A New Class of Constrained-Geometry Metallocenes: Synthesis and Crystal Structure of a Carboranyl−Thiol-Appended Half-Sandwich Titanocene and Its Conversion to Halotitanocene

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*Summary: A novel carboranyl−thiol-appended cyclopentadiene ligand, 1-SH-2-[HCpCH(Ph)]-closo-1,2-$C_2B_{10}H_{10}$ (**2**), was prepared and then reacted with $Ti(NMe_2)_4$ to form the corresponding titanium complex [1-(σ-S)-2-(η^5-$C_5H_4CH(Ph)$)-1,2-$C_2B_{10}H_{10}$)]$Ti(NMe_2)_2$ (**3**), which undergoes exclusively a monohalogenation reaction on the metal center, in the presence of Me_3SiCl or Me_3NHCl, leading to the formation of [1-(σ-S)-2-(η^5-$C_5H_4CH(Ph)$)-1,2-$C_2B_{10}H_{10}$)]$TiCl(NMe_2)$ (**4**) in 71% yield.*

Metallocenes of constrained geometries, in which an early transition metal is simultaneously bonded to a cyclopentadienide ligand (Cp) and to an η^1-bonding pendant group of Cp, have been shown to be effective catalysts, or cocatalysts, for olefin polymerizations.[1,2] Some of the earliest, and most successful, constrained-geometry catalyst precursors were those based on the *ansa*-monocyclopentadienide−amido ligand, $[C_5R_4{-}SiMe_2R'N]^{2-}$ (CpA), in which an amido nitrogen is the η^1-bonding site and is linked to the Cp by a dimethylsilyl group.[3] Early-transition-metal complexes of CpA have been the basis of both single-site and binuclear catalytic systems.[2,4] Because of these early successes, modifications of the ansa ligands have been the subject of intensive research. Such modifications have involved changes to the Cp, the linking group, and the η^1-bonding moiety or combinations thereof.[2a,5−7] Many of these changes have resulted in effective catalytic systems.[5−7] One particularly interesting modification was found in $\{CpC({=}CH_2)OZr(NEt_2)_2\}_2$, which exhibited no specific steric constraints but which, on activation with MAO, generated an active Ziegler−Natta catalyst.[8] Recently, there have been reports of group 4 constrained-geometry complexes in which phenol has been used both as the linking group and for the η^1-bonding site.[9] Since these complexes have been shown to be the bases of highly efficient catalytic systems, a further investigation of the early-transition-metal, constrained-geometry complexes having group 16 base sites seemed warranted. In this study we have sought to take advantage of the high electron-withdrawing ability of the carboranyl−thiol moiety by introducing it onto a Cp ligand. Here we report the synthesis of the novel ansa ligand 1-SH-2-[HCpCH(Ph)]-*closo*-1,2-$C_2B_{10}H_{10}$ and its metalation product [1-(σ-S)-2-(η^5-$C_5H_4CH(Ph)$)-1,2-$C_2B_{10}H_{10}$)]$Ti(NMe_2)_2$, in which the appended carboranyl−thiol unit acts as both the linking and η^1-bonding group.

The reaction of 6-phenylfulvene with the dilithium salt of 1-SH-*closo*-1,2-$C_2B_{10}H_{11}$ (**1**) in a molar ratio of 1:1 in THF, followed by hydrolysis, gave the carboranyl−thiol-appended cyclopentadiene ligand 1-SH-2-[HCpCH(Ph)]-*closo*-1,2-$C_2B_{10}H_{10}$ (**2**) in 85% yield (see

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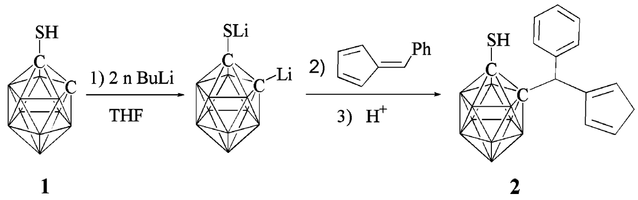
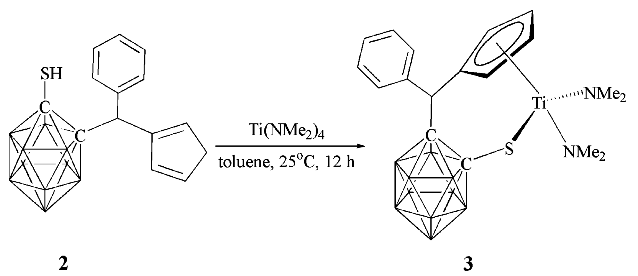
Scheme 1



