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Synthesis, Structural Characterization, Reactivity, and Thermal Stability of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti(R)($NMe_2$)

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Reaction of [η:$^5\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]TiCl($NMe_2$) (**1**) with 1 equiv of $PhCH_2K$, MeMgBr, or Me_3SiCH_2Li gave corresponding organotitanium alkyl complexes [η:$^5\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti(R)($NMe_2$) (R = CH_2Ph (**2**), CH_2SiMe_3 (**4**), or Me (**5**)) in good yields. Treatment of **1** with 1 equiv of *n*-BuLi afforded the decomposition product {[η:$^5\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti}$_2$($\mu$-NMe)($\mu$:$\sigma$-$CH_2NMe$) (**3**). Complex **5** slowly decomposed to generate a mixed-valence dinuclear species {[η:$^5\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti}$_2$($\mu$-$NMe_2$)($\mu$:$\sigma$-$CH_2NMe$) (**6**). Complex **1** reacted with 1 equiv of PhNCO or 2,6-$Me_2C_6H_3NC$ to afford the corresponding monoinsertion product [η:$^5\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti(Cl)[$\eta^2$-OC($NMe_2$)NPh] (**7**) or [$\eta$:$^5\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti(Cl)[$\eta^2$-C($NMe_2$)=N(2,6-$Me_2C_6H_3$)] (**8**). Reaction of **4** or **5** with 1 equiv of R′NC gave the titanium η^2-iminoacyl complexes [η:$^5\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti($NMe_2$)[$\eta^2$-C(R)=N(R′)] (R = CH_2SiMe_3, R′ = 2,6-$Me_2C_6H_3$ (**9**) or ^{t}Bu (**10**); R = Me, R′ = 2,6-$Me_2C_6H_3$ (**11**) or ^{t}Bu (**12**)). The results indicated that the unsaturated molecules inserted into the Ti–N bond only in the absence of the Ti–C(alkyl) bond and that the Ti–C(cage) bond remained intact. All complexes were fully characterized by various spectroscopic techniques and elemental analyses. Molecular structures of **2**, **3**, **6**–**8**, and **10**–**12** were further confirmed by single-crystal X-ray analyses.

Introduction

Our previous work showed that group 4 metal complexes of the types [η^5:σ-$Me_2A(C_5H_4)(C_2B_{10}H_{10})$]M($NR_2$)$_2$, [$\eta$:$^5\sigma$-$Me_2A(C_9H_6)(C_2B_{10}H_{10})$]M($NR_2$)$_2$,[1] and [$\eta^5$:$\sigma$-$^iPr_2NA'(C_9H_6)$-$(C_2B_{10}H_{10})$]M($NR_2$)$_2$[2] (A = C, Si; A′ = B, P; M = group 4 metals; R = Me, Et) were active catalysts for ethylene polymerization upon activation with MAO (methylalumoxane).[3] The active species were suggested to be $L_2MCH_3^+$ (L_2 = linked cyclopentadienyl−carboranyl ligands) cations containing both M−C(cage) and M−CH_3 bonds. A question subsequently arises as to whether the M−C(cage) bond is active in polymerization. Reactivity studies on [η^5:σ-Me_2C-$(C_9H_6)(C_2B_{10}H_{10})$]Zr($NMe_2$)$_2$ indicated that the unsaturated molecules inserted exclusively into the Zr−N bond and the Zr−C(cage) bond remained intact. Such a preference of the Zr−N over Zr−C insertion was suggested to most likely be governed by steric factors.[4] This is a very rare example,[5] because the insertion into M−N bonds would be possible only if no alkyl substituents are present.[6]

On the other hand, [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]$_2$Zr was reported to catalyze the polymerization of MMA (methyl methacrylate) in the absence of any cocatalyst through the action of the nucleophilic cage atom.[7] Complexes [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]M($\eta^5$-$C_5Me_5$)Cl (M = Ti, Zr) were active catalysts for ethylene polymerization in the presence

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of MMAO (modified methylalumoxane). Possible involvement of the activation of the M−C(cage) σ bond was suggested.[8]

The above results prompted us to investigate the relative reactivity of M−C(alkyl), M−C(cage), and M−N bonds toward unsaturated molecules. The most convenient route for preparing such a model complex containing four different ligands is to convert one of the NMe_2 groups in $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M(NMe_2)_2$ into an alkyl unit. Controlled methylation[9] or chlorination[1] of zirconium amides was not successful using Me_3Al or Me_3SiCl as reagents. For the smaller Ti analogue, however, controlled chlorination was achieved. $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]TiCl(NMe_2)$ was conveniently prepared in 65% yield by treatment of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(NMe_2)_2$ with excess Me_3SiCl in toluene.[1] This was subsequently converted into its alkyl derivatives, which offered a unique opportunity to observe the direct competition among Ti−C(alkyl), Ti−N, and Ti−C(cage) bonds in the migratory insertion with unsaturated molecules. The Ti−alkyl complexes were thermally unstable, leading to the formation of interesting dinuclear species. We report in this article the synthesis, structural characterization, thermal stability, and reactivity of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]TiR(NMe_2)$.

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. $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]TiCl(NMe_2)$ (**1**)[1] and $PhCH_2K$[10] were prepared according to 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. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300 and 75 MHz, respectively. ^{11}B spectra were recorded on a Varian Inova 400 spectrometer at 128 MHz. All chemical shifts were reported in δ 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 $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(CH_2Ph)(NMe_2)$ (2). A THF (10 mL) solution of $PhCH_2K$ (117 mg, 0.9 mmol) was added dropwise to a THF (10 mL) solution of **1** (337 mg, 0.9 mmol) at −78 °C. The reaction mixture was slowly warmed to room temperature and stirred overnight. After the solvent was removed, the residue was extracted with toluene (5 mL × 3). The toluene solutions were combined and concentrated to about 5 mL and *n*-hexane (5 mL) was added. Complex **2** was isolated as red crystals after this solution stood at −30 °C for 3 days (210 mg, 54%). ^1H NMR (benzene-d_6): δ 7.10 (m, 2H, $CH_2C_6H_5$), 6.90 (t, J = 7.2 Hz, 1H, $CH_2C_6H_5$), 6.76 (d, J = 7.2 Hz, 2H, $CH_2C_6H_5$), 6.08 (m, 1H, C_5H_4), 5.39 (m, 1H, C_5H_4), 5.25 (m, 2H, C_5H_4), 3.04 (s, 6H, $N(CH_3)_2$), 2.42 (d, ^2J = 8.5 Hz, 1H, $CH_2C_6H_5$), 2.10 (d, ^2J = 8.5 Hz, 1H, $CH_2C_6H_5$), 1.27 (s, 3H, $(CH_3)_2C$), 1.17 (s, 3H, $(CH_3)_2C$). ^{13}C NMR (benzene-d_6): δ 150.3, 148.7, 129.6, 129.4, 126.0, 125.2 ($CH_2C_6H_5$), 123.3, 118.9, 118.7, 115.0, 113.1 (C_5H_4), 102.5, 92.4 (cage *C*), 66.2 ($CH_2C_6H_5$), 47.5 ($N(CH_3)_2$), 42.6, 32.1, 31.6 ($(CH_3)_2C$). ^{11}B NMR (benzene-d_6): δ −3.2 (2B), −6.4 (2B), −9.8 (4B), −12.9 (2B). IR (KBr, cm^{-1}): ν 2589 (s) (BH). Anal. Calcd for $C_{19}H_{33}B_{10}NTi$: C, 52.89; H, 7.71; N, 3.25. Found: C, 52.60; H, 7.71; N, 3.50.

