Novel Bent-Sandwich Titanium(III) and Titanium(IV) Organometallics

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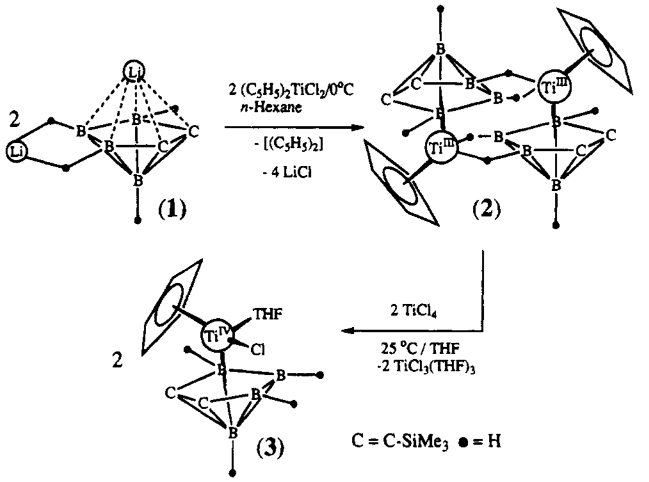
*Summary: The reaction between closo-exo-Li-1-Li-2,3-($SiMe_3$)$_2$-2,3-$C_2B_4H_4$ (**1**) and anhydrous Cp_2TiCl_2, in a molar ratio of 1:1, in a 1:1 mixture of dry benzene and n-hexane produced, in 60% yield, [commo-1-Cp-1-Ti-2,3-($SiMe_3$)$_2$-2,3−$C_2B_4H_4$]$_2$ (**2**), the first example of a paramagnetic Ti(III) d^1−d^1 dimer not having distinct bridging ligands. Chemical oxidation of **2** with anhydrous $TiCl_4$ in a 1:1 molar ratio in THF produces, in 86% yield, a previously unknown diamagnetic (d^0) Ti(IV) complex, commo-1-Cp-1-Cl-1-THF-1-Ti-2,3-($SiMe_3$)$_2$-2,3-$C_2B_4H_4$ (**3**), whose crystal structure shows a distorted tetrahedral environment about the metal center similar to those of titanocene derivatives.*

Because of their involvement in Ziegler−Natta olefin polymerization catalytic systems, the neutral, d^0, group 4 (titanium group) metal alkyl complexes of the general formula $Cp_2M(R)_2$ (Cp = C_5H_5, R = H, alkyl group) or $Cp_2M(R)X$ (X = anionic, 2-electron donor ligand) are among the most extensively studied class of organometallic compounds.[1,2] Recently, Jordan and co-workers have shown that such catalytic activity could also be found in the 14-electron, d^0, mixed-ligand, bent-metallocene complexes of the type [(Cp^*)M(Me)($C_2B_9H_{11}$)] (Cp^* = C_5Me_5, M = Zr, Hf),[3] and Grimes has also reported bent-sandwich configurations for the complexes $Cp'MXY(R_2C_2B_4H_4)$ [M = Ta or Zr; R = $SiMe_3$, Me, or Et; Cp′ = Cp or Cp^*; X, Y = Cl, alkyl, THF].[4] However, neither the synthesis nor any structural and/or reactivity information is available on titanium analogues of the carborane ligand systems. We report herein the syntheses and crystal structures of the first, bent-sandwich Ti(III) and Ti(IV) complexes, based on mixed Cp and the smaller carborane ligands.

