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Pentamethylcyclopentadienyl–Dicarbollide Derivatives of Scandium[†]

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The reactions of $[Cp^*ScCl_2]_x$ ($Cp^* = (\eta^5\text{-}C_5Me_5)$) with $Na_2[C_2B_9H_{11}]$ or $[Cp^*ScMe_2]_x$ with $C_2B_9H_{13}$, followed by treatment with THF yield $Cp^*(C_2B_9H_{11})Sc(THF)_3$. Alkylation of $Cp^*(C_2B_9H_{11})Sc(THF)_3$ with $LiCH(SiMe_3)_2$ yields $Cp^*(C_2B_9H_{11})ScCH(SiMe_3)_2Li(THF)_3$, and $\{[Cp^*(C_2B_9H_{11})ScCH(SiMe_3)_2]_2Li\}\cdot Li(THF)_3$, which is obtained by its recrystallization from pentane/toluene, has been characterized structurally. This alkyl derivative reacts slowly with H_2 to yield $[Cp^*(C_2B_9H_{11})ScH]_2[Li(THF)_n]_2$, a surprisingly unreactive scandium hydride dimer. Once again, recrystallization from toluene affords a crystalline form with less coordinated THF, $[Cp^*(C_2B_9H_{11})ScH]_2[Li(THF)_2\cdot{}^3/_2(C_6H_5CH_3)$, whose structure reveals that the two anionic $[Cp^*(C_2B_9H_{11})ScH]^-$ fragments are held together by reciprocal B–H dative bonding from the dicarbollide ligand to the electron deficient scandium. The potential of pentamethylcyclopentadienyl–dicarbollide derivatives of scandium to serve as efficient α olefin polymerization catalysts is discussed.

Introduction

A study of the kinetics of the polymerization of α-olefins, $CH_2{=}CHR$, using a well-defined, single component catalyst system with $[\{(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NCMe_3)\}(PMe_3)Sc]_2(\mu\text{-}H)_2$ or $[\{(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NCMe_3)\}Sc]_2(\mu\text{-}CH_2CH_2CH_3)_2$ as catalysts (or as catalyst precursors) revealed that the propagating species is likely to be the monomeric, PMe_3-free alkyl $\{(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NCMe_3)\}Sc{-}CH_2CHRPC$ (**PC** = polymer chain).[2] These alkyls, such as the *n*-propyl derivative, are in equilibrium with a dimeric form, and it is this tendency of the active catalyst to produce an inactive dimer that is partly responsible for the slow polymerization rates observed. It occurred to us that molecular analogs containing a dianionic equivalent of the monoanionic cyclopentadienide or amide ligand could be more active catalysts, since dimerization would be discouraged by simple Coulombic repulsion between the negatively charged monomers.

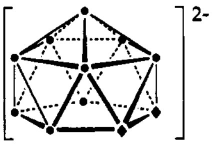
The similarity of the coordination chemistry of the dianionic dicarbollide ligand, $[C_2B_9H_{11}]^{2-}$, to monoanionic cyclopentadienide, $[C_5H_5]^-$, has been extensively documented by Hawthorne and co-workers.[3] Thus, we considered the possibility that anionic derivatives of the type $[(\eta^5\text{-}C_5R_5)(\eta^5\text{-}C_2B_9H_{11})Sc{-}R']^-$ (R, R′ = H, alkyl) might function as more active olefin polymerization catalysts. Dicarbollide complexes which are particularly relevant to the compounds reported here are the recently reported bis $[\eta^5\text{-}C_2B_9H_{11}]$ aluminate, $Tl^+[Al(C_2B_9H_{11})_2]^-$,[4] and the mono and bis $[\eta^5\text{-}C_2B_9H_{11}]$ derivatives of Sm and Yb.[5] A group 3 sandwich complex containing the smaller dicarbollide ligand $[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]^{2-}$ has been synthesized by Hosmane and co-workers.[6] Furthermore, Jordan has adopted a similar strategy for adding negative charge to some cationic zirconcene and hafnocene derivatives (rendering them neutral) by substitution of this same dicarbollide ligand for one of the cyclopentadienide ligands.[7] We report herein the synthesis and characterization of pentamethylcyclopentadienyl–dicarbollide complexes of scandium and an evaluation of their potential as catalysts for the polymerization of olefins.