Preparation of $\{[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti\}_2(\mu\text{-}NMe)(\mu{:}\sigma\text{-}NMeCH_2){\cdot}2C_6H_5CH_3$ ($3{\cdot}2C_6H_5CH_3$). A 1.6 M solution of *n*-BuLi in hexane (0.4 mL, 0.6 mmol) was slowly added to a THF (15 mL) solution of **1** (226 mg, 0.6 mmol) at −78 °C. The reaction mixture was slowly warmed to room temperature and stirred for 3 h. The color of the solution changed gradually from red to dark blue. After the solvents were removed, the residue was extracted with toluene (10 mL × 3). The toluene solutions were combined and concentrated to about 5 mL. Complex **3** was isolated as dark red crystals after this dark blue solution stood at room temperature for 3 days (188 mg, 37%). ^1H NMR (benzene-d_6): δ 7.13 (m, 4H, $CH_3C_6H_5$), 7.02 (m, 6H, $CH_3C_6H_5$), 6.67 (m, 2H, C_5H_4), 6.58 (m, 2H, C_5H_4), 6.23 (m, 2H, C_5H_4), 5.17 (m, 2H, C_5H_4), 3.54 (br s, 6H, NCH_3), 3.02 (d, ^2J = 7.0 Hz, 1H, NCH_2), 2.19 (d, ^2J = 7.0 Hz, 1H, NCH_2), 2.01 (s, 6H, $CH_3C_6H_5$), 1.41 (s, 6H, $(CH_3)_2C$), 1.21 (s, 6H, $(CH_3)_2C$). ^{13}C NMR (benzene-d_6): δ 137.9, 129.3, 125.6 ($CH_3C_6H_5$), 120.1, 115.2, 113.3, 112.5, 111.2 (C_5H_4), 67.9 (NCH_3), 65.9 (NCH_2), 31.9, 25.8, 23.0 ($(CH_3)_2C$), 21.4 ($CH_3C_6H_5$); the cage carbons were not observed. ^{11}B NMR (benzene-d_6): δ −3.7 (2B), −4.2 (2B), −6.6 (2B), −9.0 (4B), −11.1 (4B), −13.3 (6B). IR (KBr, cm^{-1}): ν 2565 (s) (BH). Anal. Calcd for $C_{30}H_{57}B_{20}N_2Ti_2$ (**3** + toluene): C, 47.55; H, 7.58; N, 3.70. Found: C, 47.40; H, 7.30; N, 3.50.

Preparation of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(CH_2SiMe_3)(NMe_2)$ (4). A 1.0 M solution of Me_3SiCH_2Li in hexane (0.5 mL, 0.5 mmol) was added dropwise to a toluene (10 mL) solution of **1** (187 mg, 0.5 mmol) with stirring at −30 °C, and the mixture was stirred at room temperature for 3 h. After the solvents were removed, the residue was extracted with *n*-hexane (20 mL x 2). The *n*-hexane solutions were combined and concentrated to about 10 mL. Complex **4** was isolated as an orange solid after this solution stood at −30 °C for 1 day (160 mg, 75%). ^1H NMR (benzene-d_6): δ 6.30 (m, 1H, C_5H_4), 6.02 (m, 1H, C_5H_4), 5.31 (m, 1H, C_5H_4), 5.26 (m, 1H, C_5H_4), 3.12 (s, 6H, $N(CH_3)_2$), 2.11 (d, ^2J = 9.0 Hz, 1H, $CH_2Si(CH_3)_3$), 1.74 (d, ^2J = 9.0 Hz, 1H, $CH_2Si(CH_3)_3$), 1.35 (s, 3H, $(CH_3)_2C$), 1.23 (s, 3H, $(CH_3)_2C$), 0.11 (s, 9H, $CH_2Si(CH_3)_3$). ^{13}C NMR (benzene-d_6): δ 147.8, 116.3, 114.3, 111.9, 111.3 (C_5H_4), 102.2, 90.9 (cage *C*), 65.8 ($CH_2Si(CH_3)_3$), 47.6 ($N(CH_3)_2$), 42.1, 31.8, 31.7 ($(CH_3)_2C$), 2.80 ($CH_2Si(CH_3)_3$). ^{11}B NMR (benzene-d_6): δ −0.8 (2B), −4.1 (2B), −7.6 (4B), −10.7 (2B). IR (KBr, cm^{-1}): ν 2574 (vs) (BH). Anal. Calcd for $C_{16}H_{37}B_{10}NSiTi$: C, 44.95; H, 8.72; N, 3.28. Found: C, 44.60; H, 8.81; N, 3.23.

Preparation of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(CH_3)(NMe_2)$ (5). A 3.0 M solution of CH_3MgBr in diethyl ether (0.33 mL, 1.0 mmol) was added dropwise to a toluene (15 mL) solution of **1** (375 mg, 1.0 mmol) with stirring at −30 °C, followed by the identical procedure reported for **4** to give **5** as a yellow solid (213 mg, 60%). ^1H NMR (benzene-d_6): δ 6.25 (m, 1H, C_5H_4), 5.58 (m, 1H, C_5H_4), 5.29 (m, 1H, C_5H_4), 5.19 (m, 1H, C_5H_4), 3.03 (s, 6H, $N(CH_3)_2$), 1.33 (s, 3H, $(CH_3)_2C$), 1.22 (s, 3H, $(CH_3)_2C$), 0.71 (s, 3H, CH_3). ^{13}C NMR (benzene-d_6): δ 147.3, 116.9, 113.6, 111.3, 109.7 (C_5H_4), 103.6, 102.1 (cage *C*), 47.6 (CH_3), 45.7 ($N(CH_3)_2$), 42.2, 31.8, 31.3 ($(CH_3)_2C$). ^{11}B NMR (benzene-d_6): δ −2.4 (2B), −6.1 (2B), −9.5

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(4B), −12.6 (2B). IR (KBr, cm^{-1}): ν 2577 (s) (BH). Satisfactory elemental analyses were not obtained because of the thermal decomposition of **5** during shipment.

Preparation of $\{[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti\}_2(\mu\text{-}NMe_2)(\mu{:}\sigma\text{-}NMeCH_2)\cdot 2THF$ (6·2THF). Complex **5** (177 mg, 0.5 mmol) was dissolved in a warm toluene (15 mL). The color of the solution turned from yellow to dark blue overnight. Removal of the solvents gave a dark blue solid. Recrystallization from THF/toluene at room temperature afforded **6**·2THF as dark green crystals (124 mg, 30%). ^{1}H NMR (pyridine-d_5): δ 3.57 (br s), 1.42 (br s) (THF), plus many broad, unresolved peaks. ^{13}C NMR (pyridine-d_5): δ 65.2, 25.7 (THF), plus many broad, unresolved peaks. ^{11}B NMR (pyridine-d_5): δ −2.7 (6B), −5.9 (6B), −9.2 (8B). IR (KBr, cm^{-1}): ν 2584 (vs) (BH). Anal. Calcd for $C_{32}H_{67}B_{20}N_2O_2Ti_2$ (**6** + 2THF): C, 46.65; H, 8.20; N, 3.40. Found: C, 46.32; H, 7.97; N, 3.54.

Preparation of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(Cl)[\eta^2\text{-}OC(NMe_2)NPh]$ (7). A toluene (10 mL) solution of phenyl isocyanate (60 mg, 0.5 mmol) was added to a toluene (10 mL) solution of **1** (187 mg, 0.5 mmol) at 0 °C, and the mixture was stirred overnight at room temperature. The precipitate was collected by filtration and redissolved in hot THF (10 mL). Complex **7** was isolated as orange crystals after this solution stood at room temperature for 3 days (160 mg, 65%). ^{1}H NMR (pyridine-d_5): δ 7.42 (m, 2H, C_6H_5), 7.29 (t, J = 6.9 Hz, 1H, C_6H_5), 7.03 (d, J = 6.3 Hz, 2H, C_6H_5), 6.99 (m, 1H, C_5H_4), 6.79 (m, 1H, C_5H_4), 6.17 (m, 1H, C_5H_4), 5.99 (m, 1H, C_5H_4), 2.87 (s, 6H, $N(CH_3)_2$), 1.70 (s, 3H, $(CH_3)_2C$), 1.58 (s, 3H, $(CH_3)_2C$). ^{13}C NMR (pyridine-d_5): δ 165.9 (NCO), 146.2, 128.2, 128.0, 124.7, 123.6, 121.7 (C_6H_5), 154.9, 120.0, 117.2, 112.3 (C_5H_4), 102.8 (cage *C*), 42.3 ($N(CH_3)_2$), 35.7, 31.4, 31.3 ($(CH_3)_2C$). ^{11}B NMR (pyridine-d_5): δ −4.7 (2B), −8.3 (4B), −10.4 (4B). IR (KBr, cm^{-1}): ν 2576 (vs) (BH), 1596 (vs) (NCO). Anal. Calcd for $C_{19}H_{31}B_{10}ClN_2OTi$: C, 46.11; H, 6.31; N, 5.66. Found: C, 46.45; H, 6.13; N, 5.68.

