# Synthesis, Characterization, and Reactivity of Terminal Titanium Imido Complexes Incorporating Constrained-Geometry Carboranyl Ligands

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Reaction of $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]Li_2$ with $Ti(=NR)Cl_2(Py)_3$ afforded the corresponding titanium imido complexes $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(=NR)(Py)$ (R = $^t$Bu (**1**), 2,6-$Me_2C_6H_3$ (**2**), 2,6-$^i Pr_2C_6H_3$ (**3**)). Complexes **2** and **3** were also prepared by an imido exchange reaction of **1** with $RNH_2$ (R = 2,6-$Me_2C_6H_3$, 2,6-$^i Pr_2C_6H_3$). Similarly, $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Ti(=N^tBu)(Py)$ (**4**) was prepared from the reaction of $[Me_2C(C_9H_6)(C_2B_{10}H_{10})]Li_2$ with $Ti(=N^tBu)Cl_2(Py)_3$. The reactivity of **1** toward a series of unsaturated organic compounds was examined. Complex **1** underwent imido/oxo exchange reactions with carbonyl compounds such as $Ph_2CO$, PhCHO, and PhNCO to generate the corresponding imines or carbodiimide and oxotitanium oligomers. The resulting insoluble oxotitanium oligomer was trapped by $Me_3SiCl$, resulting in the formation of a chloride complex, $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(OSiMe_3)Cl$ (**5**). Interaction of **1** with $CS_2$ gave $^t$BuN=C=N$^t$Bu and $^t$BuN=C=S with a molar ratio of 1:3 as well as an insoluble sulfidotitanium complex. **1** was able to catalyze the hydroamination of phenyl acetylene with amines to afford both Markovnikov and *anti*-Markovnikov products. The product ratio was dependent upon the steric hindrance of the amines used. High regioselectivity was observed for sterically demanding amines such as *t*-$BuNH_2$. The *anti*-Markovnikov [2+2] cycloaddition intermediate $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(\eta^3\text{-}N^tBuCH{=}CPh)$ (**6**) was successfully isolated from a stoichiometric reaction of **1** with phenyl acetylene in toluene. The molecular structures of **3**−**6** were further confirmed by single-crystal X-ray analyses.

## Introduction

Group 4 metal imido complexes have attracted considerable interest in the past decade.[1] These complexes are finding many applications in C−H activation,[2] [2+2] cycloadditions,[3] catalytic hydroamination of alkynes,[4] and NR group transfer reactions.[5] A wide range of ancilliary ligands has been used to support the M=NR unit. However, group 4 metal imido complexes with constrained-geometry ligands have not been reported in the literature.[1e] It has been well documented that the constrained-geometry ligands can offer group 4 metal complexes very high activities in the copolymerization of α-olefins due to the increased electron deficiency and more open coordination environment of the central metal ions.[6] They may also provide metal imido complexes with some interesting properties since the identity of the ancilliary ligands has a large effect on the reactivity of the resulting imido complexes.[1−5]

In view of the role of the carboranyl moiety of group 4 metal complexes bearing $[Me_2A(C_5H_4)(C_2B_{10}H_{10})]^{2-}$, $[Me_2A(C_9H_6)(C_2B_{10}H_{10})]^{2-}$ (A = C, Si),[7] and $[^i Pr_2NB(C_9H_6)(C_2B_{10}H_{10})]^{2-}$ [8] in the polymerization/insertion reactions and the impact of the supporting ligands on the reactivity of metal imido complexes, we have incorporated the above constrained-geometry carboranyl ligands into group 4 metal imido complexes. Herein we report the

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synthesis and structural characterization of several terminal titanium imido complexes bearing $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]^{2-}$ and $[Me_2C(C_9H_6)(C_2B_{10}H_{10})]^{2-}$ ligands and their reactivities toward unsaturated organic molecules such as $CS_2$, PhNCO, ketone, aldehyde, and alkyne.

## Experimental Section

**General Procedures.** All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. $Ti(NR)Cl_2(Py)_3$ (Py = pyridine; R = $^t$Bu, 2,6-$Me_2C_6H_3$, 2,6-$^i Pr_2C_6H_3$),[9] $Me_2C(C_5H_5)(C_2B_{10}H_{11})$,[7,10] and $Me_2C(C_9H_7)(C_2B_{10}H_{11})$[11] were prepared according to the literature methods. All other chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets prepared in the glovebox on a Perkin-Elmer 1600 Fourier transform spectrometer. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300.13 and 75.47 MHz, respectively. $^{11}$B NMR spectra were recorded on a Varian Inova 400 spectrometer at 128.32 MHz. All chemical shifts were reported in $\delta$ units with reference to the residual protons of the deuterated solvents for proton and carbon chemical shifts, and to external $BF_3{\cdot}OEt_2$ (0.00 ppm) for boron chemical shifts. Elemental analyses were performed by MEDAC Ltd., U.K. or Shanghai Institute of Organic Chemistry, CAS, China.

**Preparation of [$\eta^5$:$\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti(=N$^t$Bu)(Py) (1).** A 1.6 M solution of *n*-BuLi in hexane (0.63 mL, 1.0 mmol) was added dropwise to a THF solution (20 mL) of $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ (125 mg, 0.5 mmol) at 0 °C, and the mixture was stirred at room temperature overnight. After removal of the solvent, toluene (25 mL) was added to the resulting solid. To this toluene suspension was slowly added $Ti(=N^tBu)Cl_2(Py)_3$ (213 mg, 0.5 mmol) at room temperature, and the reaction mixture was then refluxed overnight. After removal the precipitate, the clear red solution was concentrated to about 10 mL. Complex **1** was isolated as a dark red crystalline solid after this solution stood at room temperature for 3 days (156 mg, 70%). $^1$H NMR (benzene-$d_6$): $\delta$ 8.59 (d, $J$ = 5.1 Hz, 2H, $C_5H_5N$), 6.88 (m, 2H, $C_5H_5N$ + $C_5H_4$), 6.50 (m, 3H, $C_5H_5N$ + $C_5H_4$), 5.44 (d, $J$ = 2.4 Hz, 1H, $C_5H_4$), 5.02 (d, $J$ = 2.4 Hz, 1H, $C_5H_4$), 1.49 (s, 3H, $(CH_3)_2C$), 1.48 (s, 3H, $(CH_3)_2C$), 1.20 (s, 9H, $(CH_3)_3C$). $^{13}$C NMR (benzene-$d_6$): $\delta$ 153.2, 139.8, 124.5 ($C_5H_5N$), 149.8, 110.2, 108.3, 107.9, 104.7 ($C_5H_4$), 103.0, 101.7 (cage *C*), 68.0 ($(CH_3)_3C$), 42,1, 32.6, 31.4 ($(CH_3)_2C$), 32.0 ($(CH_3)_3C$). $^{11}$B NMR (benzene-$d_6$): $\delta$ −3.2 (3B), −8.5 (2B), −10.9 (2B), −13.5 (3B). IR (KBr, cm$^{-1}$): $\nu$ 3060 (w), 2962 (s), 2589 (vs), 1602 (s), 1442 (m), 1219 (s), 1183 (s), 1042 (m), 801 (s), 702 (m), 618 (w). Anal. Calcd for $C_{19}H_{34}B_{10}N_2Ti$: C, 51.11; H, 7.68; N, 6.27. Found: C, 51.38; H, 7.70; N, 6.03.