Scheme 1



Treatment of the unsolvated *closo-exo*-Li-1-Li-2,3-($SiMe_3$)$_2$-2,3-$C_2B_4H_4$ (**1**)[5] with anhydrous Cp_2TiCl_2 in a molar ratio of 1:1 in a 1:1 mixture of dry benzene and *n*-hexane produced dihydrofulvalene, $(C_5H_5)_2$, and a novel dimeric Ti(III) sandwich, [*commo*-1-Cp-1-Ti-2,3-($SiMe_3$)$_2$-2,3-$C_2B_4H_4$]$_2$ (**2**),[5] in 60% yields. Chemical oxidation of **2** with anhydrous $TiCl_4$ in a 1:1 molar ratio in THF resulted in the formation of a monomeric Ti(IV) sandwich complex, *commo*-1-Cp-1-Cl-1−THF-1-Ti-2,3-($SiMe_3$)$_2$-2,3-$C_2B_4H_4$ (**3**),[6] along with the reduced Ti(III) species, $(THF)_3TiCl_3$, in 86% yields (Scheme 1). The elimination of a Cp ligand during the formation of the titanium sandwich complex, with concomitant dimerization of the metal products and without the benefit of distinct bridging groups, is quite unusual. The incorporation of an anionic ligand (Cl^-) and a labile group

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(6) **Synthesis of 2:** A 3.13 mmol (0.73 g) sample of unsolvated *closo-exo*-Li-1-Li-2,3-($SiMe_3$)$_2$-2,3-$C_2B_4H_4$ (**1**)[5a] was allowed to react with 3.13 mmol (0.78 g) of anhydrous Cp_2TiCl_2 in a 1:1 mixture of dry benzene and *n*-hexane (20 mL) at 0 °C for 5 h and then at room temperature for 8 h, during which time the mixture turned from red to green turbid solution. The solution was then filtered through a frit in vacuo, and all the volatiles including solvents were removed from the filtrate by vacuum distillation to collect a green solid which was later recrystallized from dry benzene solution to obtain 0.62 g (0.94 mmol, 60% yield) of air-sensitive deep-green crystals of **2** (mp 250 °C dec). The contents of the mother-liquor were identified as a mixture of unreacted **1** and Cp_2TiCl_2 (not measured). The volatiles were fractionated through traps held at 0, −45, −78, and −196 °C, and the trap at 0 °C collected a syrupy liquid, identified by NMR (Hedaya, E.; McNeil, D. W.; Schissel, P.; McAdoo, D. J. *J. Am. Chem. Soc.* **1968**, *90*, 5284) and IR spectra and by analysis as $(Cp)_2$ in 61% yield (0.124 g, 0.95 mmol). The white solid on the frit (not measured) was identified as LiCl by qualitative analysis and by ^7Li NMR spectra. **Synthesis of 3:** In a procedure identical to that described elsewhere,[5b] a 0.76 mmol (0.5 g) sample of **2** in a 20 mL mixture of dry benzene (60%) and dry THF (40%) was allowed to react with 1.52 mmol (0.29 g) of anhydrous $TiCl_4$ in vacuo at 25 °C for 24 h to produce 0.56 g (1.51 mmol) of blue crystals of $(THF)_3TiCl_3$ (Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135) and 0.58 g (1.31 mmol, 86% yield) of dark-brown platelike air-sensitive crystals of **3** (mp 155−160 °C dec). The solids were separated by extraction with hexane, which dissolves **3**, but not $(THF)_3TiCl_3$.

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(THF) on the metal atom in **3**, as well as the π-interactions with the Cp and carborane bonding faces, resulting in a distorted tetrahedral geometry of the Ti(IV) center, is very similar to those found in the $Cp_2M(R)X$ system.[1,2] Therefore, the present methodology constitutes an important general synthetic route to a series of organometallic compounds possessing both inherently interesting structures and potentially useful properties.

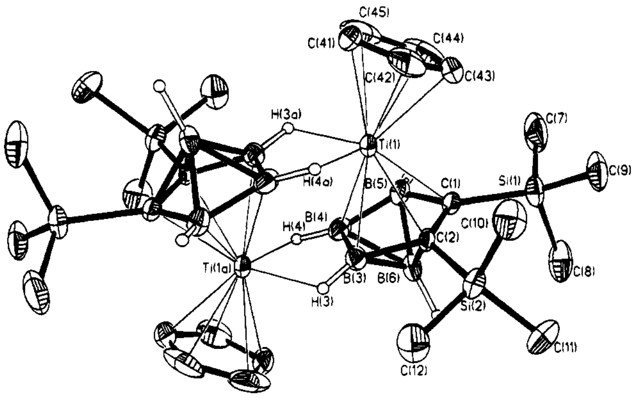

Figure 1. Perspective view of **2** drawn at the 40% probability level. Pertinent distances (Å) and angles (deg): Ti(1,1a)–(C_2B_3 centroid-1,2) 1.964, 1.976; Ti(1,1a)–(Cp centroid-3,4) 2.039, 2.029; (centroid-1,2)–Ti(1,1a)–(centroid-3,4) 142.8, 142. 5 (see supplementary Table S-2 for detailed bond lengths and angles).

