Supplementary Material (ESI) for Chemical Communications

Supporting Information for the Paper Entitled “Latent low-coordinate titanium imides supported by a sterically encumbering beta-diketiminate ligand”

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Experimental Section

General Considerations. Unless otherwise stated, all operations were performed in a M. Braun Lab Master double-dry box under an atmosphere of purified nitrogen or using high vacuum standard Schlenk techniques under an argon atmosphere.[1] 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.[2] Diethylether and CH_2Cl_2 were dried by passage through a column of activated alumina.[2] 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 dry box. FC_6H_5 was purchased from Acros Organics and filtered through activated alumina. C_6D_6 was purchased from Cambridge Isotope Laboratory (CIL), degassed and dried over CaH_2, then vacuum transferred to 4 Å molecular sieves. C_6D_5F and C_6D_5Cl were purchased from CIL and passed through a thin mat of activated alumina. 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) ($Nacnac^- = [ArNC(tBu)]_2CH$, Ar = 2,6-$i Pr_2C_6H_3$) was prepared according to the literature.[3] $LiCH_2SiMe_3$ was recrystallized from pentane at −35 °C and $LiMe(Et_2O)_x$ (x = 1-2) was obtained as a powder from a concentrated Et_2O solution at −35 °C. $[HNMe_2Ph][B(C_6F_5)_4]$ and $B(C_6F_5)_3$ were purchased from Boulder Scientific, recrystallized from benzene and dried under reduced pressure. Note: The boron containing materials should not be exposed to coordinating solvents such as Et_2O and THF. All other chemical were used as received. CHN analyses were performed by Desert Analytics, Tucson, AZ. ^1H, ^{13}C, ^{19}F, ^{11}B, and ^{31}P NMR spectra were recorded on Varian 400 or 300 MHz NMR spectrometers. ^1H and ^{13}C NMR are reported with reference to solvent resonances (residual C_6D_5H in C_6D_6, 7.16 ppm and 128.0 ppm; THF in THF-d_8 3.58, 1.73 and 67.4, 25.3 ppm; C_6H_5F in C_6D_5F 7.09, 6.92, 6.89 and 163.1, 129.5, 123.5, 115.0 ppm; C_6H_5Cl in C_6D_5Cl 7.09, 6.95, 6.92 and 134.2, 129.2, 128.3, 126.0 ppm). ^{19}F NMR chemical shifts are reported with respect to external $HOCOCF_3$ (–78.5 ppm). ^{11}B NMR spectra were reported with respect to external BF_3•(OEt_2) (0.0 ppm). X-ray diffraction data were collected on a SMART6000 (Bruker) system under a stream of N_2 (g) at low temperatures.[4,5]

Synthesis of (Nacnac)Ti=NAr(Cl) (1)

LiNacnac (1.51 g, 2.97 mmol) was sifted to a toluene (~50 mL) suspention of $TiCl_3(THF)_3$ [1.00 g, 2.70 mmol] at –35 °C. The mixture was stirred for 20 min then transferred to a bomb and heated to 80 °C for 3 days. The solution was filtered and all volatiles were removed *in vacuo*. The residue was extracted with hexane and the solution was passed through a pad of celite. The celite was washed with hexane and the filtrate was concentrated and cooled to −35 °C to yield red crystals of (Nacnac)Ti=NAr(Cl) (**1**) [800 mg, 1.05 mmol, 39% yield].

^1H NMR (23°C, 399.8 MHz, C_6D_6): δ 7.06-6.72 (m, 9H, Ar-*H*), 5.98 (ArN(*t*Bu)CC*H*C(*t*Bu)NAr), 3.69 (septet, 2H, C*H*Me$_2$), 3.30 (septet, 2H, C*H*Me$_2$), 3.23 (septet, 2H, C*H*Me$_2$), 1.56 (d, 6H, CH*Me$_2$*), 1.32 (d, 6H, CH*Me$_2$*), 1.16 (d, 6H, CH*Me$_2$*), 1.09-1.04 (m, 36H, CH*Me$_2$* and ArN(*tBu*)CCHC(*tBu*)NAr). ^{13}C NMR (23°C, 100.6 MHz, C_6D_6): δ 175.8 (ArN(*t*Bu)*C*CH*C*(*t*Bu)NAr), 146.2 (*C*$_6$H$_3$), 142.2 (*C*$_6$H$_3$), 140.6 (*C*$_6$H$_3$), 129.3 (*C*$_6$H$_3$), 128.6 (*C*$_6$H$_3$), 127.1 (*C*$_6$H$_3$), 125.3 (*C*$_6$H$_3$), 124.0 (*C*$_6$H$_3$), 122.5 (*C*$_6$H$_3$), 122.4 (*C*$_6$H$_3$), 94.8 (ArN(*t*Bu)C*C*HC(*t*Bu)NAr), 45.12 (ArN(*C*Me$_3$)CCHC(*C*Me$_3$)NAr), 32.01 ((ArN(C*Me$_3$*)CCHC(C*Me$_3$*)NAr), 29.23 (*C*HMe$_2$), 28.71 (*C*HMe$_2$), 28.05 (*C*HMe$_2$), 26.67

(*Me*), 25.29 (*Me*), 25.20 (*Me*), 25.07 (*Me*), 24.72 (*Me*). Anal. Calcd. for $C_{47}H_{70}N_3ClTi$: C, 74.27; H, 9.27; N, 5.52. Found: C, 74.29; H, 8.96; N, 5.31.