**Preparation of [$\eta^5$:$\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti(=$NC_6H_3Me_2$-2,6)(Py) (2).** A toluene solution (10 mL) of 2,6-dimethylaniline (62 mg, 0.5 mmol) was added to a toluene solution (15 mL) of **1** (223 mg, 0.5 mmol) with stirring at room temperature, and the mixture was stirred overnight. The color of the solution turned from orange to dark brown. After removal of the solvent, the residue was extracted with a mixed solvent of toluene/*n*-hexane (5:1, 10 × 2 mL). The organic solutions were combined and concentrated to about 10 mL. Complex **2** was isolated as a dark red solid after this solution stood at room temperature for 3 days (129 mg, 52%). $^1$H NMR (benzene-$d_6$): $\delta$ 8.59 (d, $J$ = 5.1 Hz, 2H, $C_5H_5N$), 7.27 (dd, $J$ = 7.5 Hz, 1H, $C_6H_3(CH_3)_2$), 7.09 (d, $J$ = 7.5 Hz, 2H, $C_6H_3(CH_3)_2$), 6.86 (dd, $J$ = 5.1 Hz, 2H, $C_5H_5N$), 6.67 (m, 1H, $C_5H_4$), 6.50 (dd, $J$ = 5.1 Hz, 1H, $C_5H_5N$), 6.37 (m, 1H, $C_5H_4$), 5.63 (m, 1H, $C_5H_4$), 5.25 (m, 1H, $C_5H_4$), 2.45 (s, 6H, $C_6H_3(CH_3)_2$), 1.56 (s, 3H, $(CH_3)_2C$), 1.54 (s, 3H, $(CH_3)_2C$). $^{13}$C NMR (benzene-$d_6$): $\delta$ 152.5, 140.3, 124.7 ($C_5H_5N$), 159.4, 137.8, 132.5, 129.2, 125.6, 121.7 ($C_6H_3(CH_3)_2$), 149.3, 111.5, 111.3, 109.3, 109.0 ($C_5H_4$), 104.6, 102.8 (cage *C*), 42.1, 32.2, 31.5 ($(CH_3)_2C$), 20.2, 20.1 ($C_6H_3(CH_3)_2$). $^{11}$B NMR (benzene-$d_6$): $\delta$ -2.5 (3B), −4.7 (2B), −6.8 (2B), −9.4 (3B). IR (KBr, cm$^{-1}$): $\nu$ 3015 (w), 2973 (m), 2923 (m), 2579 (vs), 1608 (m), 1459 (s), 1280 (m), 1050 (m), 803 (vs), 512 (w). Anal. Calcd for $C_{20.5}H_{31.5}B_{10}N_{1.5}Ti$ (**2** − 0.5Py): C, 54.12; H, 6.98; N, 4.62. Found: C, 53.88; H, 7.27; N, 4.50.

This complex was also prepared in 50% yield via the reaction of the $[Me_2C(C_5H_4)(C_2B_{10}H_{11})]Li_2$ (prepared in situ from $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ (125 mg, 0.5 mmol) and *n*-BuLi (0.7 mL, 1.0 mmol) in THF) with $Ti(=NC_6H_3Me_2\text{-}2,6)Cl_2(Py)_3$ (237 mg, 0.5 mmol) in toluene using the same procedure reported for **1**.

**Preparation of [$\eta^5$:$\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti(=$NC_6H_3{}^iPr_2$-2,6)(Py)·$C_6H_5CH_3$ (3·$C_6H_5CH_3$).** A toluene solution (10 mL) of 2,6-diisopropylaniline (89 mg, 0.5 mmol) was slowly added to a toluene solution (10 mL) of **1** (233 mg, 0.5 mmol) with stirring at room temperature, followed by the identical procedure reported for **2** to give **3**·$C_6H_5CH_3$ as dark red crystals (161 mg, 50%). $^1$H NMR (benzene-$d_6$): $\delta$ 8.51 (d, $J$ = 5.1 Hz, 2H, $C_5H_5N$), 7.13 (dd, $J$ = 7.2 Hz, 1H, $C_6H_3Pr^i_2$), 7.04−6.91 (m, 7H, $C_6H_3Pr^i_2$ + $C_6H_5CH_3$), 6.74 (m, 1H, $C_5H_4$), 6.72 (dd, $J$ = 5.4 Hz, 2H, $C_5H_5N$), 6.45 (m, 1H, $C_5H_4$), 6.38 (dd, $J$ = 5.1 Hz, 1H, $C_5H_5N$), 5.58 (m, 1H, $C_5H_4$), 5.29 (m, 1H, $C_5H_4$), 3.69 (m, 2H, $CH(CH_3)_2$), 2.11 (s, 3H, $C_6H_5CH_3$), 1.49 (s, 3H, $(CH_3)_2C$), 1.45 (s, 3H, $(CH_3)_2C$), 1.26 (d, $J$ = 6.9 Hz, 6H, $CH(CH_3)_2$), 1.13 (d, $J$ = 6.9 Hz, 6H, $CH(CH_3)_2$). $^{13}$C NMR (benzene-$d_6$): $\delta$ 152.9, 140.3, 123.0 ($C_5H_5N$), 156.3, 143.9, 137.9, 129.3, 125.7, 124.7 ($C_6H_3Pr^i_2$ + $C_6H_5CH_3$), 149.6, 111.5, 110.4, 109.3 ($C_5H_4$), 103.2 (cage *C*), 42.1, 31.9, 27.9, 25.8, 24.3, 23.0 ($CH(CH_3)_2$ + $(CH_3)_2C$), 21.4 ($C_6H_5CH_3$). $^{11}$B NMR (benzene-$d_6$): $\delta$ −6.4 (3B), −8.7(2B), −10.5 (2B), −12.8 (3B). IR (KBr, cm$^{-1}$): $\nu$ 3020 (w), 2954 (s), 2583 (vs), 1614 (s), 1450 (s), 1369 (m), 1265 (m), 1051 (s), 806 (vs), 521 (m). Anal. Calcd for $C_{25.5}H_{41}B_{10}NTi$ (**3** + 0.5 toluene − Py): C, 59.17; H, 7.98; N, 2.71. Found: C, 58.78; H, 7.88; N, 3.08.

This complex was also obtained in 40% yield via the reaction of $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]Li_2$ (prepared in situ from $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ (125 mg, 0.5 mmol) and *n*-BuLi (0.7 mL, 1.0 mmol) in THF) with $Ti(=NC_6H_3Pr^i_2\text{-}2,6)Cl_2(Py)_3$ (266 mg, 0.5 mmol) in toluene using the same procedure reported for **1**.