Preparation of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(Cl)[\eta^2\text{-}C(NMe_2){=}N(C_6H_3Me_2\text{-}2,6)]$ (8). A toluene (10 mL) solution of 2,6-dimethylphenyl isocyanide (66 mg, 0.5 mmol) was added to a toluene (15 mL) solution of **1** (187 mg, 0.5 mmol) with stirring at room temperature. The resulting solution was refluxed for 2 days and then concentrated to about 10 mL. Complex **8** was isolated as yellow crystals after this solution stood at room temperature for 1 day (152 mg, 60%). ^{1}H NMR (benzene-d_6): δ 6.80 (m, 3H, $C_6H_3(CH_3)_2$), 6.45 (m, 1H, C_5H_4), 5.98 (m, 1H, C_5H_4), 5.59 (m, 1H, C_5H_4), 5.29 (m, 1H, C_5H_4), 2.99 (s, 3H, $N(CH_3)_2$), 1.95 (s, 3H, $N(CH_3)_2$), 1.90 (s, 3H, $C_6H_3(CH_3)_2$), 1.66 (s, 3H, $C_6H_3(CH_3)_2$), 1.39 (s, 3H, $(CH_3)_2C$), 1.26 (s, 3H, $(CH_3)_2C$).^{13}C NMR (benzene-d_6): δ 206.8 ($ArN{=}CN(CH_3)_2$), 149.8, 132.6, 130.4, 126.9 ($C_6H_3(CH_3)_2$), 154.9, 118.3, 116.7, 113.5, 111.8 (C_5H_4), 108.3, 102.7 (cage *C*), 44.1, 36.9 ($N(CH_3)_2$), 41.7, 31.9, 31.4 ($(CH_3)_2C$), 18.9, 18.5 ($C_6H_3(CH_3)_2$). ^{11}B NMR (benzene-d_6): δ −4.1 (3B), −8.1 (2B), −10.6 (3B), −12.6 (1B), −13.9 (1B). IR (KBr, cm^{-1}): ν 2569 (vs) (BH), 1622 (s) ($C{=}N$). Anal. Calcd for $C_{21}H_{35}B_{10}ClN_2Ti$: C, 49.75; H, 6.96; N, 5.53. Found: C, 49.51; H, 6.97; N, 5.46.

Preparation of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(NMe_2)[\eta^2\text{-}C(CH_2SiMe_3){=}N(C_6H_3Me_2\text{-}2,6)]$ (9). A toluene (10 mL) solution of 2,6-dimethylphenyl isocyanide (66 mg, 0.5 mmol) was slowly added to a toluene (10 mL) solution of **4** (213 mg, 0.5 mmol) at 0 °C. The resulting solution was stirred at room temperature for 6 h and then concentrated to 10 mL. The clear solution stood at −30 °C for 2 days to afford **9** as a yellow solid (173 mg, 62%). ^{1}H NMR (benzene-d_6): δ 7.00 (m, 3H, $C_6H_3(CH_3)_2$), 6.11 (m, 1H, C_5H_4), 5.51 (m, 2H, C_5H_4), 5.03 (m, 1H, C_5H_4), 2.85 (s, 6H, $N(CH_3)_2$), 2.55 (d, ^2J = 9.0 Hz, 1H, $CH_2Si(CH_3)_3$), 2.11 (s, 3H, $C_6H_3(CH_3)_2$), 1.85 (d, ^2J = 9.0 Hz, 1H, $CH_2Si(CH_3)_3$), 1.62 (s, 3H, $C_6H_3(CH_3)_2$), 1.57 (s, 3H, $(CH_3)_2C$), 1.41 (s, 3H, $(CH_3)_2C$), −0.25 (s, 9H, $CH_2Si(CH_3)_3$). ^{13}C NMR (benzene-d_6): δ 244.2 ($ArN{=}CCH_2Si(CH_3)_3$), 144.8, 131.1, 129.1, 128.8, 128.0, 125.7 ($C_6H_3(CH_3)_2$), 148.0, 111.9, 110.0, 109.2, 107.6 (C_5H_4), 102.6 (cage *C*), 49.2 ($CH_2Si(CH_3)_3$), 47.1 ($N(CH_3)_2$) 41.5, 32.5, 32.1 ($(CH_3)_2C$), 21.1, 18.9 ($C_6H_3(CH_3)_2$), −1.0 ($CH_2Si(CH_3)_3$). ^{11}B NMR (benzene-d_6): δ −2.8 (2B), −5.2 (3B), −8.8 (5B). IR (KBr, cm^{-1}): ν 2585 (vs) (BH), 1562 (s) ($C{=}N$). Anal. Calcd for $C_{25}H_{46}B_{10}N_2SiTi$: C, 53.74; H, 8.30; N, 5.01. Found: C, 53.53; H, 8.35; N, 4.83.

Preparation of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(NMe_2)[\eta^2\text{-}C(CH_2SiMe_3){=}N^tBu]\cdot 2/3C_6H_5CH_3$ (10·2/3 toluene). This compound was prepared as orange crystals from the reaction of **4** (213 mg, 0.5 mmol) with *t*-butyl isocyanide (41 mg, 0.5 mmol) in toluene (15 mL) using the same procedure reported for **9**; yield: 134 mg (47%). ^{1}H NMR (benzene-d_6): δ 7.05 (m, 3H, $C_6H_5CH_3$), 6.00 (m, 1H, C_5H_4), 5.47 (m, 1H, C_5H_4), 5.23 (m, 1H, C_5H_4), 5.05 (m, 1H, C_5H_4), 3.23 (d, ^2J = 9.0 Hz, 1H, $CH_2Si(CH_3)_3$), 3.16 (s, 6H, $N(CH_3)_2$), 2.68 (d, ^2J = 9.0 Hz, 1H, $CH_2Si(CH_3)_3$), 2.05 (s, 2H, $C_6H_5CH_3$), 1.56 (s, 3H, $(CH_3)_2C$), 1.49 (s, 3H, $(CH_3)_2C$), 0.95 (s, 9H, $C(CH_3)_3$), 0.11 (s, 9H, $CH_2Si(CH_3)_3$). ^{13}C NMR (benzene-d_6): δ 236.6 ($^tBuN{=}CCH_2Si(CH_3)_3$), 137.5, 129.5, 126.5, 124.5 ($C_6H_5CH_3$), 150.3, 111.5, 108.3, 107.4, 103.9 (C_5H_4), 101.4 (cage *C*), 60.4 ($C(CH_3)_3$), 49.2 ($CH_2Si(CH_3)_3$), 46.8 ($N(CH_3)_2$), 41.9, 32.9, 32.7 ($(CH_3)_2C$), 29.5 ($C(CH_3)_3$), 23.0 ($C_6H_5CH_3$), 1.1 ($CH_2Si(CH_3)_3$. ^{11}B NMR (benzene-d_6): δ −3.2 (2B), −5.9 (3B), −9.5 (3B), −10.8 (2B). IR (KBr, cm^{-1}): ν 2574 (vs) (BH), 1622 (m) ($C{=}N$). Anal. Calcd for $C_{21}H_{46}B_{10}N_2SiTi$ (**10**): C, 49.39; H, 9.08; N, 5.49. Found: C, 49.44; H, 8.91; N, 5.38.