Results and Discussion

Synthesis and Characterization of a Cp*–Dicarbollide Scandium Alkyl Complex. The dicarbollide ligand may be introduced either via the reaction of $[Cp^*ScCl_2]_x$[8] with $Na_2[C_2B_9H_{11}]$ in diethyl ether, followed by treatment with THF (eq 1), or by following the

$$[Cp^*ScCl_2]_x + Na_2[C_2B_9H_{11}] \xrightarrow{\substack{\text{(i) } Et_2O\\ \text{(ii) toluene extraction}\\ \text{(iii) THF}}} \underset{30\%}{Cp^*(C_2B_9H_{11})Sc(THF)_3} \quad (1)$$

$$[Cp^*ScMe_2]_x + [C_2B_9H_{13}] \xrightarrow[-2CH_4]{\substack{\text{(i) toluene}\\ \text{(ii) THF}}} \underset{80\%}{Cp^*(C_2B_9H_{11})Sc(THF)_3} \quad (2)$$



$= [C_2B_9H_{11}]^{2-}$ (• = BH; ♦ = CH)

[†] Contribution No. 8755.

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[2] Pamela J. Shapiro, W. Donald Cotter, William P. Schaefer, Jay A. Labinger, and John E. Bercaw, manuscript in preparation.

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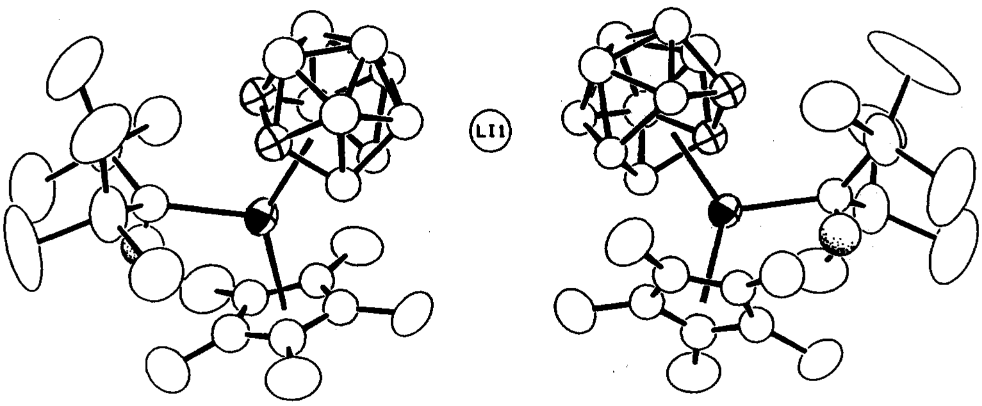
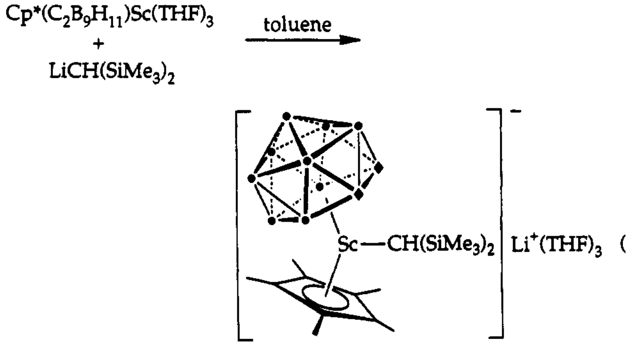


Figure 1. ORTEP drawing of $\{[Cp^*(C_2B_9H_{11})ScCH(SiMe_3)_2]_2Li\}\cdot Li(THF)_3$ showing the two anions with the bridging lithium atom with 50% probability ellipsoids. Only the $CH(SiMe_3)_2$ hydrogens are shown. Carbon atoms of the dicarbolide ligands are shown with outlined octants.

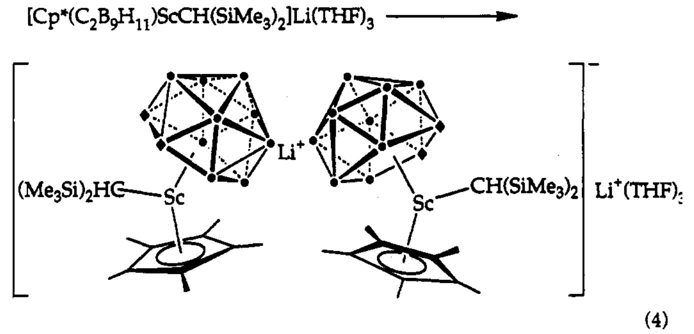
procedure of THF (eq 2) to yield the same compound, $Cp^*(C_2B_9H_{11})Sc(THF)_3$. This material is easily isolated due to its insolubility in THF. Although the yield from the second method is higher, both reagents, $[Cp^*ScMe_2]_x$ and $[C_2B_9H_{13}]$, are rather unstable, their preparations are cumbersome and unpredictable, and they normally produce low yields. Thus, we favor the first method.