Synthesis of (Nacnac)Ti=NAr(OTf) (2)

In a flask was dissolved **1** [632 mg, 0.83 mmol] in THF (40 mL) and the solution was cooled to −35 °C. To the solution was added a cold THF (20 mL) solution containing AgOTf [277.6 mg, 1.08 mmol]. The solution was allowed to stir for 30 min, filtered and then dried in vacuo. The red residue was extracted with Et_2O and filtered. The resulting filtrate was concentrated and cooled to −35 °C to yield red crystals of (Nacnac)Ti=NAr(OTf) (**2**) [533 mg, 0.63 mmol, 76% yield].

^{1}H NMR (23°C, 399.8 MHz, C_6D_6): δ 7.04-6.68 (m, 9H, Ar-*H*), 5.80 (ArN(*t*Bu)CC*H*C(*t*Bu)NAr), 3.65 (septet, 2H, C*H*Me$_2$), 3.52 (septet, 2H, C*H*Me$_2$), 2.87 (septet, 2H, C*H*Me$_2$), 1.45 (d, 6H, CH*Me$_2$*), 1.43 (d, 6H, CH*Me$_2$*), 1.18 (d, 6H, CH*Me$_2$*), 1.11 (d, 6H, CH*Me$_2$*), 1.06 (s, 18H, ArN(*tBu*)CCHC(*tBu*)NAr), 1.02 (d, 12H, CH*Me$_2$*). ^{13}C NMR (23°C, 100.6 MHz, C_6D_6): δ 175.5 (ArN(*t*Bu)*C*CH*C*(*t*Bu)NAr), 159.2 (*C*$_6$H$_3$), 146.5 (*C*$_6$H$_3$), 144.0 (*C*$_6$H$_3$), 142.7 (*C*$_6$H$_3$), 139.8 (*C*$_6$H$_3$), 127.5 (*C*$_6$H$_3$), 125.3 (*C*$_6$H$_3$), 123.9 (*C*$_6$H$_3$), 123.6 (*C*$_6$H$_3$), 122.8 (*C*$_6$H$_3$), 91.98 (ArN(*t*Bu)C*C*HC(*t*Bu)NAr), 44.96 (ArN(*C*Me$_3$)CCHC(*C*Me$_3$)NAr), 31.98 ((ArN(C*Me$_3$*)CCHC(C*Me$_3$*)NAr), 30.48 (*C*HMe$_2$), 28.69 (*C*HMe$_2$), 27.90 (*C*HMe$_2$), 26.86 (*Me*), 25.92 (*Me*), 25.04 (*Me*), 24.82 (*Me*), 24.61 (*Me*). ^{19}F NMR (23°C, 282.3 MHz, C_6D_6): δ −77.44 (OSO$_2$C*F$_3$*). Anal. Calcd. for $C_{48}H_{70}N_3O_3SF_3Ti$: C, 65.96; H, 8.07; N, 4.81. Found: C, 65.82; H, 8.07; N, 4.79.

Synthesis of (Nacnac)Ti=NAr(Me) (3)

In a vial was dissolved **2** [372 mg, 0.43 mmol] in Et_2O (10 mL) and the solution was cooled to −35 °C. To the solution was added a cold THF solution of MeMgCl [3M solution, 0.14 mL, 0.43 mmol]. The solution was allowed to stir for 2 h and then dried in vacuo. The red residue was extracted with Et_2O and filtered. The resulting filtrate was concentrated and cooled to −35 °C to afford red crystals of (Nacnac)Ti=NAr(Me) (**3**) [283 mg, 0.38 mmol, 88% yield].