Preparation of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(NMe_2)[\eta^2\text{-}C(CH_3){=}N(C_6H_3Me_2\text{-}2,6)]\cdot C_6H_5CH_3$ (11·toluene). This compound was prepared as orange crystals from the reaction of **5** (177 mg, 0.5 mmol) with 2,6-dimethylphenyl isocyanide (66 mg, 0.5 mmol) in toluene (15 mL) using the same procedure reported for **9**; yield: 202 mg (70%). ^{1}H NMR (benzene-d_6): δ 6.90 (m, 8H, aromatic), 6.03 (m, 1H, C_5H_4), 5.54 (m, 1H, C_5H_4), 5.24 (m, 1H, C_5H_4), 5.16 (m, 1H, C_5H_4), 2.81 (s, 6H, $N(CH_3)_2$), 2.05 (s, 3H, $C_6H_5CH_3$), 1.84 (s, 3H, CH_3), 1.82 (s, 3H, $C_6H_3(CH_3)_2$), 1.65 (s, 3H, $C_6H_3(CH_3)_2$), 1.55 (s, 3H, $(CH_3)_2C$), 1.42 (s, 3H, $(CH_3)_2C$). ^{13}C NMR (benzene-d_6): δ 245.0 ($ArN{=}CCH_3$), 149.6, 144.6, 131.1, 129.9, 129.2, 127.7, 126.5 ($C_6H_3(CH_3)_2 + C_6H_5CH_3$), 111.8, 109.6, 107.5, 102.9, 101.8 (C_5H_4), 49.2 ($N(CH_3)_2$), 41.8, 32.5, 32.1 ($(CH_3)_2C$), 22.3 (CH_3), 22.2, 18.7 ($C_6H_3(CH_3)_2 + C_6H_5CH_3$); the cage carbons were not observed. ^{11}B NMR (benzene-d_6): δ −2.9 (2B), −5.6 (2B), −9.2 (4B), −10.9 (2B). IR (KBr, cm^{-1}): ν 2584 (vs) (BH), 1597 (s) ($C{=}N$). Anal. Calcd for $C_{29}H_{46}B_{10}N_2Ti$ (**11** + toluene): C, 60.19; H, 8.01; N, 4.84. Found: C, 60.36; H, 7.96; N, 4.81.

Preparation of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(NMe_2)[\eta^2\text{-}C(CH_3){=}N^tBu]$ (12). This compound was prepared as orange crystals from the reaction of **5** (177 mg, 0.5 mmol) with *t*-butyl isocyanide (41 mg, 0.5 mmol) in toluene (15 mL) using the same procedure reported for **9**; yield: 142 mg (65%). ^{1}H NMR (benzene-d_6): δ 5.91 (m, 1H, C_5H_4), 5.47 (m, 1H, C_5H_4), 4.84 (m, 1H, C_5H_4), 4.80 (m, 1H, C_5H_4), 2.99 (s, 6H, $N(CH_3)_2$), 2.34 (s, 3H, CH_3), 1.50 (s, 3H, $(CH_3)_2C$), 1.41 (s, 3H, $(CH_3)_2C$), 0.88 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (benzene-d_6): δ 238.9 ($^tBuN{=}CCH_3$), 150.6, 110.8, 108.9, 107.1, 102.9 (C_5H_4), 103.3, 100.8 (cage *C*), 60.5 ($C(CH_3)_3$), 51.9 ($N(CH_3)_2$), 42.1, 33.1, 31.4 ($(CH_3)_2C$), 28.7 ($C(CH_3)_3$), 19.5 (CH_3). ^{11}B NMR (benzene-d_6): δ −3.6 (2B), −5.6 (1B), −6.5 (1B), −9.8 (5B), −11.7 (1B). IR (KBr, cm^{-1}): ν 2572 (vs) (BH), 1635 (m) ($C{=}N$). Anal. Calcd for $C_{18}H_{38}B_{10}N_2Ti$: C, 49.30; H, 8.73; N, 6.39. Found: C, 49.32; H, 8.63; N, 6.27.

Table 1. Crystal Data and Summary of Data Collection and Refinement for **2**, **3**, **6**, and **7**

	2	**3**·$2C_6H_5CH_3$	**6**·2THF	**7**
formula	$C_{19}H_{33}B_{10}NTi$	$C_{37}H_{64}B_{20}N_2Ti_2$	$C_{32}H_{67}B_{20}N_2O_2Ti_2$	$C_{19}H_{31}B_{10}ClN_2OTi$
cryst size (mm^3)	0.50 × 0.30 × 0.20	0.80 × 0.30 × 0.20	0.60 × 0.50 × 0.30	0.40 × 0.30 × 0.20
fw	431.5	848.9	823.9	494.9
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$C2/c$	$P2_1/n$
a (Å)	23.563(5)	20.823(3)	16.862(1)	14.314(1)
b (Å)	18.323(4)	11.980(2)	18.266(1)	12,667(1)
c (Å)	17.636(4)	21.382(3)	15.437(1)	14.937(1)
β (deg)	107.07(3)	119.14(1)	98.66(1)	111.58(1)
V (Å^3)	7279.0(3)	4658.6(10)	4700.5(5)	2518.6(3)
Z	12	4	4	4
D_{calcd} (Mg/m^3)	1.181	1.210	1.164	1.305
λ, Mo Kα (Å)	0.71073	0.71073	0.71073	0.71073
2θ range (deg)	2.9−51.3	2.2−50.0	4.0−50.0	3.4−50.0
μ (mm^{-1})	0.360	0.374	0.372	0.463
F(000)	2712	1776	1732	1024
no. of obsd reflns	5174	8225	4144	3292
no. of params refined	838	550	281	307
GOF	1.061	0.871	1.012	1.002
R1	0.051	0.071	0.087	0.067
wR2	0.136	0.152	0.249	0.158

Table 2. Crystal Data and Summary of Data Collection and Refinement for **8** and **10**−**12**

	8	**10**·$2/3C_6H_5CH_3$	**11**·$C_6H_5CH_3$	**12**
formula	$C_{21}H_{35}B_{10}ClN_2Ti$	$C_{77}H_{154}B_{30}N_6Si_3Ti_3$	$C_{29}H_{46}B_{10}N_2Ti$	$C_{18}H_{38}B_{10}N_2Ti$
cryst size (mm)	0.30 × 0.20 × 0.10	0.40 × 0.30 × 0.20	0.20 × 0.15 × 0.10	0.30 × 0.20 × 0.10
fw	506.9	1716.3	578.7	438.5
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1$	$P2_1/n$
a (Å)	14.167(1)	15.436(1)	10.614(1)	9.952(1)
b (Å)	13.801(1)	16.349(1)	19.818(2)	12.559(1)
c (Å)	13.747(1)	21.805(2)	16.727(2)	20.798(1)
α (deg)	90	92.25(1)	90	90
β (deg)	96.06(1)	108.67(1)	106.87(1)	102.80(1)
γ (deg)	90	98.42(1)	90	90
V (Å^3)	2672.7(3)	5134.8(6)	3367.1(5)	2534.7(3)
Z	4	2	4	4
D_{calcd} (Mg/m^3)	1.260	1.110	1.142	1.149
λ, Mo Kα (Å)	0.71073	0.71073	0.71073	0.71073
2θ range (deg)	2.9−56.1	2.0−50.0	2.5−50.0	3.8−56.0
μ, mm^{-1}	0.435	0.304	0.277	0.347
F(000)	1056	1832	1224	928
no. of obsd reflns	6451	18006	9955	6097
no. of params refined	316	1072	758	280
GOF	0.933	0.997	0.963	0.911
R1	0.067	0.062	0.061	0.059
wR2	0.142	0.166	0.137	0.143

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 either a Bruker SMART 1000 CCD diffractometer using Mo−Kα radiation for **3**, **8**, **10**, and **12** or an MSC/Rigaku RAXIS-IIC imaging plate using Mo−Kα radiation from a Rigaku rotating-anode X-ray generator operating at 50 KV and 90 mA for **2**, **6**, **7**, and **11**. An empirical absorption correction was applied using the SADABS program[11a] for CCD data or by correlation of symmetry-equivalent reflections using the ABSCOR program for IP data.[11b] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on F^2 using the SHELXTL program package.[12a] For the noncentrosymmetric structure of **11**, the appropriate enantiomorph was chosen by refining Flack's parameter x toward zero.[12b] All hydrogen atoms were geometrically fixed using the riding model. There were three crystallographically independent molecules in the unit cells of **2** and **10** and two independent molecules in the unit cell of **11**. In addition, the following solvated molecules were found in the unit cells of different structures: two toluene molecules in **3**, **10**, and **11** and two THF molecules in **6**. Thus, each molecule of **10** shared two-thirds of a toluene molecule in the unit cell. Crystal data and details of data collection and structure refinements are given in Tables 1 and 2. Selected bond distances and angles are compiled in Table 3. Further details are included in the Supporting Information.