**Preparation of [$\eta^5$:$\sigma$-$Me_2C(C_9H_6)(C_2B_{10}H_{10})$]Ti(=N$^t$Bu)(Py) (4).** A 1.6 M solution of *n*-BuLi in hexane (0.63 mL, 1.0 mmol) was added dropwise to a THF solution (20 mL) of

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$Me_2C(C_9H_7)(C_2B_{10}H_{11})$ (150 mg, 0.5 mmol) at 0 °C. The reaction mixture was stirred overnight at room temperature. After removal of the solvent and addition of toluene (25 mL), Ti(=N$^t$Bu)$Cl_2(Py)_3$ (213 mg, 0.5 mmol) was slowly added to this suspension at room temperature, followed by the same procedure reported for **1** to give **4** as dark red crystals (104 mg, 42%). $^1$H NMR (benzene-$d_6$): $\delta$ 8.71 (d, $J$ = 5.1 Hz, 2H, $C_5H_5N$), 7.92 (d, $J$ = 8.7 Hz, 1H, indenyl), 7.57 (dd, $J$ = 5.1 Hz, 2H, $C_5H_5N$), 7.52 (d, $J$ = 3.3 Hz, 1H, indenyl), 7.20 (dd, $J$ = 5.1 Hz, 1H, $C_5H_5N$), 7.17 (d, $J$ = 3.3 Hz, 1H, indenyl), 7.12 (d, $J$ = 8.7 Hz, 1H, indenyl), 6.93 (t, $J$ = 8.7 Hz, 1H, indenyl), 6.48 (t, $J$ = 8.7 Hz, 1H, indenyl), 1.90 (s, 3H, $(CH_3)_2C$), 1.76 (s, 3H, $(CH_3)_2C$), 1.25 (s, 9H, $(CH_3)_3C$). $^{13}$C NMR (benzene-$d_6$): $\delta$ 150.6, 136.1, 123.1 ($C_5H_5N$), 128.7, 127.9, 125.2, 124.3, 123.4, 120.7, 115.9, 104.7, 103.7 (indenyl), 93.0 (cage *C*), 69.7 ($(CH_3)_3C$), 44.2, 33.3, 32.1 ($(CH_3)_2C$), 31.1 ($(CH_3)_3C$). $^{11}$B NMR (benzene-$d_6$): $\delta$ −3.4 (3B), −5.4 (2B), −6.5 (2B), −9.5 (3B). IR (KBr, cm$^{-1}$): $\nu$ 3050 (w), 2956 (s), 2563 (vs), 1603 (w), 1451 (m), 1366 (m), 1121 (vs), 1043 (m), 802 (m), 744 (s). Anal. Calcd for $C_{23}H_{36}B_{10}N_2Ti$: C, 55.64; H, 7.31; N, 5.64. Found: C, 55.42; H, 7.17; N, 5.69.

**Reaction of 1 with $CS_2$.** An NMR tube was loaded with **1** (12.0 mg, 2.7 × 10$^{-2}$ mmol) and $C_6D_6$ (0.5 mL). $CS_2$ (2.3 mg, 3.0 × 10$^{-2}$ mmol) was added to this solution at room temperature in the glovebox. The color of the solution turned from orange to lime green after the reaction mixture was heated at 50 °C overnight. A yellow solid $[\{\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})\}TiS]_n$ was produced (8.4 mg, 95%). There was no $^{11}$B NMR signal in the solution. The $^1$H NMR spectrum indicated the formation of 1,3-di-*tert*-butylcarbodiimide ($^t$BuN=C=N$^t$Bu) and *tert*-butyl isothiocyanate ($^t$BuN=C=S) with a molar ratio of 1:3. The $^1$H NMR spectrum and GC/MS of $^t$BuN=C=N$^t$Bu and $^t$BuN=C=S were identical to those of authentic samples. The solid-state IR spectrum of the resulting yellow solid showed a characteristic B−H absorption at 2570 cm$^{-1}$.

**Reactions of 1 with Organic Carbonyls.** An NMR tube was charged with **1** (14.0 mg, 3.0 × 10$^{-2}$ mmol) and $C_6D_6$ (0.5 mL). Benzophenone (5.5 mg, 3.0 × 10$^{-2}$ mmol) was added to this solution at room temperature. A pale yellow solid, $[\{\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})\}TiO]_n$, was produced upon mixing the reagents (8.9 mg, 95%). There was no $^{11}$B NMR signal in the solution. The $^1$H NMR spectrum showed the formation of $Ph_2C$=N$^t$Bu by comparison with literature data.[12] The solid-state IR spectrum of the resulting pale yellow solid showed a characteristic B−H absorption at about 2570 cm$^{-1}$.

Treatment of **1** (14.0 mg, 3.0 × 10$^{-2}$ mmol) with phenyl aldehyde (3.2 mg, 3.0 × 10$^{-2}$ mmol) in $C_6D_6$ in an NMR tube resulted in the immediate formation of the corresponding imine (PhCH=N$^t$Bu) and a pale yellow solid, $[\{\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})\}TiO]_n$ (9.0 mg, 96%). The imine was identified by comparison of its $^1$H NMR spectrum with the literature one.[5b] The solid-state IR spectrum of the resulting pale yellow solid showed a characteristic B−H absorption at about 2570 cm$^{-1}$.

**Reaction of 1 with Phenyl Isocyanate.** An NMR tube was charged with **1** (12.0 mg, 2.7 × 10$^{-2}$ mmol) and $C_6D_6$ (0.5 mL). The phenyl isocyanate (3.6 mg, 3.0 × 10$^{-2}$ mmol) was added to this solution at room temperature, and the reaction mixture was put in an ultrasonic bath for 8 h, whereupon the color of the solution turned from orange to dark red. A yellow solid, $[\{\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})\}TiO]_n$, was formed (8.9 mg, 95%). There was no $^{11}$B NMR signal in the solution. The$^1$H NMR spectrum indicated the formation of $^t$BuN=C=NPh. Its $^1$H NMR spectrum and GC-MS data were identical with those of the authentic sample. The solid-state IR spectrum of the resulting yellow solid showed a characteristic B−H absorption at 2570 cm$^{-1}$.

