^{13}C NMR solution spectra (vide supra). The $Ti(1)-N_{\{imine\}}$ distances are considerably longer [$Ti(1)-N_{\{imine\}}$, 2.187(9) and 2.477(2) Å] when compared to the $Ti-N_{\{Nacnac\}}$ distances of the former $(L_1)Ti{=}NAr(OTf)$ complex [$Ti-N_{\{Nacnac\}}$, 1.978(5) and 2.029(5) Å].[18b] In fact, the latter bond length for Ti(1)−N(6) suggests that the imine is weakly bound to the metal. The structure of the titanium complex containing the L_2^- ligand also reveals an olefinic functionality [C(34)−C(35), 1.356(3) Å] present in the β-carbon of the now-bound α-alkoxide [Ti(1)−O(33), 1.930(5) Å]. Complex $(L_2)Ti{=}NAr(OTf)$ is stable both as a solid and in solution, which is not surprising as η^2-coordination of the $^-$OTf and π-donation of the alkoxo, the two imines, and the imide functionalities saturate the coordination environment as well as supply the titanium center with sufficient electron density. Facile and clean coordination of diphenylketene across the γ-carbon and titanium center of complex $(L_1)Ti{=}NAr(OTf)$ is intriguing because it provides a strategy to assemble novel ligands on titanium retaining the Nacnac−Ti core.

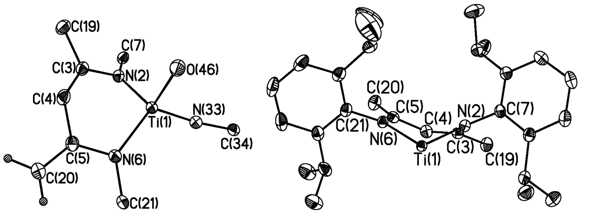

Figure 4. Molecular structure of $(L_3)Ti{=}NAr(OEt_2)$ showing atom-labeling scheme with thermal ellipsoids at the 50% probability level. H-atoms with the exception of those on C(20), ethyl groups on O(46), and aryl groups on the nitrogen atoms with the exception of the ipso-carbons have been omitted for clarity (left). A perspective view of the ligand down the Ti(1)−C(4) axis is also shown (right), and the imide and OEt_2 groups on titanium, as well as H-atoms, have been omitted for clarity.

Deprotonation of the β-carbon methyl group on the Nacnac$^-$ ligand has been reported for Ge complexes bearing this ligand.[25] Likewise, when ether-based solutions of $(L_1)Ti{=}NAr(OTf)$ are treated with nucleophiles such as LiR (R = Me, $CH_2{}^tBu$, and CH_2SiMe_3), complex $(L_3)Ti{=}NAr(OEt_2)$ is formed cleanly (Scheme 2). Significant and diagnostic features for $(L_3)Ti{=}NAr(OEt_2)$ include observation by ^1H NMR spectroscopy of two methylene protons of the former β-carbon methyl centered at 3.61 and 3.33 ppm. The two resonances were unambiguously correlated to the sp^2-hydridized carbon at 86.3 ppm by HMQC experiments (J_{C-H} = 157 Hz).[40] A result from the methyl being deprotonated is the loss of symmetry from C_s to C_1, which is evident by the spectroscopic observation of four nonequivalent isopropyl groups on Nacnac$^-$, each having two diasteriotopic methyl groups. Hindered rotation of the aryl group attached to the imido gives rise to two additional nonequivalent isopropyl groups. Coordination of Et_2O is also observed in both the ^1H and ^{13}C NMR spectra of $(L_3)Ti{=}NAr(OEt_2)$. Overall, deprotonation concurrent with triflate elimination generates a dianionic amide ligand lacking C_2 symmetry. Thus, complex $(L_3)Ti{=}NAr(OEt_2)$ represents a unique example of a four-coordinate titanium imide complex supported by an anionic and chelate bis-anilide ligand. When $(L_1)Ti{=}NAr(OTf)$ is treated with LiR in hexane or toluene, no reaction is observed (even upon heating of the mixture), hinting that solvent plays a key role in the formation of $(L_3)Ti{=}NAr(OEt_2)$. Complex $(L_3)Ti{=}NAr(OEt_2)$ is remarkably stable, and heating samples under dynamic vacuum does not lead to substantial decomposition or evidence of Et_2O loss [even in the presence of a Lewis acid such as $B(C_6F_5)_3$].