Results

Alkylation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]$TiCl(NMe_2)$. Treatment of [$\eta^5$:$\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]$TiCl(NMe_2)$ (**1**) with 1 equiv of alkylating reagents such as $PhCH_2K$, Me_3SiCH_2Li, and CH_3MgBr resulted in the isolation of the corresponding titanium alkyl complexes [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]$TiR(NMe_2)$ (R = CH_2Ph (**2**), CH_2SiMe_3 (**4**), CH_3 (**5**)) in good yields (Scheme 1). The ^1H NMR spectra of **2**, **4**, and **5** showed the common features of several multiplets of Cp protons, two singlets of the Me_2C linkage protons, and one singlet of the NMe_2 group. In addition, two doublets at 2.42 and 2.10 ppm with ^2J = 8.5 Hz assignable to the methylene protons of the benzyl in **2**, two doublets at 2.11 and 1.74 ppm with ^2J = 9.0 Hz attributable to the methylene protons of the Ti−CH_2SiMe_3 in **4**, and one singlet at 0.71 ppm corresponding to the Ti−Me methyl protons in **5** were also observed in the ^1H NMR spectra. Their ^{11}B NMR spectra all exhibited a 2:2:4:2 pattern.

The solid-state structure of **2** was confirmed by single-crystal X-ray analyses. Its representative structure is shown in Figure 1. The Ti atom is η^5-bound to the five-membered ring of the cyclopentadienyl and σ-bound to a carborane cage carbon atom, an amido group, and a benzyl unit in a distorted-tetrahedral geometry. The average Ti−C(benzyl) distance of 2.106(2) Å and the Ti−C−C(aryl) angle of 129.1(3)° are close to the corresponding values of 2.134(1) Å and 127.2(7)° in (TCP)Ti$(CH_2Ph)_2$ (TCP = tetramethylcyclopentadienyl-4-methyl phenolate),[13] 2.162(1) Å and 124.3(1)° in {η^5−C_5H_3-1,3-[$SiMe_2$(η^1−N^{t}Bu)]$_2$}Ti(CH_2Ph),[14] and 2.147(5) Å in $(Pr^i_2$-2,6-ArO$)_2$Ti(η^2-^{t}BuNCCH$_2$Ph)(CH$_2$Ph).[15] The average Ti−C(ring) distance of 2.349(3) Å, Ti−C(cage) distance of 2.189(3) Å, and Ti−N(1) distance of 1.873(2) Å are very comparable to the corresponding values of 2.341(2), 2.179(2), and 1.862(2) Å, respectively, observed in **1**[1]

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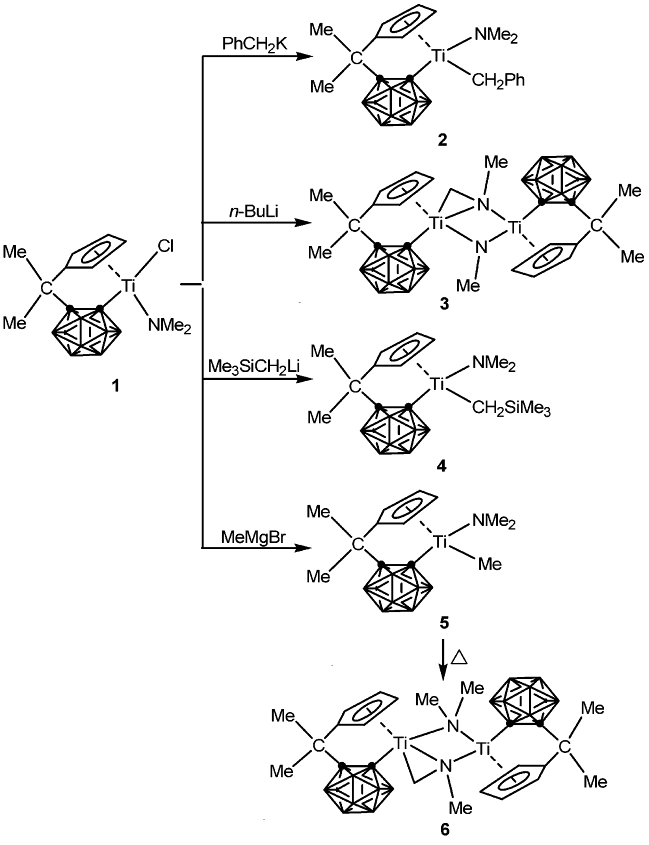
Table 3. Selected Bond Distances (Å) and Angles (deg)

	2[a]	**3**	**6**	**7**	**8**	**10**[a]	**11**[a]	**12**
avg Ti−C(ring)	2.349(3)	2.343(1)	2.337(1)	2.344(5)	2.376(5)	2.370(1)	2.392(1)	2.366(4)
Ti−C(cage)	2.189(3)	2.219(1)	2.254(1)	2.242(5)	2.197(5)	2.259(1)	2.241(1)	2.251(3)
Ti−C(alkyl)	2.106(2)	2.169(1)	2.097(1)					
Ti−Cl				2.256(2)	2.305(2)			
Ti−N(NMe_2)	1.873(2)	2.081(1)	2.131(1)			1.908(1)	1.868(1)	1.913(3)
Ti−N(C═N)				2.086(4)	1.955(4)	2.044(1)	2.156(1)	2.033(3)
C═N				1.317(7)	1.303(6)	1.256(1)	1.278(1)	1.256(4)
C(ring)−C−C(cage)	109.2(3)	109.0(1)	108.8(1)	108.7(4)	108.6(4)	109.7(1)	108.8(3)	108.7(3)
cent−Ti−C(cage)[b]	107.0	105.8	104.8	103.6	104.0	104.0	105.4	104.0

[a] Average values of several crystallographically independent molecules in the unit cell. [b] cent = the centroid of the five-membered ring of the cyclopentadienyl.

Scheme 1



and those found in [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti($NR_2$)$_2$.[1,3]

Compound **5** was not very thermally stable. Its toluene solution gradually turned from red to blue overnight at room temperature, from which a dark blue solid was isolated. Recrystallization from THF gave dinuclear complex {[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti}$_2$($\mu$-$NMe_2$)($\mu$:$\sigma$-$NMeCH_2$)·2THF (**6**·2THF) as dark green crystals in 30% yield (Scheme 1). It was a paramagnetic species, and the ^{1}H and ^{13}C NMR did not give much useful information. Its ^{11}B NMR spectrum exhibited a 3:3:4 pattern. The green color and paramagnetic nature of **6** suggested that it may contain Ti(III) ion.[16] Its molecular structure was ultimately established by single-crystal X-ray diffraction study and is shown in Figure 2.