**Preparation of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(OSiMe_3)Cl$ (5).** A THF solution (10 mL) of PhNCO (119 mg, 1.0 mmol) was slowly added to a THF solution (15 mL) of **1** (466 mg, 1.0 mmol) at room temperature, and the mixture was stirred for 5 h. The yellow precipitate was collected by filtration and washed with THF (5 mL × 2). A THF solution (10 mL) of $Me_3SiCl$ (163 mg, 1.5 mmol) was then added to a THF (10 mL) suspension of the above resulting solid (oligomeric oxotitanium) at room temperature. The reaction mixture was stirred overnight to afford an orange solution. After removal of the solvent, the residue was extracted with a mixed solvent of toluene/*n*-hexane (2:1, 10 mL × 2). The organic solutions were combined and concentrated to about 5 mL, from which **5** was isolated as red crystals after this solution stood at room temperature for 3 days (285 mg, 68%). $^1$H NMR (benzene-$d_6$): 6.09 (m, 1H, $C_5H_4$), 5.86 (d, $J$ = 2.4 Hz, 1H, $C_5H_4$), 5.74 (m, 1H, $C_5H_4$), 5.39 (d, $J$ = 2.4 Hz, 1H, $C_5H_4$), 1.32 (s, 3H, $(CH_3)_2C$), 1.22 (s, 3H, $(CH_3)_2C$), 0.11 (s, 9H, $Si(CH_3)_3$). $^{13}$C NMR (benzene-$d_6$): $\delta$ 156.4, 118.8, 108.3, 117.1, 112.3 ($C_5H_4$), 106.9, 103.8 (cage *C*), 42.6, 31.2, 31.1 ($(CH_3)_2C$), 1.18 ($Si(CH_3)_3$). $^{11}$B NMR (benzene-$d_6$): −1.9 (2B), −5.8 (4B), −8.9 (2B), −11.6 (2B). IR (KBr, cm$^{-1}$): $\nu$ 3010 (w), 2956 (m), 2596 (vs), 1469 (w), 1380 (w), 1253 (s), 1093 (m), 1053 (s), 945 (vs), 835 (vs), 756 (s). Anal. Calcd for $C_{13}H_{29}B_{10}ClOSiTi$: C, 37.10; H, 6.94. Found: C, 37.28; H, 7.15.

**Preparation of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(\eta^3\text{-}N^tBuCH{=}CPh)$ (6).** Phenyl acetylene (61 mg, 0.6 mmol) was added to a toluene (15 mL) solution of **1** (233 mg, 0.5 mmol) at room temperature, and the reaction mixture was heated at 90 °C overnight. The color of the solution turned from orange to dark red. After removal of the solvent, the residue was extracted with a mixed solvent of THF/toluene (1:5, 10 mL × 2). The organic solutions were combined and concentrated to about 10 mL, from which **6** was isolated as dark red crystals after this solution stood at −30 °C for 2 days (70 mg, 30%). $^1$H NMR (benzene-$d_6$): $\delta$ 10.6 (s, 1H, PhC=CN*H*), 7.17−7.08 (m, 5H, $C_6H_5$), 6.52 (m, 1H, $C_5H_4$), 5.89 (m, 1H, $C_5H_4$), 5.21 (d, $J$ = 3.0 Hz, 1H, $C_5H_4$), 4.53 (d, $J$ = 3.0 Hz, 1H, $C_5H_4$), 1.44 (s, 3H, $(CH_3)_2C$), 1.41 (s, 3H, $(CH_3)_2C$), 0.96 (s, 9H, $(CH_3)_3C$). $^{13}$C NMR (benzene-$d_6$): $\delta$ 221.8, 146.9 (Ph*C*=*C*NH), 142.1, 128.8, 128.4, 127.1 ($C_6H_5$), 150.6, 112.9, 111.9, 110.0, 103.6 ($C_5H_4$), 102.4, 100.2 (cage *C*), 61.5 ($(CH_3)_3C$), 42.7, 31.8, 31.6 ($(CH_3)_2C$), 31.0 ($(CH_3)_3C$). $^{11}$B NMR (benzene-$d_6$): $\delta$ −4.2 (2B), −7.0 (2B), −10.3 (4B), −13.3 (2B). IR (KBr, cm$^{-1}$): $\nu$ 3075 (w), 2967 (m), 2572 (vs), 1616 (w), 1463 (s), 1380 (s), 1267 (m), 1198 (m), 1038 (s), 812 (s), 693 (m), 501 (s). Anal. Calcd for $C_{22}H_{35}B_{10}NTi$: C, 56.28; H, 7.51; N, 2.98. Found: C, 56.11; H, 7.25; N, 3.18.

**General Procedure for Hydroamination Reaction.** All manipulations were done in the glovebox. A screw cap flask was loaded with **1** (23.0 mg, 5.1 × 10$^{-2}$ mmol) as the catalyst, amine (1.5 mmol), phenyl acetylene (102 mg, 1.0 mmol), and 10 mL of toluene. The flask was heated with stirring at 90 °C for 2 days. The yields and the ratios of *anti*-Marlovnikov to Marlovnikov products were determined by GC-MS in comparison with authentic samples after hydrolysis with 5% HCl and for ketone/aldehyde.

**X-ray Structure Determination.** All single crystals were immersed in Paraton-N oil and sealed under $N_2$ in thin-walled glass capillaries. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation. An empirical absorption correction was applied using the SADABS program.[13] All structures were solved by direct methods and subsequent Fourier difference techniques and refined aniso-

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(13) Sheldrick, G. M. *SADABS*: Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen: Germany, 1996.

**Table 1. Crystal Data and Summary of Data Collection and Refinement for 3−6**

| | **3**·toluene | **4** | **5** | **6** |
|---|---|---|---|---|
| formula | $C_{34}H_{50}B_{10}N_2Ti$ | $C_{23}H_{36}B_{10}N_2Ti$ | $C_{13}H_{29}B_{10}ClOSiTi$ | $C_{22}H_{35}B_{10}NTi$ |
| cryst size, mm | 0.40 × 0.30 × 0.20 | 0.50 × 0.40 × 0.30 | 0.30 × 0.20 × 0.10 | 0.30 × 0.20 × 0.10 |
| fw | 642.8 | 496.5 | 420.9 | 469.5 |
| cryst syst | triclinic | monoclinic | monoclinic | monoclinic |
| space group | $P(-1)$ | $P2_1/c$ | $P2_1$ | $P2_1/n$ |
| $a$, Å | 9.561(2) | 14.710(3) | 7.380(1) | 13.172(1) |
| $b$, Å | 10.511(2) | 10.463(2) | 15.544(1) | 14.591(1) |
| $c$, Å | 20.781(2) | 17.836(4) | 10.070(1) | 13.973(1) |
| α, deg | 97.47(1) | 90 | 90 | 90 |
| $\beta$, deg | 91.46(1) | 94.98(3) | 102.28(1) | 105.39(1) |
| $\gamma$, deg | 115.18(1) | 90 | 90 | 90 |
| $V$, Å$^3$ | 1866.4(4) | 2734.9(9) | 1128.7(1) | 2589.1(3) |
| $Z$ | 2 | 4 | 2 | 4 |
| $D_{calcd}$, Mg/m$^3$ | 1.144 | 1.206 | 1.238 | 1.204 |
| radiation ($\lambda$), Å | Mo Kα (0.71073) | Mo Kα (0.71073) | Mo Kα (0.71073) | Mo Kα (0.71073) |
| 2$\theta$ range, deg | 2.0 to 50.0 | 2.8 to 51.0 | 4.1 to 50.0 | 3.8 to 50.0 |
| $\mu$, mm$^{-1}$ | 0.256 | 0.329 | 0.552 | 0.343 |
| $F$(000) | 680 | 1040 | 436 | 984 |
| no. of obsd reflns | 3965 | 4812 | 3856 | 3385 |
| no. of params refnd | 409 | 325 | 245 | 307 |
| goodness of fit | 1.140 | 1.105 | 0.994 | 1.081 |
| R1 | 0.106 | 0.045 | 0.052 | 0.069 |
| wR2 | 0.253 | 0.122 | 0.114 | 0.167 |