Alkylation of $Cp^*(C_2B_9H_{11})Sc(THF)_3$ proceeds essentially quantitatively by using bulky $LiCH(SiMe_3)_2$ to yield $Cp^*(C_2B_9H_{11})ScCH(SiMe_3)_2Li(THF)_3$ (eq 3). Smaller alkylating reagents do not work well.



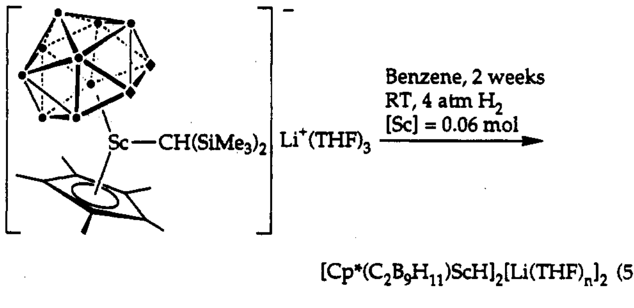
(3)

Slow recrystallization by pentane diffusion into a concentrated toluene solution affords crystals of overall composition $[Cp^*(C_2B_9H_{11})ScCH(SiMe_3)_2]Li(THF)_{3/2}$. X-ray crystallographic analysis revealed that the dicarbollide ligand is indeed bonded in an η^5 fashion to yield a sandwich complex, as expected.[9] In the solid state two scandium cores share a lithium ion loosely bonded to the triangular [BH] faces of their two dicarbollide ligands, while a second lithium ion is coordinated to three THF molecules. Therefore the solid state formula is $\{[Cp^*(C_2B_9H_{11})ScCH(SiMe_3)_2]_2Li\}^-\cdot Li^+(THF)_3$ (eq 4). A drawing of the structure as determined from X-ray data is shown in Figure 1. The ability of the B–H units of dicarbollide ligands to effectively compete with THF for coordination to the lithium ion has been observed previously in the structure of $\{YCl(THF)[\eta^5\text{-}C_2(SiMe_3)_2B_4H_4]_2\}^{2-}$, having a complexed exo-polyhedral $Li^+(THF)$ and a discrete $Li^+(THF)_4$ outside the coordination sphere to balance charges.



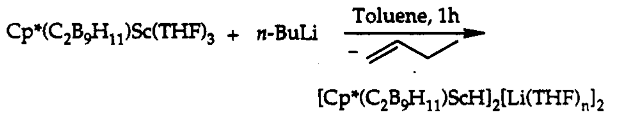
(4)

Synthesis and Characterization of a Cp*–Dicarbollide Scandium Hydride Complex. $[Cp^*(C_2B_9H_{11})ScCH(SiMe_3)_2]Li(THF)_3$ does not react with Lewis bases such as PMe_3, 2-butyne, or even with ethylene, presumably because of steric congestion around the metal. Alternatively, this lack of reactivity could be attributed to a reduced electrophilicity due to the formal negative charge on the complex, some of which must reside at scandium. Hence, by both steric and electronic arguments the reactivity of the Sc–R group is expected to be reduced. The alkyl group does, however, react with H_2, albeit slowly, to yield $CH_2(SiMe_3)_2$ and $[Cp^*(C_2B_9H_{11})ScH]_2[Li(THF)_n]_2$ (eq 5). This reaction is rather slow when compared with the rates observed for hydrogenation of $Cp^*_2Sc\text{–}CH(SiMe_3)_2$ which is complete after only a few hours under similar conditions.[10]



(5)

This hydride may also be synthesized by the reaction of $Cp^*(C_2B_9H_{11})Sc(THF)_3$ with 1 equiv of n-butyllithium (eq 6).



$$Cp^*(C_2B_9H_{11})Sc(THF)_3 + n\text{-BuLi} \xrightarrow{\text{Toluene, 1h}} [Cp^*(C_2B_9H_{11})ScH]_2[Li(THF)_n]_2 \quad (6)$$

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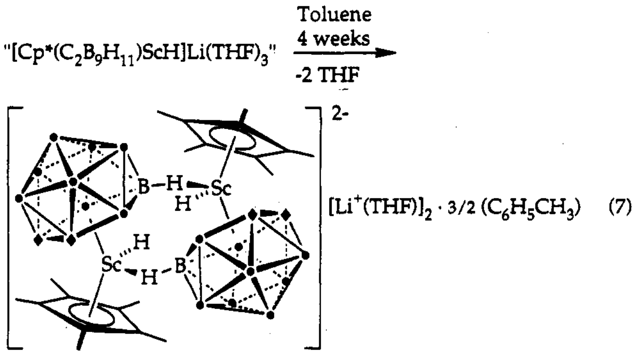
If the hydrogenation of $[Cp^*(C_2B_9H_{11})ScCH(SiMe_3)_2]Li(THF)_3$ is carried out in the presence of unsaturated substrates such as 2-butyne or propene, once again only the formation of $[Cp^*(C_2B_9H_{11})ScH]_2[Li(THF)_n]_2$ is observed along with the expected organic products from hydrogenation (i.e. butene, butane, and propane). Similarly, only $[Cp^*(C_2B_9H_{11})ScH]_2[Li(THF)_n]_2$ is produced when the hydrogenation reaction is carried out with excess PMe_3. Moreover, isolated samples of $[Cp^*(C_2B_9H_{11})ScH]_2[Li(THF)_n]_2$ are found to be surprisingly unreactive toward the same substrates (PMe_3, propene, ethylene, or 2-butyne.