Single crystals of $(L_3)Ti{=}NAr(OEt_2)$ were grown from a saturated pentane solution cooled to −35 °C. Upon inspection, the molecular structure of $(L_3)Ti{=}NAr(OEt_2)$ displays a rare four-coordinate titanium imide complex supported by a chelating bis-anilide ligand (Figure 4). Crystal data and

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(39) Hofmann, P.; Perez-Moya, L. A.; Steigelmann, O.; Riede, J. *Organometallics* **1992**, *11*, 1167.

(40) For a detailed description of HMQC experiments: Summers, M. F.; Marzilli, L. G.; Bax, A. J. *J. Am. Chem. Soc.* **1986**, *108*, 4285.

relevant metrical parameters for the structure of $(L_3)Ti{=}NAr(OEt_2)$ are listed in Tables 1 and 2, respectively. The dianionic nature of the ligand is supported clearly by the short Ti(1)−N$_{\{anilide\}}$ bonds [1.939(2) and 1.966(1) Å], which are substantially shorter than typical Ti(IV)-N$_{\{Nacnac\}}$ distances.[18,37k] As a consequence of the Ti−N distances being shorter, the N−β-C distances are longer for L_3^{2-} [N(2)−C(3), 1.365(2) Å; N(6)−C(5), 1.330(2) Å] than that reported for the Nacnac$^-$ ligand L_1 (vide supra).[18b] Most notably, deprotonation of the methyl on the β-carbon is evident from shortening of the H_3C-C bond to an sp^2 $H_2C{=}C$ bond [1.501(3) Å for an sp^3 CH_3-C bond vs 1.348(2) Å for the sp^2 $CH_2{=}C$ bond]. When $(L_3)Ti$ is viewed down the Ti(1)−C(4) axis, it is apparent that the ligand has distorted considerably from planarity (Figure 4, right view). More indicative of this distortion are the dihedral angles defined between the carbons $H_2C(20){=}C(5)-C(4)H{=}C(3)-C(19)H_3$ [C(20)−C(5)−C(4)−C(3), 144.2(7)°; C(19)−C(3)−C(4)−C(5), 171.2(5)°]. Such a deviation from planarity is significant when compared to the dihedral angles for the former Nacnac$^-$ ligand in $(L_1)Ti{=}NAr(OTf)$ [C(20)−C(5)−C(4)−C(3), 167.2(8)°; C(19)−C(3)−C(4)−C(5), 172.3(7)°].[18b] Other parameters are the short Ti(1)−N(33) bond of 1.726(2) Å, which is consistent with a Ti−N multiple bond,[36a] and a relatively short Ti(1)−O(46) dative bond of 2.100(1) Å for the tightly bound Et_2O. Coordination of Et_2O is not surprising because of the exceedingly low-coordinate (three-coordinate) and electron-deficient titanium center being generated during deprotonation of $(L_1)Ti{=}NAr(OTf)$.

Conclusion

The (Nacnac)Ti frame "$(L_1)Ti$" is an excellent platform for the design of both a tripodal monoanionic ligand and an asymmetric and dianionic bis-anilide chelate ligand. For instance, the present L_2^- ligand exhibits all of the traits of a robust and attractive ligand: it lacks β-hydrogens, has good donicity (yet a low overall negative charge), and is sterically encumbering. These features are also present in the dianionic and asymmetric ligand L_3^{2-}. The stability of the imido functionality in $(L_1)Ti{=}NAr(OTf)$ arises likely from thermodynamic reasons as small molecules do not appear to react under normal conditions. However, the possibility remains that the substrates themselves are too large to react with the hindered Ti═NAr fragment, which leaves unresolved the issue of thermodynamic preference. We are currently pursuing the synthesis of three-coordinate titanium imide complexes (both neutral and cationic) with the more robust Nacnac$^-$ ligand [Ar]NC(^{t}Bu)CHC(^{t}Bu)N[Ar].[6,37k] Titanium systems tuned properly for the clear illustration of this coordination environment remain attractive as synthetic targets.

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Supporting Information Available: Complete crystallographic data for compounds $(L_1)Ti{=}NAr(OTf)(XY)$ (XY = CN^{t}Bu and $NCCH_2Mes$), $(L_2)Ti{=}NAr(OTf)$, and $(L_3)Ti{=}NAr(OEt_2)$ (CIF files in text format). This material is available free of charge via the Internet at http://pubs.acs.org.

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