^1H NMR (23°C, 399.8 MHz, C_6D_6): δ 7.06-6.75 (m, 9H, Ar-*H*), 5.93 (ArN(*t*Bu)CC*H*C(*t*Bu)NAr), 3.87 (septet, 2H, C*H*Me_2), 3.58 (septet, 2H, C*H*Me_2), 3.02 (septet, 2H, C*H*Me_2), 1.40 (d, 6H, CH*Me₂*), 1.31 (d, 6H, CHMe_2), 1.20 (d, 6H, CHMe_2), 1.19 (d, 6H, CHMe_2), 1.11 (d, 12H, CHMe_2), 1.08 (s, 18H, ArN(*tBu*)CCHC(*tBu*)NAr), 0.93 (s, 3H, Ti-*Me*) . ^{13}C NMR (23°C, 100.6 MHz, C_6D_6): δ 174.8 (ArN(*t*Bu)*C*CH*C*(*t*Bu)NAr), 158.2 (C_6H_3), 146.2 (C_6H_3), 142.5 (C_6H_3), 142.1 (C_6H_3), 140.4 (C_6H_3), 126.5 (C_6H_3), 124.8 (C_6H_3), 123.8 (C_6H_3), 122.3 (C_6H_3), 120.8 (C_6H_3), 93.55 (ArN(tBu)C*C*HC(*t*Bu)NAr), 45.35 (ArN(*C*Me_3)CCHC(*C*Me_3)NAr), 34.16 (Ti-*C*H_3, $J_{C\text{-}H}$ = 114 Hz), 32.14 ((ArN(CMe_3)CCHC(CMe_3)NAr), 29.48 (*C*HMe_2), 28.62 (*C*HMe_2), 27.84 (*C*HMe_2), 26.61 (*Me*), 25.82 (*Me*), 24.84 (*Me*), 24.80 (*Me*), 24.62 (*Me*). Anal. Calcd. for $C_{48}H_{73}N_3Ti$: C, 77.91; H, 9.94; N, 5.68. Found: C, 77.59; H, 9.60; N, 5.54.

Synthesis of (Nacnac)Ti=NAr(CH_2SiMe_3) (4)

In a vial was dissolved **2** [252 mg, 0.29 mmol] in Et_2O (10 mL) and the solution was cooled to −35 °C. To the solution was added a cold solution of $LiCH_2SiMe_3$ [29.83 mg, 0.32 mmol]. The solution was allowed to stir for 2 h and then dried in vacuo. The red residue was extracted with pentane and filtered, and the resulting filtrate was concentrated and cooled to

−35 °C to yield red crystals of (Nacnac)Ti=NAr(CH$_2$SiMe$_3$) (**4**) [203 mg, 0.25 mmol, 86% yield].

^{1}H NMR (23°C, 399.8 MHz, C$_6$D$_6$): δ 7.06-6.65 (m, 9H, Ar-*H*), 5.87 (ArN(*t*Bu)CC*H*C(*t*Bu)NAr), 3.27 (two overlapping septets, 4H, C*H*Me$_2$), 3.16 (septet, 2H, C*H*Me$_2$), 1.56 (d, 6H, CH*Me*$_2$), 1.35 (d, 6H, CH*Me*$_2$), 1.31 (s, 2H, Ti-C*H*$_2$SiMe$_3$), 1.17 (d, 6H, CH*Me*$_2$), 1.07 (s, 18H, ArN(*tBu*)CCHC(*tBu*)NAr), 1.04 (d, 6H, CH*Me*$_2$), 0.97 (d, 12H, CH*Me*$_2$), 0.34 (s, 9H, Ti-CH$_2$Si*Me*$_3$). ^{13}C NMR (23°C, 100.6 MHz, C$_6$D$_6$): δ 176.8 (ArN(*t*Bu)*C*CH*C*(*t*Bu)NAr), 158.8 (*C*$_6$H$_3$), 146.0 (*C*$_6$H$_3$), 142.5 (*C*$_6$H$_3$), 141.5 (*C*$_6$H$_3$), 141.3 (*C*$_6$H$_3$), 126.6 (*C*$_6$H$_3$), 125.1 (*C*$_6$H$_3$), 124.3 (*C*$_6$H$_3$), 122.4 (*C*$_6$H$_3$), 121.0 (*C*$_6$H$_3$), 94.19 (ArN(tBu)C*C*HC(tBu)NAr), 56.14 (Ti-*C*H$_2$SiMe$_3$, $J_{\mathrm{C\text{-}H}}$ = 99 Hz), 44.59 (ArN(*C*Me$_3$)CCHC(*C*Me$_3$)NAr), 32.14 ((ArN(C*Me*$_3$)CCHC(C*Me*$_3$)NAr), 28.44 (*C*HMe$_2$), 28.32 (*C*HMe$_2$), 27.61 (*C*HMe$_2$), 26.85 (*Me*), 25.59 (*Me*), 25.39 (*Me*), 25.35 (*Me*), 24.80 (*Me*), 3.81 (Ti-CH$_2$Si(*C*H$_3$)$_3$). Anal. Calcd. for C$_{51}$H$_{81}$N$_3$SiTi : C, 75.42; H, 10.05; N, 5.17. Found: C, 75.35; H, 9.74; N, 4.81.

Synthesis of [(Nacnac)Ti=NAr(THF)][B(C$_6$F$_5$)$_4$] (5)

In a vial was dissolved **3** [273 mg, 0.37 mmol] in benzene (10 mL) and to the solution was added slowly to a solution of [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] [325.2 mg, 0.41 mmol]. The solution was allowed to stir for 5 min and then few drops of THF were added. The stirring was continued for 30 min and the orange solid thus obtained was collected by filtration. The resulting solid was washed with benzene to yield [(Nacnac**)**Ti=NAr(THF)][B(C$_6$F$_5$)$_4$] **(5)** [414 mg, 0.28 mmol, 76% yield]. Single crystals of **5** were grown slowly from the THF solution with few drops of hexane at −35 °C.