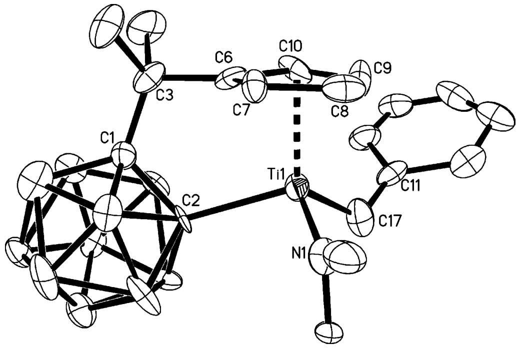


Figure 1. Molecular structure of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti($CH_2Ph$)($NMe_2$) (**2**) (all hydrogen atoms are omitted for clarity).

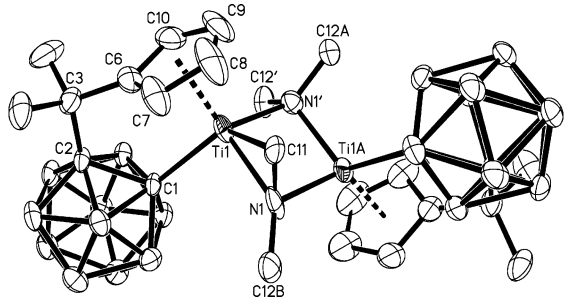


Figure 2. Molecular structure of {[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti}$_2$($\mu$-$NMe_2$)($\mu$:$\sigma$-$NMeCH_2$) (**6**) (the solvated THF molecules, the second set of the disordered C(11) and C(12) atoms, and all hydrogen atoms are omitted for clarity).

Complex **6** is a centrosymmetric dinuclear molecule, in which a crystallographically imposed C_2 axis passes through the N(1) and N(1′) atoms, thus prohibiting differentiation of the two Ti atoms. The C(11) and C(12) atoms are disordered over two sets of positions with 0.5:0.5 occupancy. As shown in Table 3, the average Ti−C(ring) distance of 2.337(1) Å and Ti−C(cage) distance of 2.254(1) Å are very close to those in **2**. The Ti(1)−C(11) distance of 2.097(1) Å is comparable to the corresponding values observed in other azatitanacyclic complexes,[17] for example, 2.150(2) Å in (Pr^i_2-2,6-ArO)$_2$Ti[η^2-^{t}BuNC(CH_2Ph)$_2$],[17a] 2.262(3) Å in (Ph_2-2,6-ArO)$_2$Ti(η^2-^{t}BuNCC$_4$Et$_4$),[17b] and 2.076(4) Å in CpTi[CpFe(η^5-$C_5H_3CH_2NMe_2$)][CpFe{η^5-$C_5H_3CH_2NCH_2$(Me)}].[17c] The N−C distances (1.432(1)/1.450(1)/1.453(1) Å) are representative of single bond distances.[17] The Ti···Ti separation of

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(16) For examples of dinuclear paramagnetic titanium(III) complexes, see: (a) Hosmane, N. S.; Wang, Y.; Zhang, H.; Lu, K.-J.; Maguire, J. A.; Gray, T. G.; Brooks, K. A.; Waldhör, E.; Kaim, W.; Kremer, R. K. *Organometallics* **1997**, *16*, 1365. (b) Samuel, E.; Harrod, J. F.; Gourier, D.; Dromzee, Y.; Robert, F.; Jeannin, Y. *Inorg. Chem.* **1992**, *31*, 3252.

(17) (a) Durfee, L. D.; Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1990**, *9*, 75. (b) Hill, J. E.; Balaich, G.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1993**, *12*, 2911. (c) Hitchcock, P. B.; Hughes, D. L.; Leigh, G. J.; Sanders, J. R.; de Souza, J. S. *J. Chem. Soc., Dalton Trans.* **1999**, 1161.

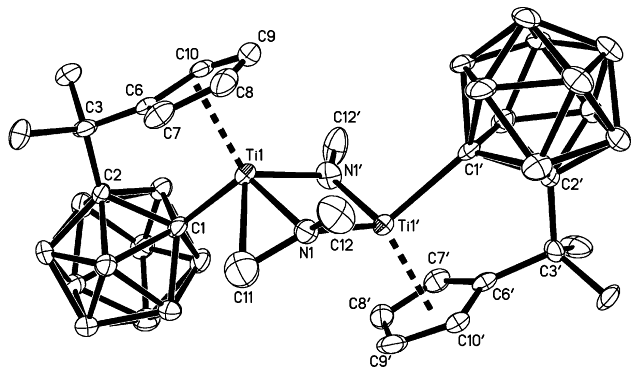


Figure 3. Molecular structure of $\{[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti\}_2(\mu\text{-}NMe)(\mu{:}\sigma\text{-}NMeCH_2)$ (**3**) (the solvated toluene molecules and all hydrogen atoms are omitted for clarity).

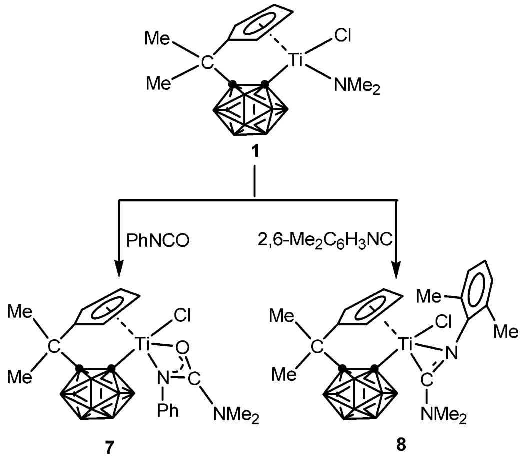
2.898(1) Å can be compared to the 2.707(1) Å in $\{[(Me_3Si)_3C_5H_2]TiCl(\mu\text{-}O)\}_2O$,[18a] 2.931(3) Å in $\{[(Me_3SiNCH_2CH_2)_2NSiMe_3]Ti(\mu\text{-}H)\}_2$,[18b] and 2.942(2) Å in $[\{CyNC(H)NCy\}_2Ti(\mu\text{-}Cl)]_2$ (Cy = cyclohexyl).[18c] In view of the molecular structure of **6** and its dark green color and paramagnetic nature,[16] it is best described as a mixed-valence Ti(IV)−Ti(III) dinuclear complex.

To gain some insight into the formation of **6**, we carried out the reaction of **1** with 1 equiv of *n*-BuLi under the same reaction condition as that for **5**. The results showed that the color of the reaction mixture changed from red to dark blue upon the reaction temperature being increased from −78 °C to room temperature. These observations were the same as those displayed by a toluene solution of **5** at room temperature. From this dark blue solution, $\{[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti\}_2(\mu\text{-}NMe)(\mu{:}\sigma\text{-}NMeCH_2)\cdot 2C_6H_5CH_3$ ($\mathbf{3}\cdot 2C_6H_5CH_3$) was isolated as dark red crystals in 37% yield (Scheme 1). Concentration of the mother liquor gave a dark blue solid, which was a paramagnetic species, as indicated by the ^1H NMR. Many attempts to isolate a pure species from the mother liquor failed.

The ^1H NMR of **3** confirmed its diamagnetic nature, in which four multiplets in the range 5.17−6.67 ppm attributable to the Cp protons, one broad singlet at 3.54 ppm assignable to the methyl protons of the two NMe groups, two doublets at 3.02 and 2.19 ppm with $^2J = 7.0$ Hz corresponding to the methylene protons of the NCH_2 unit, and two singlets of the Me_2C protons were observed. Its ^{11}B NMR spectrum showed a 1:1:1:2:2:3 pattern.