In order to establish the nuclearity of this hydride and confirm the mode of coordination of the dicarbollide ligand, an X-ray diffraction study was undertaken. Slow recrystallization from a concentrated toluene solution gave crystals of composition $[Cp^*(C_2B_9H_{11})ScH]_2[Li(THF)]_2\cdot{}^3/_2(C_6H_5CH_3)$ (eq 7).



(7)

Unfortunately, although the X-ray data for this compound are of good quality, there are three molecules of toluene of crystallization in the asymmetric unit, each disordered differently, causing the overall residual electron density to be high especially in the regions of the disordered toluenes. Fortunately, the atoms near the scandium were reliably located (Tables I and II) and are shown in Figure 2.[11] The complex is dimeric with the two scandium cores held together by what can be best considered as a two-electron dative bond between an electron rich boron hydride and the Lewis acidic scandium center. The scandium hydride has not been observed crystallographically but can be detected by ^1H NMR spectroscopy (δ 5.23 broad). Moreover, the ^1H NMR data for benzene-d_6 solutions of $[Cp^*(C_2B_9H_{11})ScH]_2[Li(THF)_n]_2$ indicate that the solid state structure is maintained in solution.

Table I. Final Refined Parameters for the Cp*–Dicarbollide Scandium Dimer (x, y, z, and $U_{eq}{}^a \times 10^4$)

atom	x	y	z	U_{eq} or B,[a] Å^2
Sc1	1182(1)	970(2)	1999(1)	411(7)
Cp1	1135(3)	−727(8)	1455(8)	3.3(3)[b]
Cp2	913(3)	−584(8)	1844(7)	3.4(3)[b]
Cp3	1041(3)	−462(8)	2665(8)	3.4(3)[b]
Cp4	1344(3)	−533(8)	2831(8)	3.5(3)[b]
Cp5	1403(3)	−667(8)	2095(7)	3.6(3)[b]
Cp6	1087(3)	−907(9)	576(8)	840(46)
Cp7	588(3)	−743(8)	1422(8)	688(42)
Cp8	892(3)	−332(9)	3309(8)	846(46)
Cp9	1562(3)	−646(8)	3654(8)	808(52)
Cp10	1686(3)	−909(9)	1968(8)	728(44)
Cc1	680(2)	1658(8)	1576(7)	3.8(3)[b]
Cc2	757(2)	1345(8)	784(7)	4.6(3)[b]
Bc3	1037(3)	1889(10)	681(8)	3.3(4)[b]
Bc4	1138(3)	2693(10)	1494(8)	3.9(4)[b]
Bc5	902(3)	2470(11)	2088(8)	4.2(3)[b]
Bc6	553(3)	2826(10)	1491(9)	4.4(4)[b]
Bc7	451(3)	2041(11)	654(10)	5.3(4)[b]
Bc8	692(3)	2219(10)	67(9)	4.7(4)[b]
Bc9	924(3)	3135(11)	543(9)	4.5(4)[b]
Bc10	840(3)	3484(10)	1440(9)	4.6(4)[b]
Bc11	561(3)	3162(11)	532(10)	5.0(4)[b]
Sc2	3228(1)	2485(2)	7518(1)	426(6)
Cp11	2786(3)	1709(9)	7687(8)	3.8(3)[b]
Cp12	3021(3)	1336(9)	8303(7)	3.6(3)[b]
Cp13	3133(2)	2097(8)	8855(7)	3.3(3)[b]
Cp14	2973(3)	2935(9)	8532(8)	3.9(3)[b]
Cp15	2761(2)	2688(9)	7797(7)	3.6(3)[b]
Cp16	2565(2)	1103(9)	7088(7)	594(40)
Cp17	3114(3)	311(10)	8431(8)	848(47)
Cp18	3353(3)	1999(9)	9686(8)	830(54)
Cp19	3009(3)	3871(9)	8981(7)	852(49)
Cp20	2539(3)	3348(9)	7337(8)	789(47)
Cc21	3133(3)	1436(9)	6291(8)	5.6(4)[b]
Cc22	2926(2)	2340(8)	6062(6)	3.8(3)[b]
Bc23	3108(3)	3325(9)	6173(8)	2.6(3)[b]
Bc24	3463(3)	3016(10)	6432(9)	3.5(4)[b]
Bc25	3473(3)	1782(10)	6524(9)	4.0(4)[b]
Bc26	3304(3)	1274(11)	5527(9)	4.9(4)[b]
Bc27	2941(3)	1627(11)	5251(10)	5.2(4)[b]
Bc28	2930(3)	2886(10)	5178(9)	4.6(4)[b]
Bc29	3276(3)	3334(10)	5390(9)	4.1(4)[b]
Bc30	3532(3)	2329(10)	5662(8)	3.9(3)[b]
Bc31	3186(3)	2238(11)	4855(9)	5.6(4)[b]
O1	3883(5)	465(9)	1793()	1587(62)
C1	3760(9)	1842(32)	2397(29)	2445(199)
C2	3989(11)	1922(38)	2126(37)	2967(233)
C3	4096(7)	1119(25)	1847(14)	1771(111)
C4	3664(5)	823(19)	2087(16)	1501(96)
O2	4189(5)	991(18)	5942(16)	2436(86)
C5	4423(6)	1755(21)	6018(23)	2097(128)
C6	4507(6)	1608(26)	5310(21)	2499(151)
C7	4269(10)	1176(19)	4762(15)	2355(162)
C8	4221(11)	711(23)	5462(39)	4537(280)
Li1	3915(10)	−764(35)	1418(29)	18.3(16)[b]