Scheme 2



Scheme 1).[10] It is important that care be taken to completely remove the original THF solvent before the reaction mixture is hydrolyzed.[10] Otherwise, a polymeric material will result. It should also be noted that, while the purified ligand precursor **2** is a yellow solid, the impure product is a dark green residue. However, the spectroscopic and analytical data are all consistent with the formulation of **2**, given in Scheme 1. The constrained-geometry titanium complex [1-(σ-S)-2-(η^5-$C_5H_4CH(Ph)$)-1,2-$C_2B_{10}H_{10}$)]Ti$(NMe_2)_2$ (**3**) could be obtained in 83% yield from the reaction of **2** with $Ti(NMe_2)_4$ in toluene via an amine elimination reaction (see Scheme 2).[11] While the reactivity of **3** toward excess Me_3SiCl results in the formation of [1-(σ-S)-2-(η^5-$C_5H_4CH(Ph)$)-1,2-$C_2B_{10}H_{10}$)]TiCl(NMe_2) (**4**) in 71% yield,[12] with 2 equiv of Me_3NHCl the yield of **4** is only 41% (see Scheme 3).[13] In neither case was there evidence for the dichlorination of the titanium.

Several other η^1 group 16 atom appended with η^5-Cp complexed organometallic species have been synthesized and their structures determined. The (sp^2-C_1)-bridged Cp/oxido−titanium complex {Cp-C(=CH_2)-O−Zr$(NEt_2)_2$}$_2$[8] was found to be a dimer, as were [η^5:σ-$C_5H_4Si(Me)_2$−O−$TiCl_2$]$_2$[14] and {[η^5:σ-$C_5H_4(CH_2)_2O$]-$TiCl_2$}$_2$.[6b] However, the dimers have quite different structures, in that each oxygen of the latter species formed a bridge between two titanium atoms, while the first two compounds are not constrained within the single unit; instead, the oxygens were bonded to one neighboring titanium in the dimeric structure. On the other hand, [η^5:σ-$C_5H_4(CH_2)_3O$]$TiCl_2$ was found to be monomeric.[6b] Since analysis and NMR data could not rule out the possibility that **3** could exist as a dimer, the unambiguous structure of compound **3** was determined by X-ray diffraction studies.[15] The ORTEP draw-

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(10) **Synthesis of 2.** A 1.00 g (5.68 mmol) sample of *closo*-1-SH-1,2-$C_2B_{10}H_{11}$ (**1**) in 40 mL of dry THF was charged into a 100 mL Schlenk flask. To this flask was added 4.55 mL of ^{n}BuLi (11.40 mmol, 2.5 M in hexanes) dropwise with stirring at −78 °C. The reaction mixture was warmed to room temperature and stirred for 12 h, during which time a white precipitate formed. The mixture was then cooled to −78 °C again, and a 10 mL THF solution of 6-phenylfulvene (0.88 g, 5.68 mmol) was added dropwise over a 10 min interval. The resulting reaction mixture was then warmed to room temperature and stirred overnight, during which time the suspension mixture became a clear orange solution. The solvents from the reaction mixture were removed in vacuo, and the remaining solid was dried in vacuo for 5 h to remove any remaining THF. The solid was then redissolved in 100 mL of water, and to this solution was added 10 mL of concentrated HCl was added up to pH 1. The solution was extracted by 100 mL of CH_2Cl_2, and the organic layer was separated and dried over anhydrous $MgSO_4$. After complete removal of the solvent, a dark green solid was obtained. The solid was further purified by column chromatography using CH_2Cl_2 as the mobile phase to give a yellow solid, identified as 1-thiol-2-[cyclopentadienylmethyl(phenyl)]-1,2-dicarba-*closo*-dodecaborane(12) (**2**; 1-SH-2-[HCpCH(Ph)]-*closo*-1,2-$C_2B_{10}H_{10}$), in 85% yield (1.60 g, 4.83 mmol). Anal. Calcd (found) for $C_{14}B_{10}H_{22}S$ (**2**): C, 50.88 (50.70); H, 6.71 (6.72). NMR data for compound **2**: ^{1}H NMR ($CDCl_3$, external Me_4Si) δ 2.93−3.34 (2H, m, CH_2 in C_5H_5), 3.78 (1H, s, S*H*), 5.05 (1H, s, br, Ph(C*H*)), 6.40−6.62 (4H, m, C=C*H* in C_5H_5), 6.94−7.52 (5H, m, C_6H_5); ^{13}C NMR ($CDCl_3$, external Me_4Si) δ 40.7, 42.1 (*C*H_2 in C_5H_5), 51.7, 52.5 (Ph(*C*H)), 85.3 (PhCC_{cage}), 86.3 (C_{cage}SH), 83.52 (Ph−C_{cage}), 127.8−134.8 (*C*=*C*H in C_5H_5), 129.7−146.3 (C_6H_5); ^{11}B NMR ($CDCl_3$, relative to external BF_3·OEt_2) δ −2.06, −4.54, −7.01, −10.03, −11.29 (d (br, overlapping), BH's, $^1J(^{11}B-^1H)$ unresolved). IR (cm^{-1}, KBr cell): 3134 (br, s), 3052 (s, m), 3021 (s, m), 2960 (s, s), 2919 (s, s), 2863 (s, m), 2847 (s, s), 2582 (br, s), 1618 (s, w), 1398 (s, s), 1255 (s, s), 1117 (s, s), 1071 (s, s), 1024 (s, w), 794 (s, w), 702 (s, s).