^{1}H NMR (23°C, 399.8 MHz, THF-d_8): δ 7.40-6.66 (m, 9H, Ar-*H*), 6.07 (ArN(*t*Bu)CC*H*C(*t*Bu)NAr), 3.63 (br, 4H, THF), 3.06 (septet, 2H, C*H*Me$_2$), 2.94 (septet, 2H, C*H*Me$_2$), 2.79 (septet, 2H, C*H*Me$_2$), 1.77 (br, 4H, THF), 1.50 (d, 12H, CH*Me$_2$*), 1.25 (d, 6H, CH*Me$_2$*), 1.23 (s, 18H, ArN(*tBu*)CCHC(*tBu*)NAr), 1.02 (d, 6H, CH*Me$_2$*), 0.67 (d, 12H, CH*Me$_2$*). ^{13}C NMR (23°C, 100.6 MHz, THF-d_8): δ 178.6 (ArN(*t*Bu)*C*CH*C*(*t*Bu)NAr), 160.5 (C_6H_3), 149.6 (br, ($C_6F_5)_4B$), 147.2 (br, ($C_6F_5)_4B$), 145.2 (C_6H_3), 143.9 (C_6H_3), 141.2 (C_6H_3), 140.3 (C_6H_3), 137.5 (br, ($C_6F_5)_4B$), 135.1 (br, ($C_6F_5)_4B$), 128.5 (C_6H_3), 122.3 (C_6H_3), 125.3 (C_6H_3), 125.2 (C_6H_3), 122.9 (C_6H_3), 89.17 (ArN(*t*Bu)C*C*HC(*t*Bu)NAr), 67.43 (THF), 45.55 (ArN(*C*Me$_3$)CCHC(*C*Me$_3$)NAr), 31.22 ((ArN(C*Me$_3$*)CCHC(C*Me$_3$*)NAr), 30.76, 30.11, 28.94, 27.91, 25.58, 25.39, 25.04, 24.84, 24.01, 23.79. ^{19}F NMR (23 °C, 282.3 MHz, THF-d_8): δ −133.3 ($C_6F_5)_4B$), −165.5 ($C_6F_5)_4B$), −169.1 ($C_6F_5)_4B$). ^{11}B NMR (23 °C, 128.4 MHz, THF-d_8): δ −16.54 ($C_6F_5)_4B$). Anal. Calcd. for $C_{75}H_{78}N_3OF_{20}BTi$: C, 61.03; H, 5.32; N, 2.85. Found: C, 60.54; H, 5.28; N, 2.81.

Synthesis of [(Nacnac)Ti=NAr(Et_2O)][B(C_6F_5)$_4$] (6)

In a vial was dissolved **3** [200 mg, 0.27 mmol] in benzene (10 mL) and to the solution was added a solution of [HNMe$_2$Ph][B(C_6F_5)$_4$] [225.8 mg, 0.28 mmol]. The solution was allowed to stir for 5 min and then few drops of Et_2O were added. The stirring was continued for 30 min and the orange solid thus obtained was collected by filtration. The resulting solid was washed with benzene to yield [(Nacnac)Ti=NAr(Et_2O)][B(C_6F_5)$_4$] **(6)** [328 mg, 0.22 mmol, 82% yield]. Single crystals were grown by layering the C_6H_5F solution of **6** with hexane at room tempareture. THF readily displaces Et_2O in complex **6**.