**Table 2. Selected Structural Data for 3−6[a]**

| | **3** | **4** | **5** | **6** |
|---|---|---|---|---|
| Ti−C(ring) | 2.340(9) | 2.404(2) | 2.378(4) | 2.331(5) |
| | 2.398(8) | 2.532(2) | 2.328(5) | 2.372(4) |
| | 2.342(10) | 2.473(2) | 2.292(5) | 2.311(5) |
| | 2.356(9) | 2.332(2) | 2.327(5) | 2.330(6) |
| | 2.408(9) | 2.331(2) | 2.365(5) | 2.385(5) |
| av Ti−C(ring) | 2.369(10) | 2.414(2) | 2.338(5) | 2.346(6) |
| Ti−C(cage) | 2.224(8) | 2.233(2) | 2.156(4) | 2.172(5) |
| Ti−C(cycle) | | | | 1.969(5) |
| | | | | 2.182(5) |
| Ti−N(py) | 2.163(7) | 2.174(2) | | |
| Ti−N(imido) | 1.713(7) | 1.704(2) | | 1.887(4) |
| Ti−O | | | 1.755(3) | |
| Ti−Cl | | | 2.340(2) | |
| Ti−N(imido)−C | 168.1(6) | 166.5(2) | | |
| Cent−Ti−C(cage) | 105.9 | 106.0 | 104.8 | 105.7 |

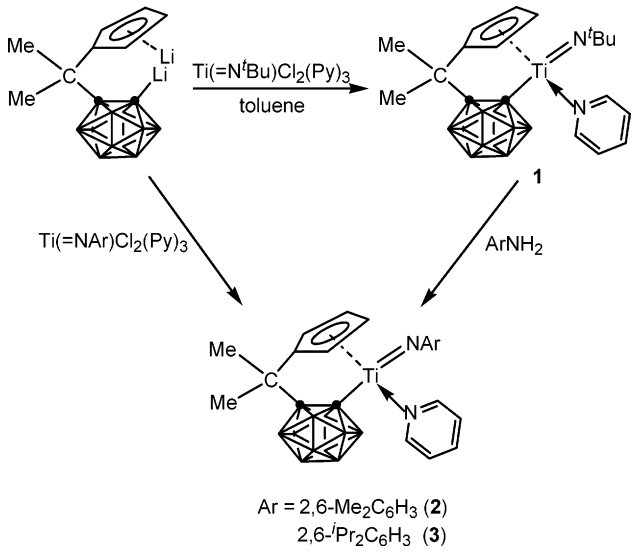
[a] Distances are in Å and angles are in deg; Cent = the centroid of the five-membered ring of Cp or indenyl.

tropically for all non-hydrogen atoms by full-matrix least-squares calculations on $F^2$ using the SHELXTL program package.[14a] For noncentrosymmetric structure **5**, the appropriate enantiomorph was chosen by refining Flack's parameter $x$ toward zero.[14b] Most of the carborane hydrogen atoms were located from difference Fourier syntheses. All other hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements are given in Table 1. Selected bond distances and angles are compiled in Table 2. Further details are included in the Supporting Information.

## Results and Discussion

**Synthesis and Characterization.** Titanium imido compound Ti(=N$^t$Bu)Cl$_2$(Py)$_3$ was reported to be a very useful synthon to a series of titanium imido complexes,[1b,15] in which the two chloro groups offer a valuable entry point to introduce various kinds of ligands through simple metathesis reactions. Treatment of Ti(=NR)Cl$_2$(Py)$_3$ (R = $^t$Bu, 2,6-Me$_2$C$_6$H$_3$, 2,6-$^i$Pr$_2$C$_6$H$_3$) with 1 equiv of dilithium salt of the carbon-bridged ligand [Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Li$_2$ gave new constrained-geometry titanium imido complexes [$\eta^5$:$\sigma$-Me$_2$C(C$_5$H$_4$)-(C$_2$B$_{10}$H$_{10}$)]Ti(=NR)(Py) (R = $^t$Bu (**1**), 2,6-Me$_2$C$_6$H$_3$ (**2**), 2,6-$^i$Pr$_2$C$_6$H$_3$ (**3**)) in 50−70% isolated yields. Complexes **2** and **3** were also prepared by the imido exchange reaction. Addition of 1 equiv of 2,6-dimethylaniline or 2,6-diisopropylaniline into a toluene solution of **1** at room temperature resulted in the rapid formation of **2** and **3** in about 50% isolated yield, respectively. The above synthetic routes were summarized in Scheme 1. Complexes **1**−**3** represent the first examples of group 4 metal imido complexes supported by constrained-geometry (Cp-D) ligands.

**Scheme 1**




Complexes **1**−**3** were air- and moisture-sensitive, very soluble in toluene, and even slightly soluble in $n$-hexane. The $^1$H NMR spectra of **1**−**3** showed four multiplets of the cyclopentadienyl ring protons and two singlets in the region 1.49−1.55 ppm attributable to the bridging Me$_2$C unit. In addition, one singlet at 1.20 ppm assign-

(14) (a) Sheldrick, G. M. *SHELXTL 5.10 for windows NT*: Structure Determination Software Programs; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997. (b) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.

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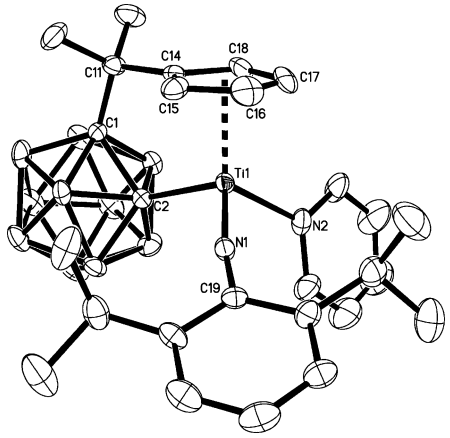
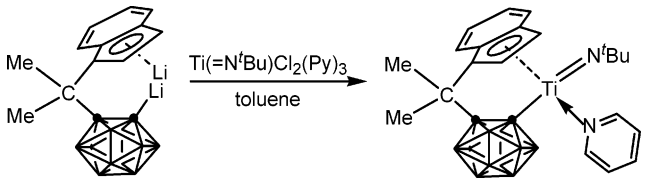



**Figure 1.** Molecular structure of [$\eta^5$:$\sigma$-$Me_2C(C_5H_4)$-$(C_2B_{10}H_{10})$]Ti(=$NC_6H_3Pr^i_2$-2,6)(Py) (**3**).

