Cationic Actinide Metallocene Alkyls and Hydrides. Metal Bis(dicarbollides) as Counterions

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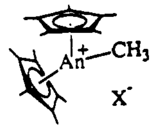
Received May 10, 1993[⊛]

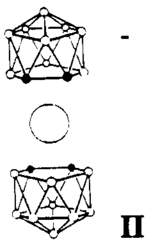
Summary: Metal bis(dicarbollides) of the type $M(B_9C_2H_{11})_2^-$ *(M = Co, Fe) have been incorporated into cationic organothorium complexes* $[Cp'_2ThR]^+X^-$ *(Cp′ =* η^5*-*$(CH_3)_5C_5$*; R = alkyl, H) as potential weakly coordinating anions. The reaction of* $Cp'_2Th(CH_3)_2$ *with* $[HNEt_3]^+[Co(B_9C_2H_{11})_2]^-$ *and* $[HNEt_3]^+[Fe(B_9C_2H_{11})_2]^-$ *in hydrocarbon solvents affords* $[Cp'_2ThCH_3]^+[Co(B_9C_2H_{11})_2]^-$ *(1) and* $[Cp'_2ThCH_3]_2^{2+}[Fe(B_9C_2H_{11})_2]^{2-}$ *(2), respectively. The structure of 2 reveals tight ion-pairing with three close Th···H–B bridging interactions (2.42(3), 2.50(3), 2.67(4) Å). This level of Th coordinative saturation explains the unexpected chemical inertness of 1 and 2. The reaction of* $Cp'_2Th[CH_2Si(CH_3)_3]_2$ *with* $[HNEt_3]^+[Co(B_9C_2H_{11})_2]^-$ *affords* $[Cp'_2ThCH_2Si(CH_3)_3]^+[Co(B_9C_2H_{11})_2]^-$ *(3), which slowly undergoes hydrogenolysis to yield* $[Cp'_2ThH]^+[Co(B_9C_2H_{11})_2]^-$ *(4).*

Table I. Summary of the Crystal Structure Data for $[Cp'_2ThMe]_2^{2+}[Fe(B_9C_2H_{11})_2]^{2-}$ **(2)**

formula	$(Th_2FeC_{46}H_{70}B_{18})\cdot C_6H_6$
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	9.225(2)
b, Å	9.831(3)
c, Å	17.414(3)
α, deg	81.75(2)
β, deg	87.85(2)
γ, deg	73.74(2)
V, Å^3	1508(1)
Z	2
d(calc), g/cm^3	1.598
cryst size, mm	0.34 × 0.27 × 0.22
color, habit	purple, transparent
diffractometer	Enraf-Nonius, CAD4
μ, cm^{-1}	50.83
transm factors range	0.84–1.38 (empirical)
radiation (λ, Å)	graphite monochromator; Mo Kα (0.710 69)
scan type	$\theta/2\theta$
2θ range, deg	4–55 ($\pm h, \pm k, \pm l$)
intensities (unique, R_i)	5651 (5291, 0.013)
intensities $>3\sigma(I)$	4937
no. of params	507
R	0.017
R_w for $w = 1/\sigma^2(F_o) + \rho F_o^2$	0.024
max density in ΔF map, e/Å^3	0.821
temp, °C	−120



I



II

Cationic group 4 metallocene alkyls and hydrides form the basis for several broad families of highly efficient olefin polymerization catalysts.[1,2] Surface spectroscopic and chemical evidence likewise indicates that cationic actinide metallocenes (e.g., **I**) play a major role in organoactinide heterogeneous and homogeneous olefin polymerization catalysis.[1a,3] As this field has developed, it has become apparent that the ion-pairing in species such as **I** can be very tight in low dielectric media[1,2,4] and that the reactivity of the cation may be strongly modulated by the weakly coordinating/sterically encumbering characteristics of the X^- counterion. An ideal weakly coordinating counterion[5] should be dimensionally large, charge-delocalized, and sheathed in nonpolar, electron-withdrawing substituents. In this contribution, we describe the properties of metal bis(dicarbollides) (**II**) as thorium metallocene counterions.[6,7] The characteristics of these large anions include a high degree of electron deficiency which should be further tunable via the encapsulated trivalent transition metal ion (e.g., the Fe(III) complex is moderately oxidizing[8]). It

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[⊛] Abstract published in *Advance ACS Abstracts*, September 15, 1993.