^{1}H NMR (23^{o}C, 399.8 MHz, C_6D_5F): δ 7.20-6.50 (m, 9H, Ar-*H*), 5.70 (ArN(*t*Bu)CC*H*C(*t*Bu)NAr), 3.27 (quartet, 4H, Et_2O), 2.80 (septet, 2H, C*H*Me$_2$), 2.71 (septet, 2H, C*H*Me$_2$), 2.46 (septet, 2H, C*H*Me$_2$), 1.24 (d, 6H, CH*Me$_2$*), 1.18 (d, 6H, CH*Me$_2$*), 1.05 (t, 6H, Et_2O) 1.02 (d, 6H, CH*Me$_2$*), 0.91 (s, 18H, ArN(*tBu*)CCHC(*tBu*)NAr), 0.82 (d, 6H, CH*Me$_2$*), 0.56 (d, 12H, CH*Me$_2$*). ^{13}C NMR (23^{o}C, 100.6 MHz, C_6D_5F): δ 178.6 (ArN(*t*Bu)*C*CH*C*(*t*Bu)NAr), 160.8 (*C*$_6$H$_3$), 150.2 (br, (*C$_6$*F$_5$)$_4$B), 147.8 (br, (*C$_6$*F$_5$)$_4$B), 145.0 (*C*$_6$H$_3$), 144.1 (*C*$_6$H$_3$), 141.2 (*C*$_6$H$_3$), 139.9 (*C*$_6$H$_3$), 138.2 (br, (*C$_6$*F$_5$)$_4$B), 135.7 (br, (*C$_6$*F$_5$)$_4$B), 128.8 (*C*$_6$H$_3$), 125.4 (*C*$_6$H$_3$), 125.1 (*C*$_6$H$_3$), 124.3 (*C*$_6$H$_3$), 123.4 (*C*$_6$H$_3$), 88.49 (ArN(*t*Bu)C*C*HC(*t*Bu)NAr), 65.96 (Et_2O), 45.51 (ArN(*C*Me$_3$)CCHC(*C*Me$_3$)NAr), 31.58 ((ArN(C*Me$_3$*)CCHC(C*Me$_3$*)NAr), 30.13 (*C*HMe$_2$), 29.04 (*C*HMe$_2$), 28.18 (*C*HMe$_2$), 25.67 (*Me*), 25.48 (*Me*), 25.01 (*Me*), 24.98 (*Me*), 24.47 (*Me*), 24.25 (*Me*), 15.58 (Et_2O). ^{19}F NMR (23 ^{o}C, 282.3 MHz, C_6D_5F): δ −133.1 (C$_6$*F$_5$*)$_4$B), −164.1 (C$_6$*F$_5$*)$_4$B), −168.0 (C$_6$*F$_5$*)$_4$B). ^{11}B NMR (23 ^{o}C, 128.4 MHz, C_6D_5F): δ -16.28 (C$_6$F$_5$)$_4$*B*). Anal. Calcd. for $C_{75}H_{80}N_3OF_{20}BTi$: C, 60.94; H, 5.45; N, 2.84. Found: C, 61.09; H, 5.28; N, 2.80.

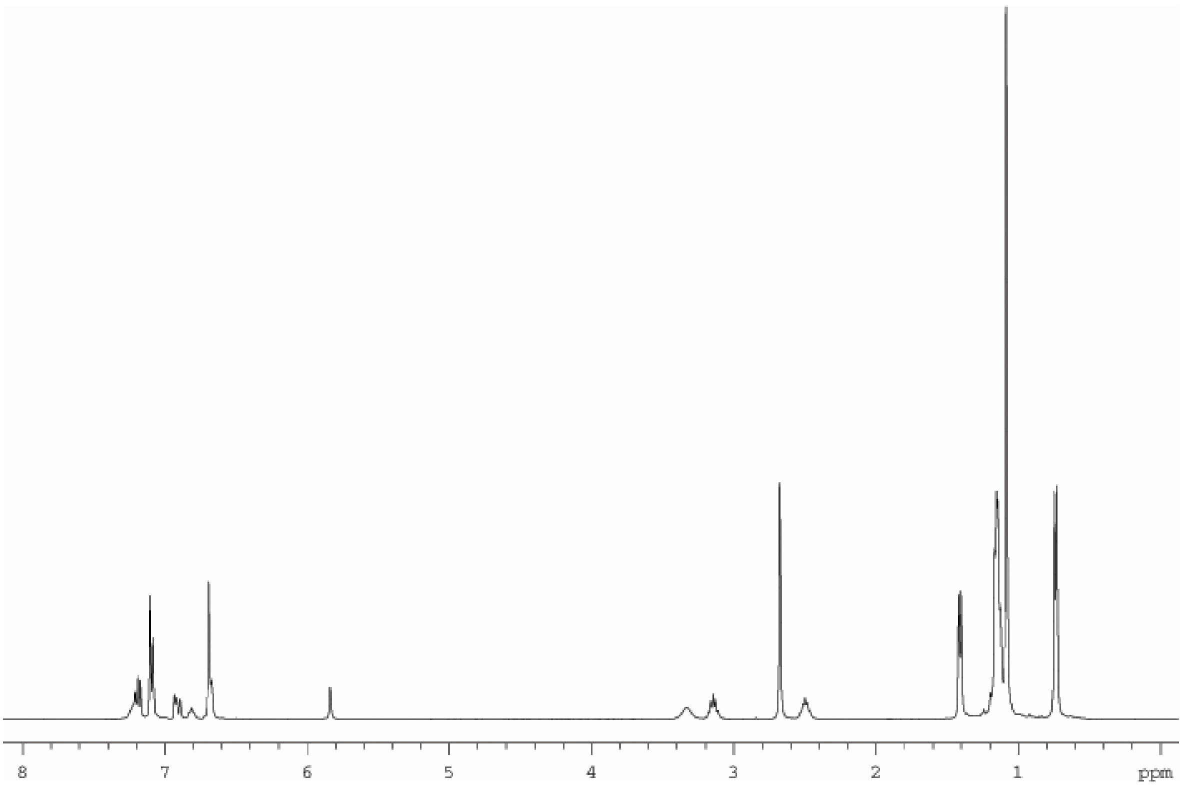
Synthesis of [(Nacnac)Ti=NAr(η^1-C$_6$H$_5$NMe$_2$)][B(C$_6$F$_5$)$_4$] (7)

C_6D_5F (0.6 mL) was added to the mixture of **3** [33 mg, 0.04 mmol] and [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] [37.52 mg, 0.05 mmol] in a J. Young NMR tube. Effervescence was noticed immediately. After allowing the reaction to proceed at room temperature for 10 min, ^{1}H NMR spectrum was collected which revealed that [(Nacnac)Ti=NAr(η^1-C$_6$H$_5$NMe$_2$)][B(C$_6$F$_5$)$_4$] **(7)** had been generated in quantitative yield. Single crystals were grown by layering the C_6H_5F solution of **7** with hexane at room tempareture. For comparison, the ^{1}H and ^{13}C NMR spectra of the free amine NMe$_2$Ph were taken in C_6D_5F.