[a] $U_{eq} = {}^1/_3\sum_i\sum_j[U_{ij}(a_i{}^*a_j{}^*)(\mathbf{a}_i\cdot\mathbf{a}_j)]$. [b] Isotropic displacement parameter, B.

Conclusions

The reciprocal B–H dative bonding interaction from the dianionic dicarbollide ligands to electrophilic scandium centers observed for $[Cp^*(C_2B_9H_{11})ScH]_2[Li(THF)_n]_2$ is very similar to that observed by Jordan and co-workers for $[Cp^*(C_2B_9H_{11})Zr]_2(\mu\text{-}CH_2)$[6] as well as for a dimeric rhodium complex, $[Rh(PPh_3)(C_2B_9H_{10}C_6H_5)]_2$, reported earlier by Hawthorne and co-workers.[12] Indeed, it is the unique B–H group in the pentagonal C_2B_3 array that provides the best donor interaction with the electron deficient metal in all three cases.[13] Unlike the zirconium and rhodium dimers there is no additional bridging interaction for the scandium derivative; rather, the two $\{[Cp^*(C_2B_9H_{11})]ScH]^-\}$ subunits bear the same charge and repel each other. Not only do these two Sc–(B–H) interactions hold the two anionic fragments firmly together, but also the dimer resists reaction with such

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[11] $[Cp^*(C_2B_9H_{11})]ScH]_2Li_n(THF)_2\cdot{}^3/_2(C_6H_5CH_3)$, MW ($n$ = 1) = 914.53, monoclinic, space group $C2/c$. a = 48.509(15) Å, b = 13.930(5) Å, c = 17.068(10) Å, β = 107.13(3)°, V = 11022(9) Å^3, Z = 8; 11 085 reflections to 2θ = 50° measured, 5130 independent and used in structure and refinement. Final R index on F for 2148 reflections with $F_o{}^2 > 3\sigma(F_o{}^2)$ = 0.090, goodness of fit = 2.22. Further details, parameters, and derived quantities are provided in the supplementary material. The analytical and spectroscopic data are most consistent with the formulation $[Cp^*(C_2B_9H_{11})]ScH]_2Li_2(THF)_2\cdot{}^3/_2(C_6H_5CH_3)$. Only one lithium atom has been reliably located crystallographically; the other is likely obscured by the disordered toluene molecules.

[12] Behnken, P. E.; Marder, T. B.; Baker, R. T.; Knobler, C. B.; Thompson, M. R.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1985**, *107*, 932.

[13] A similar dative B–H interaction has also been identified for the dicarbollide derivatives $[Cp^*{}_2ZrCH_3][C_2B_9H_{12}]$: Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728.