The solid-state structure of **3** was further confirmed by single-crystal X-ray analyses and is shown in Figure 3. It is a dinuclear complex in which two Ti atoms have different coordination environments. The structural motif of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(\eta^2\text{-}CH_2NMe)$ found in **6** is also observed in **3**. Another bridging unit between the two Ti atoms is the imido group NMe, rather than the amido group NMe_2 observed in **6**. Therefore, the formal oxidation state for both Ti atoms in **3** is +4. As expected, the Ti−N(imido) distances (1.869(1)/1.949(1) Å) are generally shorter than the Ti−N(amido) ones (1.981(1)/2.180(1) Å). The Ti(1)−C(11) distance of 2.169(1) Å is very comparable to the corresponding values observed in **6** and other azatitanacyclic complexes.[17] The N−C distances (1.403(1)−1.425(1) Å) fall in the range 1.41−1.47 Å normally found in azatitanacyclic complexes.[17] The Ti···Ti separation of 2.868(1) Å can be compared to that of 2.898(1) Å observed in **6** and those (2.707−2.942 Å) found in other dinuclear titanium complexes.[18]

Scheme 2



The reaction pathways for the formation of **3** and **6** are not clear. They may involve the intermediates $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]TiR(NMe_2)$, which undergo thermal decomposition to generate **3**, **6**, and other unidentified species.

Reaction of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(Cl)(NMe_2)$ with PhNCO and RNC. Complex **1** contains both the Ti−C(cage) and Ti−N bonds, which offers an opportunity to study the relative activity of Ti−N/Ti−C(cage) bonds toward unsaturated molecules. Reaction of **1** with 1 equiv of PhNCO or $2,6\text{-}Me_2C_6H_3NC$ gave the monoinsertion product $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(Cl)[\eta^2\text{-}OC(NMe_2)NPh]$ (**7**) in 65% yield or $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(Cl)[\eta^2\text{-}C(NMe_2){=}N(C_6H_3Me_2\text{-}2,6)]$ (**8**) in 60% yield (Scheme 2). These results showed that the unsaturated molecules inserted exclusively into the Ti−N and the Ti−C(cage) bonds remained intact. Their ^1H NMR spectra all showed four multiplets corresponding to the Cp protons and two singlets attributable to the linkage Me_2C unit. In contrast to the one singlet exhibited by NMe_2 group in the ^1H NMR spectrum of **7**, that of **8** showed two inequivalent methyl resonances at 2.99 and 1.95 ppm for the NMe_2 group and two singlets for two methyl groups on the phenyl ring due to the hindered rotation around the $C{-}N(CH_3)_2$ and N−C(aryl) bonds. The unique N*C*O resonance at 165.9 ppm and N−*C*=N resonance at 206.8 ppm were observed in the ^{13}C NMR spectra of **7** and **8**, respectively.

Figure 4 shows the solid-state structure of complex **7**. The geometry of the $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti$ fragment is almost identical with that observed in complex **1**.[1] The structural parameters of the $\eta^2\text{-}OC(NMe_2)NPh$ moiety indicate some electron delocalization over the O(1)−C(21)−N(2) atoms, which has been observed in $[\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}OC(NMe_2)NPh]_2$.[4]

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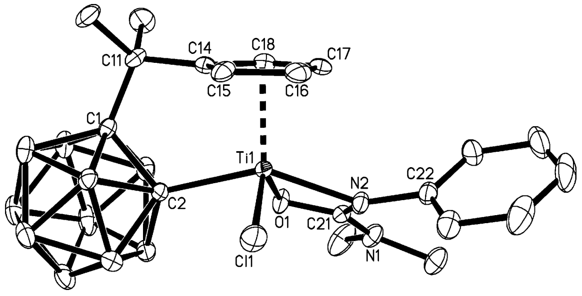


Figure 4. Molecular structure of [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Ti(Cl)-[η^2-OC(NMe$_2$)NPh] (**7**) (all hydrogen atoms are omitted for clarity).

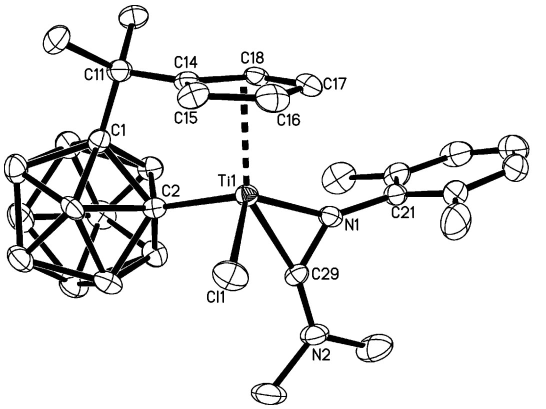
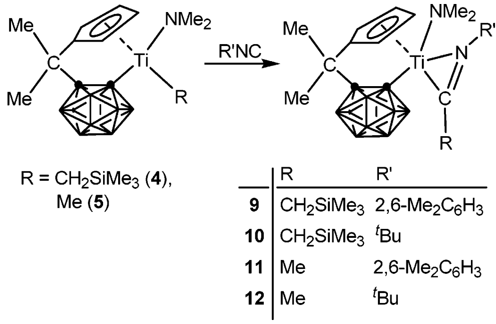


Figure 5. Molecular structure of [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Ti(Cl)-[η^2-C(NMe$_2$)=N(C$_6$H$_3$Me$_2$-2,6)] (**8**) (all hydrogen atoms are omitted for clarity).

The molecular structure of **8** is shown in Figure 5. The average Ti−C(ring), Ti−C(cage), and Ti−Cl distances are similar to those observed in **7**, as indicated in Table 3. The Ti−C(29) and Ti−N(1) distances (2.061(5) and 1.995(4) Å, respectively) are comparable to the reported Ti−C(sp^2) and Ti−N(sp^2) bond lengths,[15,19] which indicates that the iminocarbamoyl ligand in **8** is coordinated to the metal center in a η^2 fashion. The very similar C(29)−N(1) (1.303(6) Å) and C(29)−N(2) (1.318(6) Å) distances, together with the planar geometry of the N(2) atom, reveal the delocalized partial multiple bonds through the N=C−NMe$_2$ fragment, which is consistent with the ^{1}H NMR results.

Reactions of [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]TiR(NMe$_2$) with R′NC. The previous section showed that isocyanides inserted exclusively into the Ti−N bond and that the Ti−C(cage) bond remained intact. Complexes **4** and **5** offer a unique opportunity to observe the direct competition between alkyl and amido groups in the migration step. Treatment of **4** with 1 equiv of R′NC afforded the monoinsertion products [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Ti(NMe$_2$)[η^2-C(CH$_2$SiMe$_3$)=N(R′)] (R′ = 2,6-Me$_2$C$_6$H$_3$ (**9**), ^{t}Bu (**10**)) in good yields (Scheme 3). In the ^{1}H NMR spectra, the insertion of isocyanides into the Ti−CH$_2$SiMe$_3$ bond was found to result in a downfield shift of the α-protons attached to the initial alkyl complexes.[15,19] The AB pattern for the methylene protons of the C*H*$_2$SiMe$_3$ group was observed at δ = 1.85 and 2.55 in **9** and δ = 2.68 and 3.23 in **10**, with ^2J = 9.0 Hz, compared to those at δ = 1.74 and 2.11 observed in parent complex **4**. The other notable characteristic of the NMR spectra was the ^{13}C chemical shift of the iminoacyl carbon of the η^2-(Me$_3$SiCH$_2$)*C*=NR′ group, δ = 244.2 in **9** and 236.6 in **10**. Unlike in **8**, only one singlet of NMe$_2$ resonance was observed in the ^{1}H NMR spectra of both **9** and **10**, suggesting that the Ti−N bond remained intact. In addition, complexes **9** and **10** showed characteristic ν(C=N) stretching vibrations[15,20] at about 1562 and 1622 cm^{-1} in their solid-state IR spectra.