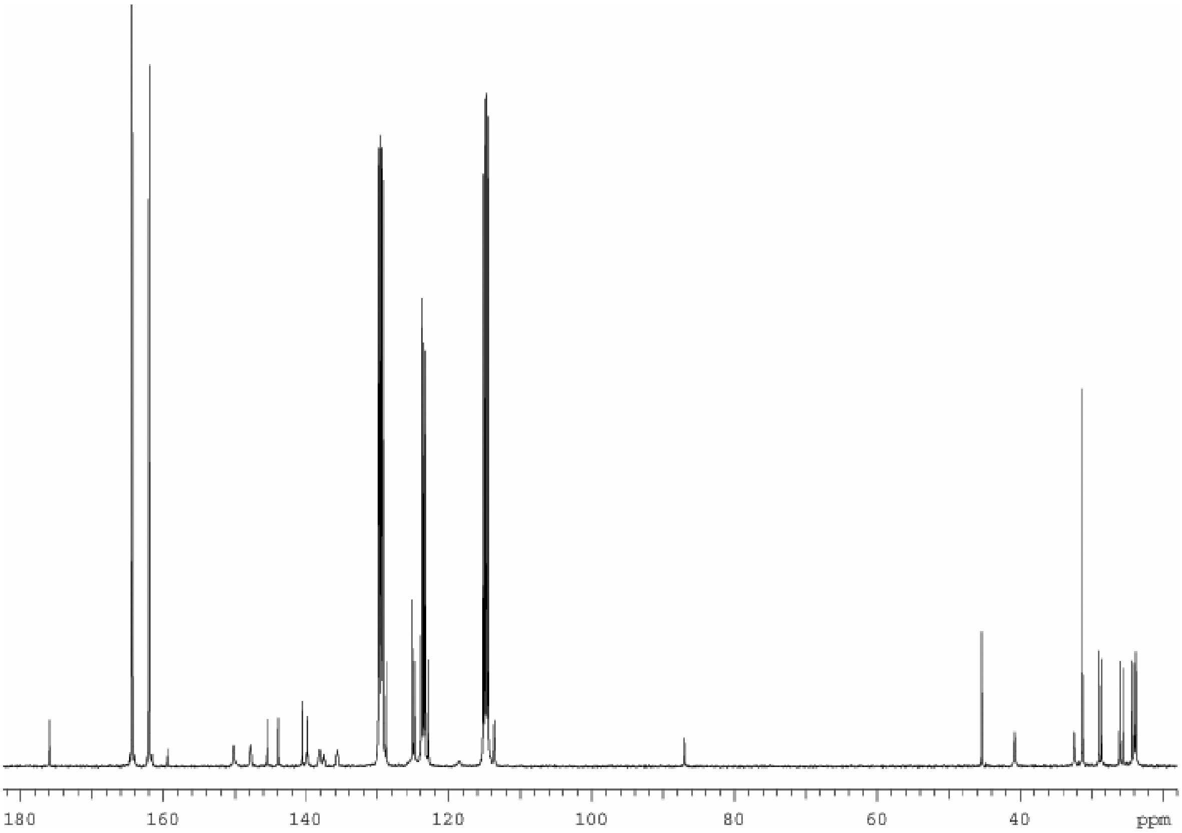
For NMe_2Ph: ^{1}H NMR (23°C, 399.8 MHz, C_6D_5F): δ 7.43 (t, 2H), 6.96 (t, 1H), 6.87 (d, 2H). ^{13}C NMR (23°C, 100.6 MHz, C_6D_5F): δ 151.0, 129.2, 116.8, 112.8.