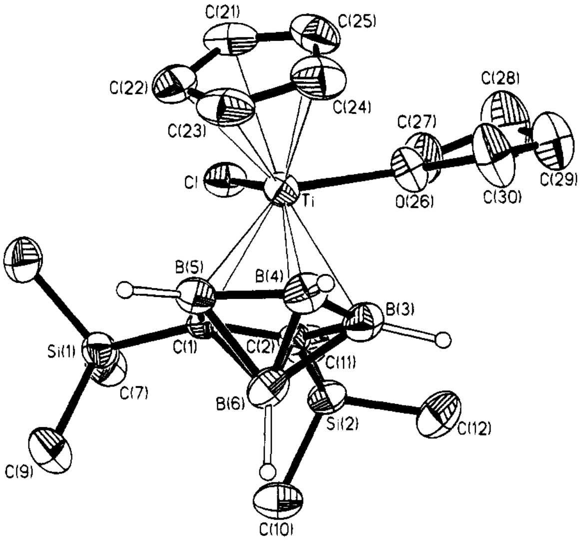

Figure 2. Perspective view of **3** drawn at the 40% probability level. Pertinent distances (Å) and angles (deg): Ti–(C_2B_3 centroid) 1.991, Ti–(Cp centroid) 2.075, Ti–Cl 2.344(2), Ti–O(26) 2.183(3), (C_2B_3 centroid)–Ti–(Cp centroid) 131.6, (C_2B_3 centroid)–Ti–Cl 107.9, (C_2B_3 centroid)–Ti–O(26) 107.7, (Cp centroid)–Ti–Cl 107.2, (Cp centroid)–Ti–O(26) 103.7, Cl–Ti–O(26) 91.4(1) (see supplementary Table S-2 for detailed bond lengths and angles).

A well-resolved EPR spectrum of **2** in frozen toluene at 105 K is indicative of a triplet state ($S = 1$) with rhombic symmetry and components at $g_x = 1.9710$, $g_y = 2.0006$, and $g_z = 1.9655$, $D = 0.0433$ cm^{-1}, and $E = 0.0033$ cm^{-1}, which would be expected for a d^1–d^1 dimer.[7] The dimer shows an interesting magnetic behavior, in that it exhibits a broad susceptibility maximum at 60 K with a sudden decrease below and Curie–Weiss behavior above this temperature.[8] The variation of the susceptibility between 14 and 300 K is best fitted using the Bleaney–Bowers formula with $\mu_{\text{eff}} = 2.7\ \mu_B$ per two Ti atoms (1.91 μ_B per one Ti atom), $J = -45.8$ K, and $\chi_o = -696 \times 10^{-4}$ emu/mol, thus indicating that the two Ti(III) centers are exchange coupled and form a magnetic dimer with the nonmagnetic singlet as the ground state and the triplet as the excited state. Although the paramagnetism precluded obtaining useful NMR data, the IR and mass spectra as well as the microanalytical data for **2** are all consistent with its molecular formula.[9] The X-ray structure of **2** (see Figure 1)[10] reveals that there are two crystallographically independent half-dimers in the unit cell and a center of symmetry exists within each dimer. Since the molecules do not differ significantly in their important atom–atom separations, average distances will be discussed. The separation of two Ti atoms in the dimers is 3.668 ± 0.032 Å, while the Ti–C_2B_3 and Ti–Cp centroid distances are 1.971 and 2.046 Å, respectively. To our knowledge, **2** is the first example of a Ti(III) dimer not having distinct bridging ligands, the interaction between the two Ti(III) centers being effected either by direct coupling through space or via hydrogen atoms on the carborane face; the relevant metal–hydrogen distances are Ti(1a)–H(3) = 1.96 Å and Ti(1a)–H(4) = 2.23 Å. The average Ti–C_2B_3 atom distance in **2** is 2.375 ± 0.039 Å and that in **3** is 2.407 ± 0.013 Å, which are close to the value of 2.344 ± 0.033 Å reported by Grimes for the anagolous average in $(C_8H_8)Ti(Et_2C_2B_4H_4)$, which neither dimerizes nor is bent.[11] Nonetheless, the geometries about the metal centers in **2** and **3** are significantly different from those found in other known titanacarborane complexes.[11,12]