**Scheme 2**




**4**

able to the methyl protons of the C($CH_3$)$_3$ unit was observed in the $^1$H NMR spectrum of **1**; the resonances at 68.0 and 32.0 ppm corresponding to the *tert*-butyl imido group (=N$C$($CH_3$)$_3$) were also found in its $^{13}$C NMR spectrum. For **2** and **3**, the $^1$H NMR spectra showed one singlet ($\delta$ = 2.45 ppm) of the ($CH_3$)$_2$$C_6H_3$ methyl protons and two doublets ($\delta$ = 1.26 and 1.13 ppm) with equal intensity for the isopropyl methyl protons, respectively. The $^{11}$B NMR spectra exhibited a 3:2:2:3 splitting pattern for **1**−**3**.

The indenyl analogue [$\eta^5$:$\sigma$-$Me_2C(C_9H_6)(C_2B_{10}H_{10})$]Ti-(=N$^t$Bu)(Py) (**4**) was prepared in 42% isolated yield from the reaction of Ti(=N$^t$Bu)$Cl_2(Py)_3$ with [$Me_2C(C_9H_6)$-$(C_2B_{10}H_{10})$]$Li_2$ in a molar ratio of 1:1 in toluene (Scheme 2). In addition to the aromatic protons, two singlets ($\delta$ = 1.90 and 1.76 ppm) assignable to the $Me_2C$ protons and one singlet at 1.25 ppm attributable to the $^t$Bu protons were also observed in the $^1$H NMR spectrum of **4**. Like complexes **1**−**3**, the $^{11}$B NMR spectrum showed a 3:2:2:3 splitting pattern.

The solid-state structures of **3** and **4** as derived from single-crystal X-ray diffraction studies confirmed that the geometry around the titanium atom in **3** and **4** is best described as a distorted tetrahedron. Figures 1 and 2 show the molecular structures of **3** and **4**, respectively. Key structural data are compiled in Table 2. The Ti−C(cage) and Ti−C(ring) distances as well as the C(Cent)−Ti−C(cage) angles in **3** and **4** are very comparable to those found in [$\eta^5$:$\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti$(NMe_2)_2$[7a] and [$\eta^5$:$\sigma$-$Me_2C(C_9H_6)(C_2B_{10}H_{10})$]Ti$(NMe_2)_2$.[7a] The Ti−N(imido) bond distances of 1.713(7) Å in **3** and 1.704(2) Å in **4** fall in the range of the Ti=NR bond lengths (1.672(7)−1.723(4) Å) for a wide variety of ancillary ligand enviroments.[9,15a,16,17] The Ti−N(imido)−C angles of 168.1(6)° in **3** and 166.5(2)° in **4** are very comparable to the C−N=Ti angles observed in titanium imido complexes.[9,15a,16,17]