Scheme 3



	R	R′
9	CH$_2$SiMe$_3$	2,6-Me$_2$C$_6$H$_3$
10	CH$_2$SiMe$_3$	^{t}Bu
11	Me	2,6-Me$_2$C$_6$H$_3$
12	Me	^{t}Bu

The isolation of **9** and **10** indicated that R′NC inserted into the Ti−CH$_2$SiMe$_3$ bond rather than the Ti−N bond. To explore the generality of these reactions, we also examined the reactivity of [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Ti(CH$_3$)-(NMe$_2$) (**5**). Treatment of **5** with 1 equiv of R′NC at room temperature gave the monoinsertion products [η^5:σ-Me$_2$C-(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Ti(NMe$_2$)[η^2-CMe=N(R′)] (R′ = 2,6-Me$_2$C$_6$H$_3$ (**11**), ^{t}Bu (**12**)) in about 65% yield (Scheme 3). The spectroscopic characteristics found in **9** and **10** were all observed in **11** and **12**. These results again showed that R′NC inserted exclusively into the Ti−CH$_3$ bond.

The proton resonance of the methyl unit (δ = 1.84 in **11** and δ = 2.34 in **12**) was downfield-shifted compared to their precursor **5** (δ = 0.71). The characteristic η^2-iminoacyl carbon resonance was found at 245.0 ppm for **11** and 238.9 ppm for **12**. Complexes **11** and **12** showed characteristic ν(C=N) stretching vibrations at about 1597 and 1635 cm^{-1}.

The molecular structures of **10**−**12** were confirmed by single-crystal X-ray analyses and are shown in Figures 6−8, respectively. The Ti atom is η^5-bound to the five-membered ring of the cyclopentadienyl, σ-bound to a cage carbon atom and a NMe$_2$ group, and η^2-bound to the iminoacyl group in a distorted-tetrahedral geometry if the iminoacyl is taken as occupying a single coordination site. Selected bond distances and angles are compiled in Table 3, which are comparable to the corresponding values reported for organotitanium iminoacyl complexes.[15,21,22] The molecular structures further confirm the migration of a CH$_3$ or CH$_2$SiMe$_3$ group from the Ti atom to the RNC carbon atom, resulting in the formation of titanium iminoacyl complexes with typical C=

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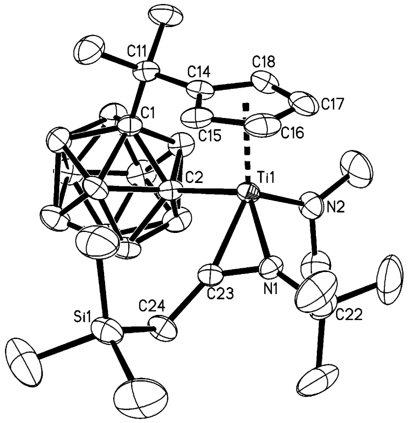


Figure 6. Molecular structure of $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(NMe_2)[\eta^2\text{-}C(CH_2SiMe_3){=}N^tBu]$ (**10**) (the solvated toluene molecule and all hydrogen atoms are omitted for clarity).

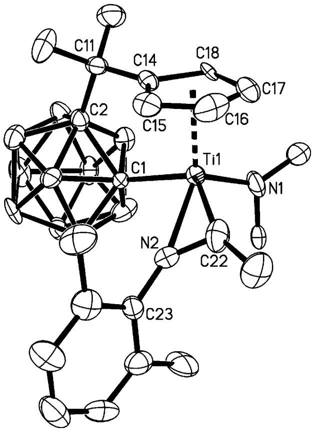


Figure 7. Molecular structure of $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(NMe_2)\text{-}[\eta^2\text{-}C(CH_3){=}N(C_6H_5Me_2\text{-}2,6)]$ (**11**) (the solvated toluene molecule and all hydrogen atoms are omitted for clarity).

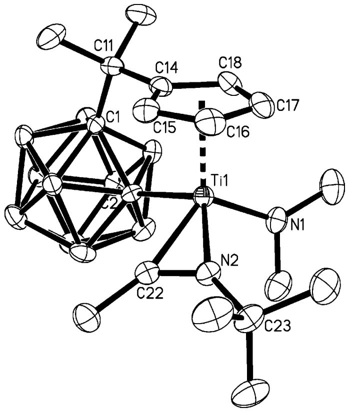


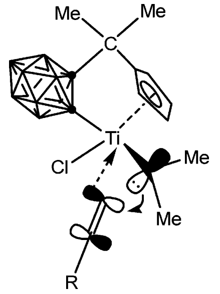
Figure 8. Molecular structure of $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(NMe_2)\text{-}[\eta^2\text{-}C(CH_3){=}N^tBu]$ (**12**) (all hydrogen atoms are omitted for clarity).

N bond distances of 1.256(1) Å in **10**, 1.278(1) Å in **11**, and 1.256(4) Å in **12**.

Discussion

The above experimental results clearly show that the unsaturated molecules insert into the Ti$-$N bond only in the absence of the Ti$-$C(alkyl) bonds and that the Ti$-$C(cage) bond remains intact, i.e., the relative reactivity follows the trend: Ti$-$C(alkyl) > Ti$-$N > Ti$-$C(cage). The migratory insertions may be proceeded by the coordination of the isocyanide and further migration of either the amido or alkyl group to the electrophilic isocyanide carbon atom to form the corresponding iminocarbamoyl or iminoacyl complexes.[22] What factors control the migration? One argument is the relative bond strengths. It has been documented that the preference of Ti$-$C(alkyl) over Ti$-$N insertion is governed by the relative bond strengths. The insertion into the weaker Ti$-$C(alkyl) bond leads to a faster reaction and a more-stable final product.[22] In view of the similar Ti$-$C(cage) and Ti$-$C(alkyl) distances (shown in Table 3) (i.e., both Ti$-$C bonds have similar bond strengths), a question is why the Ti$-$C(cage) bond is inert toward unsaturated molecules. One of the reasons may be because of the low mobility and steric bulkiness of the carboranyl unit.[4,23] Another argument is frontier orbital controlled insertion. It was used to explain the direct insertion of 2.6-$Me_2C_6H_3NC$ into the Ta$-$$NMe_2$ rather than the Ta$-$Me bond in $(\eta^5\text{-}C_5Me_5)Ta({=}N^tBu)(NMe_2)Me$.[5] This argument is made on the basis of the attack of the lone pair of the amido group in the HOMO (π-bonding orbital) on the π^* LUMO of the isocyanide molecules as the major orbital transformation of the process (Scheme 4). It may be a joint action of all factors mentioned above, which results in the inertness of the Ti$-$C(cage) bond toward unsaturated molecules.

Scheme 4



Conclusion

The chloro ligand in $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]TiCl(NMe_2)$ (**1**) was easily substituted by alkyl groups via alkylation reactions to give the corresponding chiral titanium complexes. The thermal stability of these titanium alkyls is dependent on the nature of the alkyl unit. For example, titanium methyl complex **5** is isolable, whereas the titanium butyl one is thermally very unstable. Both of the complexes underwent thermal decomposition to give a mixture of products from which two dinuclear titanium complexes were isolated and structurally characterized.

Reactions of R′NC (R′ = ^{t}Bu, 2,6-$Me_2C_6H_3$) with $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]TiCl(NMe_2)$ or $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]TiR(NMe_2)$ (R = Me, CH_2SiMe_3) were examined in order to investigate the relative reactivity of Ti$-$C/Ti$-$N bonds. The experimental results indicate that the insertion of isocyanides into the Ti$-$C(alkyl) bond is preferred over the Ti$-$N bond, whereas the Ti$-$C(cage) one remains intact in all reactions although the bond strengths of the Ti$-$

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(23) Deng, L.; Chan, H.-S.; Xie, Z. *J. Am. Chem. Soc.* **2005**, *127*, 13774.

C(alkyl) and Ti−C(cage) bonds are similar. The preferential insertion of isocyanides into the Ti−C(alkyl) bond rather than the Ti−N bond is governed by the relative bond strengths of Ti−C and Ti−N. On the other hand, a joint operation of steric factors and frontier orbital arguments may result in the inertness of the Ti−C(cage) bond toward unsaturated molecules.

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Supporting Information Available: Crystallographic data in CIF format for **2**, **3**, **6**−**8**, and **10**−**12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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