For **7**: ^{1}H NMR (23°C, 399.8 MHz, C_6D_5F): δ 7.25 (t, 2 H, Ar-*H*), 7.2-6.9 (m, 6 H, Ar-*H*), 6.87 (t, 1H, *p*-$C_6\mathit{H}_5NMe_2$), 6.8-6.6 (m, 5H, Ar-*H*) 5.90 (ArN(*t*Bu)CC*H*C(*t*Bu)NAr), 3.40 (br, 2H, C*H*Me_2), 3.21 (septet, 2H, C*H*Me_2), 2.74 (s, 6H, $C_6H_5N\mathit{Me_2}$), 2.56 (septet, 2H, C*H*Me_2), 1.47 (d, 6H, CH*Me₂*), 1.26-1.16 (overlapping doublets, 18H, CH$\mathit{Me_2}$), 1.14 (s, 18H, ArN(*tBu*)CCHC(*tBu*)NAr), 0.80 (d, 12H, CH$\mathit{Me_2}$). ^{13}C NMR (23°C, 100.6 MHz, C_6D_5F): δ 175.9 (ArN(*t*Bu)*C*CH*C*(*t*Bu)NAr), 159.5 (Ar), 150.1 (br, $(\mathit{C_6}F_5)_4B$), 147.7 (br, $(\mathit{C_6}F_5)_4B$), 145.5 (Ar), 143.9 (Ar), 140.5 (Ar), 140.0 (br, Ar), 139.8 (Ar), 138.1 (br, $(\mathit{C_6}F_5)_4B$), 137.5 (br, Ar), 135.6 (br, $(\mathit{C_6}F_5)_4B$), 128.7 (Ar), 125.1 (Ar), 124.8 (Ar), 122.8 (Ar), 118.6 (br, *p*-$\mathit{C_6}H_5NMe_2$, based on proton coupled ^{13}C NMR and HMQC experiments), 113.6 (Ar), 87.02 (ArN(*t*Bu)C*C*HC(*t*Bu)NAr), 45.35 (ArN($\mathit{C}Me_3$)CCHC($\mathit{C}Me_3$)NAr), 40.69 ($C_6H_5N\mathit{Me_2}$), 32.35 ($\mathit{C}HMe_2$), 31.21 ((ArN($C\mathit{Me_3}$)CCHC($C\mathit{Me_3}$)NAr), 28.90 ($\mathit{C}HMe_2$), 28.53 ($\mathit{C}HMe_2$), 26.03 (*Me*), 25.58 (*Me*), 24.31 (*Me*), 23.97 (*Me*), 23.72 (*Me*). ^{19}F NMR (23 °C, 282.3 MHz, C_6D_5F): δ −132.4 ($(C_6\mathit{F_5})_4B$), −163.5 ($(C_6\mathit{F_5})_4B$), −167.3 ($(C_6\mathit{F_5})_4B$). ^{11}B NMR (23 °C, 128.4 MHz, C_6D_5F): δ −16.54 ($(C_6F_5)_4\mathit{B}$). Anal. Calcd. for $C_{79}H_{81}N_4F_{20}BTi$: C, 62.21; H, 5.35; N, 3.67. Found: C, 62.10; H, 5.87; N, 3.00.

^{1}H NMR spectrum of complex 7.



^{13}C NMR spectrum of complex 7.



Synthesis of (Nacnac)Ti=NAr(μ-Me)B(C_6F_5)$_3$ (3)-B(C_6F_5)$_3$

C_6D_5Cl (0.6 mL) was added to the mixture of **3** [33 mg, 0.04 mmol] and B(C_6F_5)$_3$ [37.52 mg, 0.05 mmol] in a J. Young tube. After allowing the reaction to proceed at room temperature for 10 min, the ^{1}H NMR spectrum revealed that (Nacnac)Ti=NAr(μ-Me)B(C_6F_5)$_3$ **(3)-B(C_6F_5)$_3$** had been generated in quantitative yield. Single crystals were grown by layering a C_6H_5F solution of **(3)-B(C_6F_5)$_3$** with hexane at room temperature.

^{1}H NMR (23°C, 399.8 MHz, C_6D_5Cl): δ 7.1-6.5 (m, 9 H, Ar-*H*), 5.80 (ArN(*t*Bu)CC*H*C(*t*Bu)NAr), 3.06 (septet, 2H, C*H*Me$_2$), 2.92 (septet, 2H, C*H*Me$_2$), 2.57 (septet, 2H, C*H*Me$_2$), 1.35 (br s, 3H, *Me*B(C_6F_5)$_3$) 1.19 (d, 6H, CH*Me$_2$*), 1.15 (d, 6H, CH*Me$_2$*), 1.02 (d, 6H, CH*Me₂*), 0.96 (s, 18H, ArN(*tBu*)CCHC(*tBu*)NAr), 0.88 (d, 6H, CH*Me₂*), 0.57 (d, 12H, CH*Me₂*). ^{13}C NMR (23°C, 100.6 MHz, C_6D_5Cl): δ 176.5 (ArN(*t*Bu)*C*CH*C*(*t*Bu)NAr), 160.6 (C_6H_3), 150.2 (br, $(C_6F_5)_4B$), 147.8 (br, $(C_6F_5)_4B$), 146.0 (C_6H_3), 144.6 (C_6H_3), 141.1 (C_6H_3), 140.2 (C_6H_3), 138.4 (br, $(C_6F_5)_4B$), 137.5 (br, Ar), 136.0 (br, $(C_6F_5)_4B$), 125.3 (C_6H_3), 125.0 (C_6H_3), 124.9 (C_6H_3), 124.1 (C_6H_3), 122.9 (C_6H_3), 88.81 (ArN(tBu)C*C*HC(tBu)NAr), 45.04 (ArN(*C*Me₃)CCHC(*C*Me₃)NAr), 31.38 ((ArN(C*Me₃*)CCHC(C*Me₃*)NAr), 30.94 (*C*HMe₂), 28.63 (*C*HMe₂), 28.17 (*C*HMe₂), 25.98 (*Me*), 25.84 (*Me*), 24.75 (*Me*), 24.69(*Me*), 24.63 (*Me*), 13.94 (br, *Me*B(C_6F_5)₃). ^{19}F NMR (23 °C, 282.3 MHz, C_6D_5Cl): δ −133.4 (MeB(C_6F_5)₃), −164.5 (MeB(C_6F_5)3), −167.9 (MeB(C_6F_5)₃). ^{11}B NMR (23 °C, 128.4 MHz, C_6D_5Cl): δ −13.50 Me(C_6F_5)₃*B*). Anal. Calcd. for $C_{66}H_{73}N_3F_{15}BTi.C_6H_5F$: C, 64.14; H, 5.83; N, 3.12. Found: C, 63.67; H, 5.64; N, 3.10.