The ^1H, ^{11}B, and ^{13}C NMR, IR, and mass spectra[9] of **3** are also consistent with its molecular formula and X-ray structure (see Figure 2).[10] The Ti atom shows a distorted tetrahedral coordination with Ti–C_2B_3 and Ti–Cp centroid distances very similar to those found in **2**. The presence of a reactive Cl^- ligand and a labile THF molecule on Ti(IV) strongly suggests that **3** can

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[7] EPR spectra of **2** were recorded on a Bruker ESP 300 spectrometer in the X band (9.6 GHz).

[8] Magnetic susceptibility measurements were made on a MPMS Quantum Design magnetometer at an external field of 1 T.

[9] Complex **2**: IR 2555 (m, s), 2357 (w, s) [ν(B–H)]; Mass [M$^+$] = 661.3. Anal. Calcd for $C_{26}H_{54}B_8Si_4Ti_2$: C, 47.26; H, 8.18. Found: C, 47.64; H, 8.16. Complex **3**: IR 2580 (sh), 2540 (br, m) [ν(B–H)], 400 (s, s) [ν(Ti–Cl)]; Mass [M$^+$] = 438.18. ^1H NMR δ 6.08 (Cp), 3.33, 1.29 (THF), 0.58 (SiMe$_3$); ^{11}B NMR δ 46.10 (117 Hz, 1 basal BH), 32.99 (117 Hz, 2 basal BH), −8.62 (162 Hz, 1 apical BH); ^{13}C NMR δ 122 (cage C), 117.33 (178 Hz, Cp), 75.14, 24.77 (106 Hz, THF), 3.12 (117 Hz, SiMe$_3$).

[10] X-ray Data for **2** ($C_{26}H_{54}B_8Si_4Ti_2$; fw, 661.4; $P\bar{1}$) and **3** ($C_{17}H_{35}OB_4Si_2ClTi$; fw, 438.2; $P2_1/n$). Data were collected at 230 K on Siemens R3m/V diffractometer with a = 10.672(3) and 8.358(2) Å, b = 11.497(4) and 10.311(4) Å, c = 14.848(5) and 27.515(9) Å, α = 89.37(3) and 90.0°, β = 89.94(3) and 92.54(3)°, γ = 90.82(2) and 90.0°, V = 1822(1) and 2389(1) Å^3, Z = 2 and 4, D_{calcd} = 1.206 and 1.229 g/cm^3 for **2** and **3**, respectively. Of 3723 (2θ = 3.5–40°) and 2762 (2θ = 3.5–42°) reflections collected, 2337 and 1804 reflections were considered as observed [$F > 6.0\sigma(F)$]. Both structures were solved by the heavy-atom methods stored in *SHELXTL-PLUS* (Sheldrick, G. M. *Structure Determination Software Programs*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990). All non-H atoms were refined anisotropically. The cage H's, located in DF maps, were not refined. The final refinements converged at R = 0.055 and 0.036, wR = 0.070 and 0.048, and GOF = 1.57 and 1.18, for **2** and **3**, respectively.

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be converted to the corresponding metal alkyl derivatives, which may in turn act as precursors to a number of organic and organometallic transformations. Such an investigation is currently underway in our laboratories.

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Supplementary Material Available: Tables of positional and thermal parameters, selected bond distances, and bond angles for **2** and **3** (9 pages). Ordering information is given on any current masthead page.

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