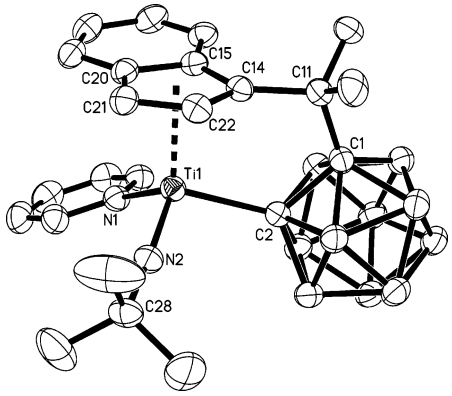



**Figure 2.** Molecular structure of [$\eta^5$:$\sigma$-$Me_2C(C_9H_6)$-$(C_2B_{10}H_{10})$]Ti(=N$^t$Bu)(Py) (**4**).

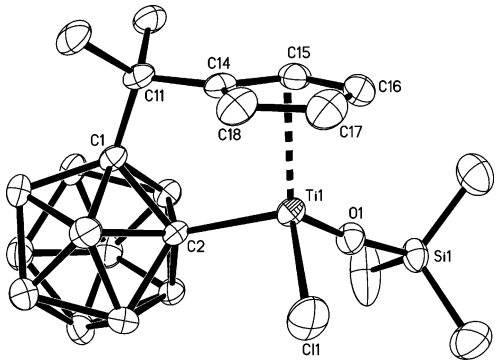


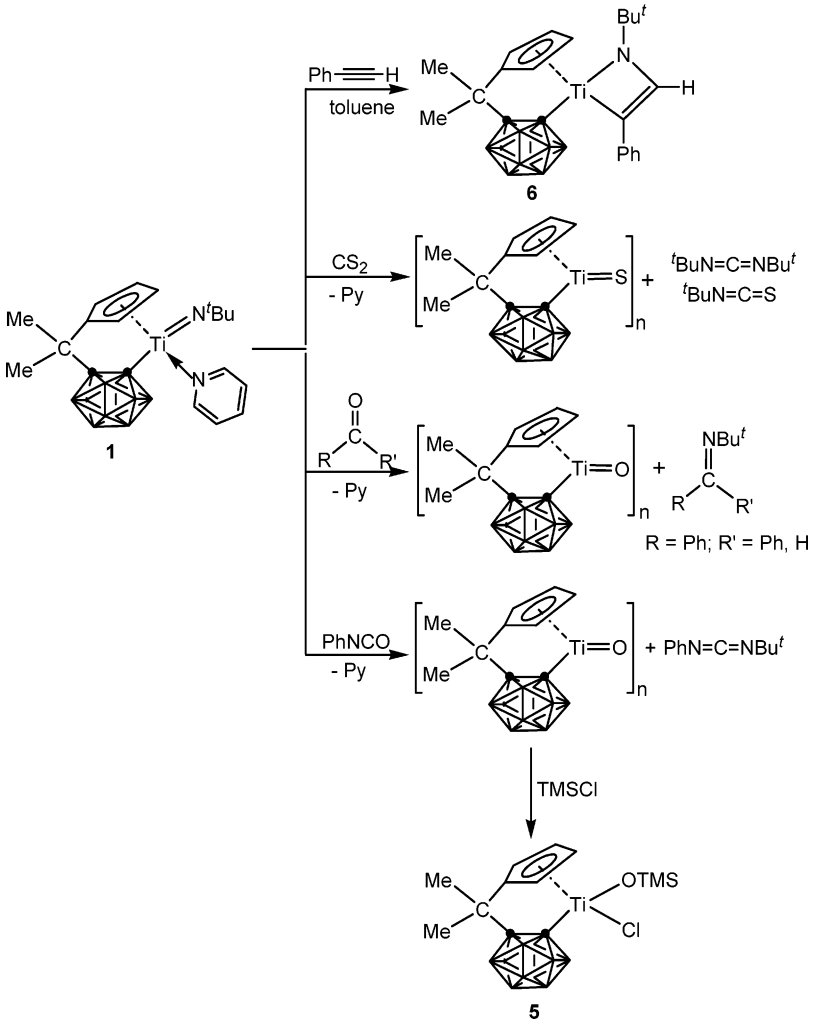

**Figure 3.** Molecular structure of [$\eta^5$:$\sigma$-$Me_2C(C_5H_4)$-$(C_2B_{10}H_{10})$]Ti($OSiMe_3$)Cl (**5**).

**Reactivity.** Metal imido complexes are useful for imido group transfer in catalytic processes as well as in organic syntheses. It is interesting to know if the constrained-geometry carboranyl ligand has any effects on the reactivity of the resulting metal imido complexes. Complex **1** underwent imido/oxo exchange reactions with $Ph_2C$=O, PhCHO, and PhN=C=O to generate the corresponding imine or carbodiimide and oxotitanium oligomer as a pale yellow solid. These reactions occurred spontaneously and quantitatively at room temperature as shown in Scheme 3. The resulting solids from the above reactions had identical solid-state IR spectra and showed a characteristic absorption at about 2570 cm$^{-1}$ for B−H. The resulting imines or carbodiimide was identified by GC-MS and by comparison with authentic samples and literature data.[5b,12] These reactions may involve initial dissociation of pyridine, followed by overall [2+2] cycloaddition between the C=O and the Ti=N moiety, to give oxoazametallacyclobutanes. Reversion of these metallacycles would generate an oxotitanium oligomer with the concurrent extrusion of $Ph_2C$=N$Bu^t$, PhCH=N$Bu^t$, or PhN=C=N$Bu^t$.

Extremely poor solubility of the resulting oxotitanium oligomer {[$\eta^5$:$\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]TiO}$_n$ in all standard solvents made its characterization by NMR techniques impossible. It has been reported that group 4 oxometallocenes can be trapped by reacting with a number of reagents, resulting in addition across the M=O bonds.[18] Treatment of {[$\eta^5$:$\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]-

(16) Stewart, P. J.; Blake, A. J.; Mountford, P. *Inorg. Chem.* **1997**, *36*, 3616.
(17) Dunn, S. C.; Mountford, P.; Robson, D. A. *J. Chem. Soc., Dalton Trans.* **1997**, 293.

**Scheme 3**




$TiO\}_n$ with excess $Me_3SiCl$ in THF gave the expected addition product $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(OSiMe_3)Cl$ (**5**) in 68% isolated yield. In addition to four multiplets of the Cp protons, its $^1H$ NMR spectrum exhibited two singlets with an equal intensity at $\delta = 1.32$ and 1.22 ppm assignable to the $(CH_3)_2C$ protons and a singlet at $\delta = 0.11$ ppm attributable to the methyl protons of the $Si(CH_3)_3$ unit. The formation of **5** was also supported by the $^{13}C$ NMR spectrum. The $^{11}B$ NMR spectrum showed a 2:4:2:2 splitting pattern. The successful isolation of **5** further confirmed the formation of the oxotitanium oligomer in the above imido/oxo exchange reactions.

The molecular structure of **5** is shown in Figure 3. The Ti atom is $\eta^5$-bound to the five-membered ring of the cyclopentadienyl and $\sigma$-bound to the cage carbon atom of the carboranyl, a chlorine atom, and an oxygen atom in a distorted-tetrahedral geometry. The average Ti−C(ring) distance of 2.339(5) Å, Ti−C(cage) distance of 2.157(4) Å, and Ti−Cl distance of 2.234(2) Å are close to the corresponding values of 2.341(2), 2.179(2), and 2.277(1) Å found in $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]TiCl(NMe_2)_2$,[7a] respectively. The Ti−O distance of 1.755(3) Å and the Ti−O−Si angle of 169.2(2)° are compared with the corresponding values of 1.806(2) Å and 174.5(1)° observed in $[\eta^5\text{-}(Me_3Si)_2C_5H_3]Ti(OSiPh_3)(CH_2Ph)$.[19] The linearity of the Ti−O−Si angle suggests the presence of O(p$\pi$)−Si(d$\pi$) and O(p$\pi$)−Ti(d$\pi$) interactions.[19]

Complex **1** also reacted with $CS_2$, but the reaction proceeded very slowly, taking 3 days at room temperature for the complete consumption of **1**. The reaction rate increased rapidly at higher temperatures. After treatment of **1** with a slight excess of $CS_2$ in $C_6D_6$ at 50 °C overnight, the $^1H$ NMR spectrum showed the formation of $^t$BuN=C=N$^t$Bu and $^t$BuN=C=S with a molar ratio of 1:3. The resulting pale yellow precipitate was presumably $\{[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]TiS\}_n$. The formation of the symmetrical carbodimide $^t$BuN=C=N$^t$Bu was the result of the consecutive reaction of **1** with the newly formed $^t$BuN=C=S.[20] The slower reaction of **1** with $CS_2$ in comparison with the above carbonyl compounds might be attributed to the lower electrophilicity of the carbon atom in $CS_2$ and the soft nature of sulfur, which makes $CS_2$ disfavor the coordination to the hard titanium center.

The crucial reaction step in the hydroamination reactions catalyzed by group 4 metal imido complexes is believed to be the formal [2+2] cycloaddition of a C≡

(18) (a) Hanna, T. A.; Baranger, A. M.; Bergman, R. G. *J. Org. Chem.* **1996,** *61*, 4532. (b) Blum, S. A.; Bergman, R. G. *Organometallics* **2004**, *23*, 4003.

(19) Duchateau, R.; Cremer, U.; Harmsen, R. J.; Mohamud, S. I.; Abbenhuis, H. C. L.; van Santen, R. A.; Meetsma, A.; Thiele, S. K.-H.; van Tol, M. F. H.; Kranenburg, M. *Organometallics* **1999**, *18*, 5447.

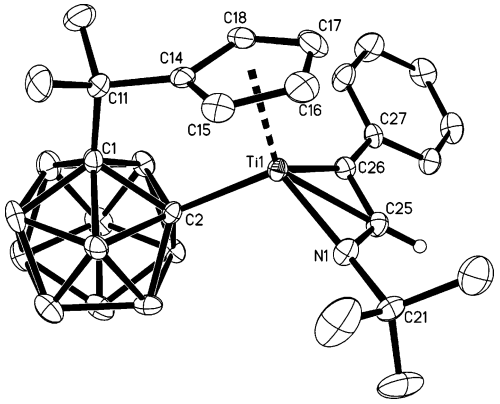
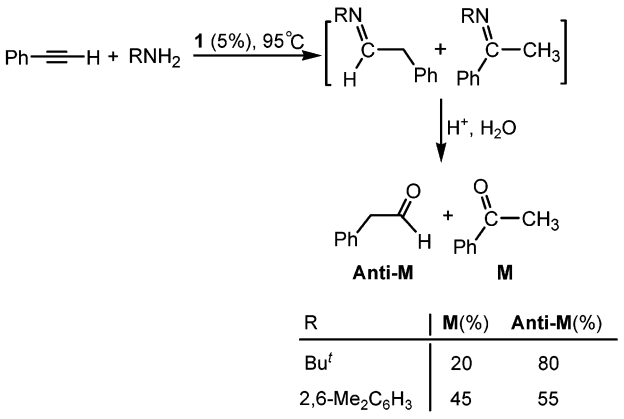



**Figure 4.** Molecular structure of [$\eta^5$:$\sigma$-$Me_2C(C_5H_4)$-$(C_2B_{10}H_{10})$]Ti($\eta^3$-N$^t$BuCH=CPh) (**6**).