Data Collection, Structure Solution and Refinement for Single Crystal X-ray Diffraction Studies of Complexes 1-3 and 5-7.

Inert atmosphere techniques were used to place the crystal onto the tip of a diameter glass capillary (0.1-0.2 mm) and mounted on a SMART6000 (Bruker) at 118-126 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 2-30 seconds with a detector distance of 5.0 cm. A randomly oriented region of a sphere in reciprocal space was surveyed. Three sections of 606 frames were collected with 0.30° steps in ω at different φ settings with the detector set at −43° in 2θ. Final cell constants were calculated from the xyz centroids of strong reflections from the actual data collection after integration (SAINT). The structure was solved using

SHELXS-97 and refined with SHELXL-97. 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, and all hydrogen atoms were refined with isotropic displacement parameters (unless otherwise specified).

Crystal data for **5**; $C_{79}H_{86}BF_{20}N_3O_2Ti$: Triclinic, $P\bar{1}$, a = 13.505(1), b = 15.087(2), c = 18.955(4) Å, α = 99.273(2), β = 104.999(2), γ = 93.197(2)°, Z = 2 μ(Mo–Kα) = 0.217 mm^{-1}, V = 3662.6(5) Å^3, D_c = 1.404 mg mm^{-3}, GoF on F^2 = 0.833, R_1 = 4.25% and wR_2 = 9.34% (F^2, all data). Out of a total of 59016 reflections collected 16905 were unique and 9698 were observed (R_{int} = 7.68%) with $I > 2\sigma I$ (red-pink prism, 0.28 × 0.18 × 0.15 mm, 27.55° ≥ θ ≥ 1.98°). Disorder occurs in the THF solvent, a *t*Bu and *i*Pr group in the molecule. With the exception of the disordered atoms, hydrogen atoms were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement. Two independent molecules were confined per asymmetric unit.

Crystal data for **3-B(C_6F_5)$_3$**; $C_{72}H_{78}BF_{16}N_3Ti$: Triclinic, $P\bar{1}$, a = 13.372(4), b = 14.027(4), c = 17.625(8) Å, α = 79.495(3), β = 88.114(3), γ = 86.204(3)°, Z = 2 μ(Mo–Kα) = 0.224 mm^{-1}, V = 3242.5(6) Å^3, D_c = 1.381 mg mm^{-3}, GoF on F^2 = 0.905, R_1 =3.84% and wR_2 = 9.41% (F^2, all data). Out of a total of 109449 reflections collected 24759 were unique and 16524 were observed (R_{int} = 6.25%) with $I > 2\sigma I$ (red-pink prism, 0.28 × 0.25 × 0.25 mm, 33.16° ≥ θ ≥ 2.05°).

Crystal data for **7**; $C_{79}H_{81}BF_{20}N_4Ti$: Triclinic, $P\bar{1}$, a = 12.645(7), b = 17.067(2), c = 17.378(2) Å, α = 94.190(4)°, β = 106.094(4), γ = 93.621(4), Z = 2, μ(Mo–Kα) = 0.220 mm^{-1}, V =

3580.0(8) Å^3, D_c = 1.415 mg mm^{-3}, GoF on F^2 = 0.874, $R(F)$ = 5.77% and $R(wF)$ = 12.93%. Out of a total of 22136 reflections collected 16157 were independent and 6812 were observed (R_{int} = 6.53%) with $I > 2\sigma I$ (orange prism, 0.25 × 0.25 × 0.20 mm, 27.54° ≥ θ ≥ 2.13°). All hydrogen atoms with the exception of the two methyl groups C59 and C60 were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement. The hydrogen atoms on C59 and C60 were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

References

(1) 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., Edx.; ACS Symposium Series 357; American Chemical Society; Washington D. C., 1987; pp 79-98.

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