Table II. Selected Distances and Angles for the Cp*-Dicarbollide Scandium Dimer

Distances (Å)			
Sc1–Cp*1	2.206	Sc2–Cp11	2.493(13)
Sc1–Cp1	2.525(12)	Sc2–Cp12	2.484(13)
Sc1–Cp2	2.502(12)	Sc2–Cp13	2.517(12)
Sc1–Cp3	2.490(12)	Sc2–Cp14	2.486(12)
Sc1–Cp4	2.523(12)	Sc2–Cp15	2.467(12)
Sc1–Cp5	2.505(12)	Sc2–Cb2	2.081
Sc1–Cb1	2.082	Sc2–Cc21	2.484(13)
Sc1–Cc1	2.514(12)	Sc2–Cc22	2.495(11)
Sc1–Cc2	2.509(12)	Sc2–Bc23	2.488(13)
Sc1–Bc3	2.501(14)	Sc2–Bc24	2.554(14)
Sc1–Bc4	2.536(14)	Sc2–Bc25	2.536(15)
Sc1–Bc5	2.521(14)	Sc1–H24	2.196
Sc2–Cp*2	2.182	Sc2–H4	2.173
Angles (deg)			
Cb1–Sc1–Cp*1	136.3	Cb2–Sc2–Cp*2	136.5
H24–Sc1–Cp*1	105.6	H4–Sc2–Cb2	106.7
H24–Sc1–Cb1	107.6	H4–Sc2–Cp*2	107.4
Bc24–H24–Sc1	148.8	Bc4–H4–Sc2	145.4

excellent Lewis bases as PMe_3. Note that this preference is likely to be for thermodynamic reasons, since the hydride dimer is the only new metal containing species present during the hydrogenation of $[Cp^*(C_2B_9H_{11})ScCH(SiMe_3)_2]Li(THF)_3$ in the presence of PMe_3. Thus, the strength of these reciprocal Sc–(B–H) interactions is truly remarkable.

The tremendous stability of this dimeric dicarbollide scandium hydride derivative augurs poorly for the utility of this class of compounds as olefin polymerization catalysts. Apart from its lack of reactivity toward PMe_3, $[Cp^*(C_2B_9H_{11})ScH]_2[Li(THF)_n]_2$ resists reaction with 2-butyne, ethylene, and propene. Moreover, β-hydride elimination from $[Cp^*(C_2B_9H_{11})ScC_4H_9]Li(THF)_n$ is apparently quite fast (eq 6), implying that chain transfer by this pathway to yield the refractory hydride dimer will dominate. Hence, we have abandoned this approach to olefin polymerization systems based on scandium derivatives with dicarbollide ligands. We are now concentrating efforts in the development of new dianionic analogs of the cyclopentadienyl ligand without B–H bonds.

Experimental Section

General Considerations. All manipulations were carried out using either high-vacuum or glovebox techniques as described earlier.[14] NMR spectra were recorded on GE300, Jeol FNM400, and Bruker AM500 spectrometers. ^{11}B NMR spectra (160.4 MHz, external reference $BF_3{\cdot}Et_2O$) were measured on a Bruker WM 500 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer. Microanalyses were performed by Galbraith Laboratories or Fenton Harvey of this department. Note that none of the dicarbollide complexes analyzed properly; carbon percentage values were found to be approximately 6% below their calculated values, and reproducibility was poor on samples which were clean as determined by ^1H NMR, even when samples were combusted with added V_2O_5. Toluene and petroleum ether were distilled from benzophenone ketyl and then vacuum distilled from titanocene[15] prior to use. All other reagents were obtained commercially and used without further purification. The preparation of $C_2B_9H_{13}$ was carried out as described by Jordan et al.[7]

Preparation of $Na_2[C_2B_9H_{11}]$. The procedure is identical to that reported by Hawthorne and co-workers[16] except that the THF solution of $Na_2[C_2B_9H_{11}]$ is pumped to dryness, toluene is condensed on the resulting white precipitate, and the resulting suspension is stirred for 1 h. The toluene is then removed in vacuo, and the resulting solids are washed with petroleum ether and placed under dynamic vacuum for 48 h. Residual THF that tends to remain must be quantitated either by titration or, more simply, by ^1H NMR spectroscopy.