C bond to the M=NR bond to form a metallacyclic complex. Many attempts to isolate such a metallacyclic intermediate have been made,[21,22] and the first isolation and structural characterization of the metallacyclic intermediate in an *anti*-Markovnikov hydroamination of terminal alkynes were reported in 2004.[21] The $^1$H NMR spectrum indicated that **1** reacted with PhC≡CH in $C_6D_6$ at 80 °C to give two [2+2] cycloaddition products with a molar ratio of 9.5:0.5. Under the same reaction conditions, or even at room temperature, interaction of **2** with 1 equiv of PhC≡CH afforded two products in a 1:1 molar ratio. No reactions were observed even at 80 °C between **1** or **2** and $Me_3SiC$≡$CSiMe_3$ in $C_6D_6$. These results suggested that [2+2] cycloaddition reactions were very sensitive to the substrates, and a pure addition product was likely isolated from the reaction of **1** with PhC≡CH. Treatment of **1** with 1 equiv of phenyl acetylene in toluene at 90 °C gave, after workup, a metallacycle, [$\eta^5$:$\sigma$-$Me_2C(C_5H_4)$-$(C_2B_{10}H_{10})$]Ti($\eta^3$-N$^t$BuCH=CPh) (**6**), in 30% isolated yield. In the $^1$H NMR spectrum, the metallacycle methine proton was observed as a singlet with a rather downfield chemical shift of $\delta$ = 10.6 ppm. The resonances at $\delta$ = 221.8 and 146.9 ppm observed in the $^{13}$C NMR spectrum were assignable to the carbons of the metallacycle in **6**. Its $^{11}$B NMR spectrum showed a 1:1:2:1 splitting pattern.

Single-crystal X-ray analyses confirmed that **6** is one of the very rare examples of a metallacyclic intermediate in an *anti*-Markovnikov hydroamination of a terminal alkyne, shown in Figure 4. The structural features of the [$\eta^5$:$\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti moiety are very similar to those observed in **3** and **5**, as judged by bond distances and angles (Table 2). The metallacycle ring is planar and the phenyl group on the C(26) is turned slightly out of the metallacycle plane. Similar structure features are also observed in ($\eta^5$-$C_5Me_5)_2$Ti[N(Ph)CH=CH] (**A**)[22b] and LTi[N($C_6H_3Pr^i$-2,6)CH=C($C_6H_5$Me-4)] (L = $MeC(C_5H_4N)(CH_2NSiMe_3)_2$) (**B**).[21] But the bond distances and angles within the metallacyclic ring in **6** are quite different from those observed in **A** and **B**. The

**Scheme 4**




| R | M(%) | Anti-M(%) |
|---|---|---|
| Bu$^t$ | 20 | 80 |
| 2,6-$Me_2C_6H_3$ | 45 | 55 |

Ti(1)−N(1) distance of 1.887(4) Å is much shorter than the corresponding values of 2.059(2) Å in **A** and 2.087(3) Å in **B**. The Ti(1)−C(26) distance of 1.969(5) Å is also shorter than the corresponding values of 2.060-(2) Å in **A** and 2.031(4) Å in **B**. The Ti(1)−C(25) distance of 2.182(5) Å is 0.213 Å longer than that of Ti(1)−C(26), but is significantly shorter than the corresponding values of 2.428(2) Å in **A** and 2.428(3) Å in **B**. As a consequent result, the C(26)−C(25)−N(1) angle of 121.1(4)° in **6** is much greater than the 115.8(2)° observed in **A** and the 115.8(3)° found in **B**. In addition, the measured Ti(1)−C(25) distance of 2.182(5) Å is much shorter than the average Ti(1)−C(ring) distance of 2.346(6) Å. All these data suggest that the $C_6H_5C$=CH−NBu$^t$ moiety is best described as a $\eta^3$ rather than $\eta^2$ $\pi$ ligand. Such bonding interactions may result from the highly electron-deficient titanium center.

**Hydroamination.** The successful isolation of the key intermediate **6** prompts us to examine the catalytic activity of **1** in hydroamination of alkynes which have received considerably current interest.[4] The catalytic reactions were carried out at 90 °C in toluene for 20 h with a 2:3 molar ratio of phenylacetylene and amines (*tert*-butylamine and 2,6-dimethylaniline) in the presence of 5% **1** as catalyst. Phenylacetylene was completely consumed after 20 h, as indicated by GC. Due to the potential susceptibility of the resulting imines to hydrolysis, the hydroamination products were directly detected by a hydrolytic workup (Scheme 4). The two amines employed in the reactions revealed an interesting regioselectivity for catalyst **1**. The reaction of *tert*-butylamine with phenylacetylene gave, after hydrolytic workup, the *anti*-Markovnikov addition product ($PhCH_2$-CHO) and Markovnikov product ($PhCOCH_3$) with a molar ratio of 4:1. When 2,6-dimethylaniline was used for the reaction, the ratio of *anti*-Markovnikov to Markovnikov products changed to 5:4. It was clear that steric factors of the amines play a key role in the hydroamination of phenylacetylene. These results were consistent with those derived from the $^1$H NMR spectra discussed previously in this paper. It was noted that complex **6** was also able to catalyze the hydroamination of phenylacetylene with a reactivity very similar to that of **1**.

## Conclusion

Several new titanium imido complexes containing the constrained-geometry carboranyl ligand [$Me_2C(C_5H_4)$-

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$(C_2B_{10}H_{10})]^{2-}$ or $[Me_2C(C_9H_6)(C_2B_{10}H_{10})]^{2-}$ were prepared by either salt metathesis or imido exchange reactions. Reactions of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(=N^tBu)(Py)$ (**1**) with various unsaturated molecules such as PhCHO, $Ph_2CO$, PhNCO, and $CS_2$ gave either N/O or N/S exchange products in addition to the formation of titanium oxo/sulfido oligomers, a reactivity pattern that is similar to that observed in other titanium imido complexes. The [2+2] cycloaddition of a C≡C to the Ti=N bond led to the isolation and structural characterization of the metallacyclic intermediate $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(\eta^3\text{-}N^tBuCH{=}CPh)$ (**6**) with unique structural features, which offers an opportunity to study the key step in hydroamination reactions. Complex **1** also catalyzed the hydroamination of phenyl acetylene with amines to give both Markovnikov and *anti*-Markovnikov products. The product ratio was dependent upon the steric hindrance of the amines used.

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**Supporting Information Available:** Tables of crystallographic data and data collection details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for complexes **3**–**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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