(11) **Synthesis of 3.** To a toluene (30 mL) solution of **2** (0.37 g, 1.12 mmol) was added a toluene (10 mL) solution of $Ti(NMe_2)_4$ (0.25 g, 1.12 mmol) at −78 °C. The resulting mixture was slowly warmed to room temperature and stirred for 24 h at this temperature until it turned to a red solution. After removal of small amounts of solid by filtration, the solvent from the clear filtrate was removed in vacuo, to collect a dark red residue. This residue was further purified repeatedly by washing with hexanes to give the corresponding titanium complex [1-(σ-S)-2-(η^5-$C_5H_4CH(Ph)$)-1,2-$C_2B_{10}H_{10}$)]Ti$(NMe_2)_2$ (**3**) in 83% yield (0.43 g, 0.93 mmol). Anal. Calcd (found) for $C_{18}H_{32}B_{10}N_2STi$ (**3**): C, 46.54 (46.70); H, 6.94 (6.72). NMR data for compound **3**: ^{1}H NMR (C_6D_6, external Me_4Si) δ 2.87, 3.29 (12H, s, N(CH_3)$_2$), 5.34 (1H, s, PhC*H*), 5.71 (2H, m, C_5H_4), 6.22 (2H, m, C_5H_4), 7.14−7.43 (5H, m, C_6H_5); ^{13}C NMR (C_6D_6, external Me_4Si) δ 48.7, 49.7 (N(*C*H_3)$_2$), 54.7 (Ph*C*H), 81.3 (Ph−C_{cage}), 83.1 (C_{cage}SH), 109.5, 113.7, 114.9, 116.2 (C_5H_4), 127.5−139.8 (C_6H_5); ^{11}B NMR (C_6D_6, relative to external BF_3·OEt_2) δ −4.86 (d, *B*H, $^1J(^{11}B-^1H) = 129$ Hz), −6.19 (d, $^1J(^{11}B-^1H) = 133$ Hz), 11.6 (d, $^1J(^{11}B-^1H) = 117$ Hz). IR (cm^{-1}, KBr cell, in C_6D_6): 3401 (s, w), 2958 (s, s), 2920 (s, s), 2845 (s, m), 2566 (vs, br), 1635 (m, s), 1465 (s, s), 1399 (s, s), 1380 (s, s), 1260 (s, s), 1097 (s, s), 1020 (s, s), 801 (vs, s), 705 (m, s).