Preparation of $Cp^*(C_2B_9H_{11})Sc(THF)_3$. Method A. In a glovebox a 100-mL round-bottom flask was charged with $[Cp^*ScCl_2]_x$ (1.40 g, 5.6 mmol) and $Na_2[C_2B_9H_{11}]$ (1.0 g, 5.6 mmol) and attached to a swivel frit assembly. Dry diethyl ether (ca. 50 mL) was vacuum transferred into a vessel at −78 °C, and the suspension was allowed to warm to room temperature under vigorous stirring and was stirred an additional 12 h. The Et_2O was removed under reduced pressure, toluene was vacuum transferred into the reaction vessel, and the suspension was stirred for 1 h and filtered. The toluene was then removed in vacuo to yield a pale yellow solid. Tetrahydrofuran (ca. 15 mL) was condensed into the flask, and the mixture was stirred until the yellow solids dissolved and was allowed to stand for 6–8 h, during which time a yellowish precipitate formed. Isolation of the solids by filtration and washing with a small amount of petroleum ether yields $Cp^*(C_2B_9H_{11})Sc(THF)_3$ (875 mg, 30%). ^1H NMR (300 MHz, benzene-d_6): δ $[C_5(CH_5]$, 1.27 (s, 15H); $-OCH_2CH_2-$, 1.40 (b, 12H); BCH, 2.86 (b, 2H); $-OCH_2CH_2-$, 3.64 (b, 12). $^{13}C\{^1H\}$ NMR (75 MHz, benzene-d_6): δ $[C_5(CH_3)]$, 11.2; $-OCH_2CH_2-$, 26.2; BCH, 52.5; $-OCH_2CH_2-$, 69.3; $[C_5(CH_3)_5]$, 118.9. ^{11}B NMR (benzene-d_6, referenced against $BF_3{\cdot}Et_2O$): δ −25.18, −13.85, −9.32, −5.06, −4.4, 0.52. Anal. Calcd: C, 54.51; H, 9.53. Found: C, 49.95, 46.34, 47.41; H, 8.90, 8.21, 8.70.

Method B. $[Cp^*ScMe_2]_x$ (0.35 g, 1.7 mmol) and $C_2B_9H_{13}$ (0.22 g, 1.7 mmol) were loaded into a 100-mL round-bottom flask which was attached to a swivel frit assembly. Dry toluene (ca. 30 mL) was vacuum transferred into the vessel at −78 °C, and the reaction mixture was allowed to warm to room temperature and was stirred for 2 h. The toluene was removed under reduced pressure, THF was condensed onto the resulting yellow solids, and the resulting solution was allowed to stand for 6–8 h during which time yellow $Cp^*(C_2B_9H_{11})Sc(THF)_3$ precipitated out of solution. The product can then be isolated by filtration and washing with a small amount of petroleum ether (700 mg, 80%).

Preparation of $[Cp^*(C_2B_9H_{11})Sc(CH(SiMe_3)_2)]Li(THF)_3$. $Cp^*(C_2B_9H_{11})Sc(THF)_3$ (0.90 g, 1.7 mmol) and $LiCH(SiMe_3)_2$ (0.29 g, 1.7 mmol) were loaded into a 50-mL round-bottom flask which was attached to a swivel frit assembly. Dry toluene (ca. 25 mL) was vacuum transferred into the vessel at −78 °C, and the reaction mixture was allowed to warm to room temperature and was stirred for 2 h. The solution was then filtered to remove a small amount of precipitate and the toluene removed in vacuo. The resulting solid was then washed with a small amount of cold petroleum ether and placed under vacuum to yield $[Cp^*(C_2B_9H_{11})Sc(CH(SiMe_3)_2)]Li(THF)_3$ (1.03 g, 87%). ^1H NMR (benzene-d_6, 300 MHz): δ $Si(CH_3)_3$, 0.31 (s, 18H); $-OCH_2CH_2-$, 1.20 (b, 12H); $ScCH(SiMe_3)_2$, 1.81 (s, 1); $[C_5(CH_3)_5]$, 2.25 (s, 15H); $-OCH_2CH_2-$, 3.30 (b, 12H); BCH, 3.10 (b, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, benzene-d_6): δ $Si(CH_3)_3$, 5.7; $ScCH(SiMe_3)_2$, 12.1; $[C_5(CH_3)_5]$, 13.2; $-OCH_2CH_2-$, 35.0; BCH, 47.8; $-OCH_2CH_2-$, 68.2; $[C_5(CH_3)]$, 121.3. ^{11}B NMR (C_6D_6) −28.8, −18.9, −17.2, −12.9, −11.0, −8.2. Anal. Calcd: C, 53.56; H, 9.93. Found: C, 49.01, 49.08; H, 9.29, 9.26.

Preparation of $[Cp^*(C_2B_9H_{11})ScH]Li(THF)_3$. Method A. A 60-mL glass bomb was charged with $[Cp^*(C_2B_9H_{11})Sc(CH(SiMe_3)_2)]Li(THF)_3$ and toluene (ca. 20 mL). The vessel was cooled to −196 °C, placed under 1 atm of H_2, warmed to room temperature, and stirred for 7 days. Removal of volatiles yields crude $[Cp^*(C_2B_9H_{11})ScH]Li(THF)_3$ essentially quantitatively,