(12) **Synthesis of 4 by reaction with Me_3SiCl.** To a toluene (30 mL) solution of **3** (0.30 g, 0.65 mmol) was added 0.85 mL (6.5 mmol) Me_3SiCl at −78 °C. The resulting solution was warmed to room temperature slowly and stirred overnight at this temperature to give a red solution. The solvents along with excess Me_3SiCl were pumped off, leaving a red solid, which was washed with *n*-hexane. Then the solid was recrystallized from toluene to give **4** as red microcrystals in 71% yield (0.21 g, 0.46 mmol). Anal. Calcd (found) for $C_{16}H_{26}B_{10}ClNSTi$ (**4**): C, 42.15 (42.40); H, 5.75 (5.72). NMR data for compound **4**: ^{1}H NMR (C_6D_6, external Me_4Si) δ 3.20 (6H, s, N(CH_3)$_2$), 5.04 (1H, s, PhC*H*), 5.16, 5.54, 6.02, 6.41 (1H, s, C_5H_4), 7.12−7.27 (5H, m, C_6H_5); ^{13}C NMR (C_6D_6, external Me_4Si) δ 51.5, 54.7 (Ph*C*H), 78.6 (PhCH−C_{cage}), 83.9 (C_{cage}−SH), 115.1, 118.0, 118.1, 119.7 (C_5H_4), 125.4−138.6 (C_6H_5); ^{11}B NMR (C_6D_6, relative to external BF_3·OEt_2) δ −4.54, −10.21. IR (cm^{-1}, KBr cell, in C_6D_6): 2958 (s, s), 2920 (s, s), 2611 (m, s), 2588 (m, s), 2571 (m, s), 2555 (m, s), 1400 (s, s), 1262 (s, s), 1099 (vs, br), 1019 (s, s), 798 (vs, s), 730 (m, s), 705 (m, s).

(13) **Synthesis of 4 by reaction with Me_3NHCl.** To a toluene (30 mL) solution of **3** (0.30 g, 0.65 mmol) was added a dry powder of Me_3-NHCl (0.62 g, 1.30 mmol) incrementally at −78 °C. The resulting solution was stirred at 0 °C over a period of several hours and then slowly warmed to room temperature and stirred further overnight at this temperature to give a red solution. The solvents from the reaction mixture were pumped off, leaving a red solid, which was washed with *n*-hexane. The solid was then recrystallized from a toluene and hexane mixture to give red microcrystals, identified as **4**, in 41% yield.

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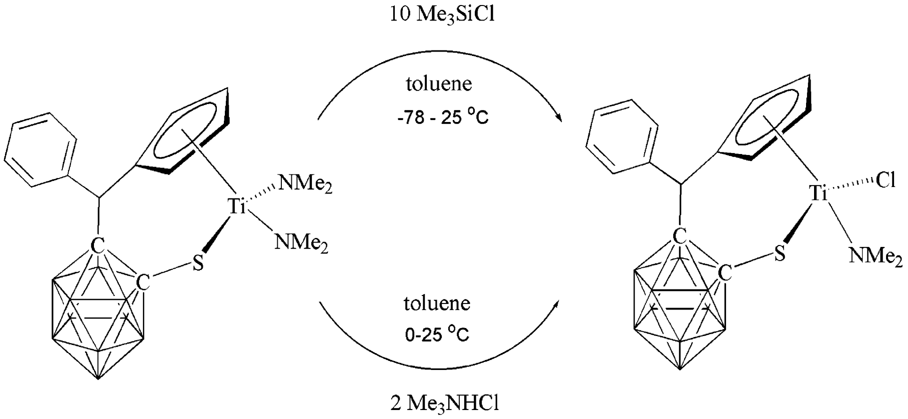
(15) X-ray data for **3** ($C_{18}H_{32}B_{10}N_2STi$; fw, 464.52; $P\bar{1}$). Data were collected at 173 (2) K on a Bruker SMART CCD PLATFORM diffractometer with $a = 10.446(2)$ Å, $b = 11.849(2)$ Å, $c = 12.280$ (2) Å, $\alpha = 114.864(3)°$, $\beta = 111.230(3)°$, $\gamma = 91.970(4)°$, $V = 1253.8$ (4) $Å^3$, $Z = 2$, and $D_{calcd} = 1.230$ g cm^{-3}. Of the 6261 reflections collected ($2\theta = 3.88-50°$), 4232 reflections were respectively considered as observed ($I > 2\sigma(I)$) and were corrected for Lorentz, polarization, and absorption effects (Sheldrick, G, M, SADABS, Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen, Göttingen, Germany, 1996). The structure was solved by direct methods and refined by full-matrix least-squares techniques using SHELXTL (Sheldrick, G. M. SHELXTL, Version 5.1; Bruker Analytical X-ray Systems, Madison, WI, 1997). All non-H atoms were refined anisotropically. The final refinements converged at R1 = 0.0618, wR2 = 0.1305, and GOF = 1.378.