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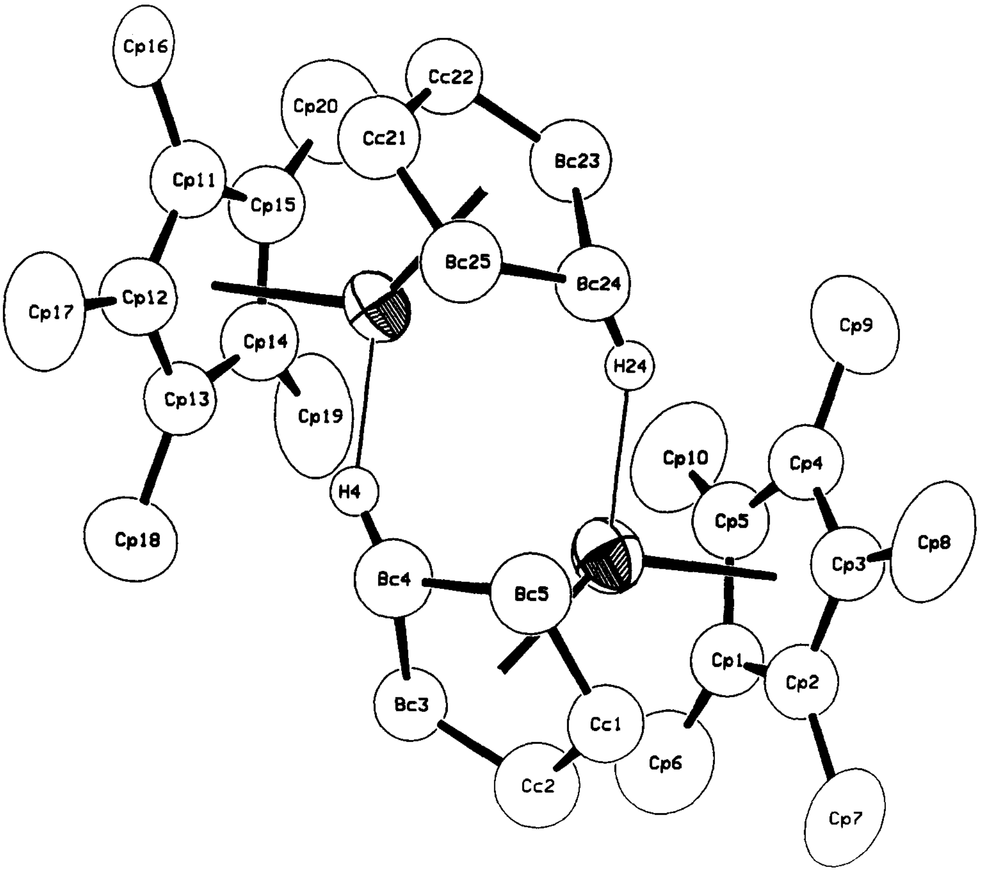

Figure 2. ORTEP drawing of the scandium core of [Cp*($C_2B_9H_{11}$)ScH]$_2^{2-}$. Only the pentagonal face of the dicarbollide ligand bound η^5 to one scandium and having the dative B–H interaction with the other is shown; atoms are drawn with 65% probability ellipsoids with the two hydrogen atoms having arbitrary, small parameters.

which can be purified by crystallization from a toluene/petroleum ether solution at –30 °C. ^{1}H NMR (300 MHz, benzene-d_6): δ –OCH_2CH_2–, 1.78 (b, 12H); [$C_5(CH_3)_5$], 1.98 (s, 15H); BC*H*, 2.31 (b, 1H); BC*H*, 2.78 (b, 1H); –OCH_2CH_2–, 3.25 (b, 12H); Sc–*H*, 5.23 (b, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, benzene-d_6): δ [$C_5(CH_3)_5$], 11.21; –OCH_2CH_2–, 23.3; BCH, 45.09; BCH, 47.3; –OCH_2CH_2–, 68.3; [$C_5(CH_3)_5$], 129.4. The resonances in the ^{11}B NMR spectrum were too broad to be identified. Anal. Calcd: C, 53.70; H, 9.58. Found: C, 49.97, 50.21; H, 8.83, 8.92.

Method B. A 1.6 M solution of *n*-BuLi in hexanes (1.2 mL) was syringed into a solution of Cp*($C_2B_9H_{11}$)Sc(THF)$_3$ (1.0 g, 1.9 mmol) in toluene at –30 °C, allowed to warm, and stirred an additional 2 h. The toluene was removed in vacuo, the residue was suspended in petroleum ether, and the product was obtained by filtration. The yield from this reaction was quite variable (in part because of the small amount of alkyllithium required) but was usually about 30%.

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Supplementary Material Available: Textual presentation of experimental data, an ORTEP diagram, and tables of nonrefined atomic positional parameters, anisotropic displacement factors, and distances and angles (18 pages). Ordering information is given on any current masthead page.

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