Scheme 3



ing of **3**, given in Figure 1, shows the compound to be a monomeric complex in which the Cp group, S, and the two NMe$_2$ groups surround the Ti in a nearly tetrahedral fashion; the Cp(centroid)−Ti−S angle is 113.4(1)°, and the N$_2$−Ti−N$_1$ angle is 107.27(13)°. The Cp(centroid)−Ti distance of 2.054 Å found in **3** is essentially the same as the value of 2.00(1) Å reported for [C$_5$H$_4$-PhCH(PhO)]TiCl$_2$[9c] but is considerably shorter than the analogous distances found in (Me$_4$CpPhO)Ti(CH$_2$Ph)$_2$ (2.36(1) Å)[9a] and Me$_2$Si(Me$_4$C$_5$)(^{t}BuN)TiCl$_2$ (2.36(1) Å),[1] indicating a tighter binding of the metal to the ligand in **3**. Consequently, the Cp(centroid)−Ti−S angle of 113.4(1)° is larger than the Cp−Ti−O angles found in [C$_5$H$_4$PhCH(PhO)]TiCl$_2$ (110.7°)[9c] and (Me$_4$CpPhO)Ti-(CH$_2$Ph)$_2$ (107.7°)[9a] as well as the Cp−Ti−N angles in Me$_2$Si(Me$_4$C$_5$)(^{t}BuN)TiCl$_2$ (107.6°).[1] These structural parameters exemplify the influence of a carboranyl−thiol group on the metal binding to a Cp ligand.

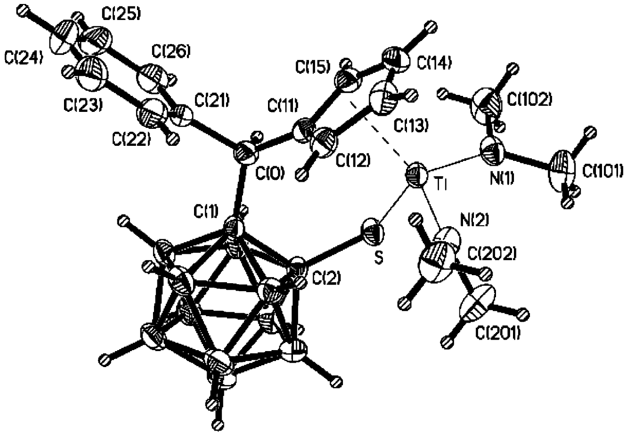


Figure 1. Perspective view of **3** with thermal ellipsoids drawn at the 50% probability level. Pertinent distances (Å) and angles (deg): Cp(centroid)−Ti, 2.054; Ti−S, 2.404(1); Ti−N(1,2), 1.908(3), 1.896(3); C(0)−C(1), 1.562(4); C(1)−C(2), 1.685(4); C(2)−S, 1.784(3); Cp(centroid)−Ti−S, 113.4(1); C(2)−S−Ti, 111.3(1); N(1)−Ti−N(2), 107.3(1), C(11)−C(0)−C(1), 118.6(3); C(11)−C(0)−C(21), 109.5(3); C(0)−C(1)−C(2), 115.5(3). See Table S-3 in the Supporting Information for a detailed list of bond lengths and angles.

The isolated good yields for **3** indicate that the methods outlined in Schemes 1 and 2 should prove to be efficient synthetic routes for a number of early-transition-metal constrained-geometry organometallics. Since the sulfur atom is known to influence the binding capability of the ligands more so than the nitrogen and phosphorus atoms, the incorporation of a thiol unit in the ansa ligand could help in enhancing the reactivity of the metallocene toward Ziegler−Natta type catalysis. Such studies are the subject of our continuing investigations.

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Supporting Information Available: Tables of crystallographic data for **3**, including fractional coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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