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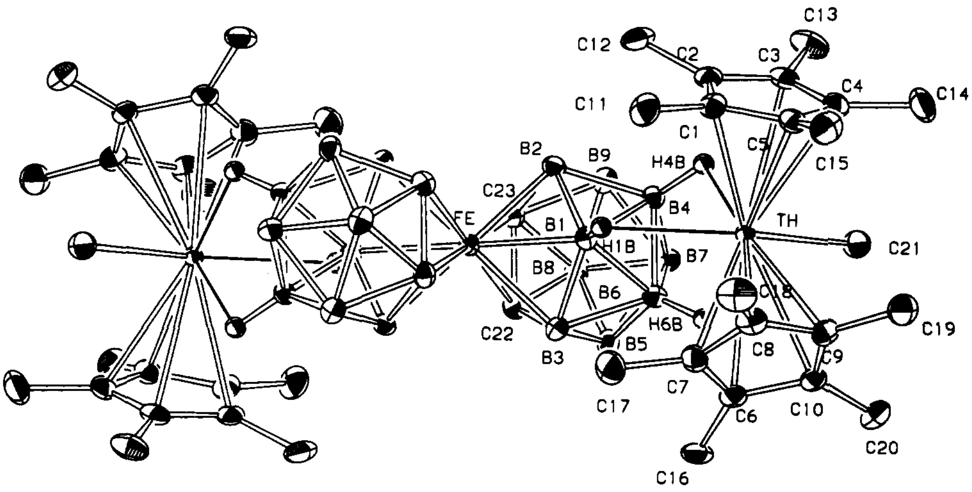

Figure 1. Perspective ORTEP drawing of the molecular structure of $[Cp'_2ThCH_3]_2^{2+}[Fe(B_9C_2H_{11})_2]^{2-}$ (**2**). The Fe atom lies on a center of inversion; therefore only half of the atoms are labeled. Ellipsoids are drawn at the 35% probability level.

will be seen that the properties of the resulting cationic complexes stand in sharp contrast to those of other weakly coordinating anions (e.g., $X^- = B(C_6F_5)_4^-$).

Experimental Section

All reactions were carried out under strictly anaerobic conditions. Solvents were purified by distillation from Na/K alloy and were stored in resealable flasks under vacuum in the presence of excess Na/K alloy. $Cp'_2Th(CH_3)_2$,[9] $Cp'_2Th[(CH_2Si(CH_3)_3]_2$,[9] and $Na^+[M(B_9C_2H_{11})_2]^-$ [8] were synthesized according to literature procedures. $[HNEt_3]^+[M(B_9C_2H_{11})_2]^-$ reagents were obtained by reacting the corresponding $Na^+[M(B_9C_2H_{11})_2]^-$ complexes with $[HNEt_3]^+Cl^-$ in water, followed by recrystallization from acetone/water. Elemental analyses were by Oneida Research Services.

$[HNEt_3]^+[Fe(B_9C_2H_{11})_2]^-$. ^1H NMR (acetone-d_6, 25 °C): δ 3.26 (q, $^3J_{H-H}$ = 6.8 Hz, 6H, CH_2), 2.82 (br, s, 4H, anion C–H), 1.22 (t, $^3J_{H-H}$ = 6.8 Hz, 9H, CH_3). Anal. Calcd for $C_{10}H_{38}B_{18}FeN$: C, 28.41; H, 9.06; N, 3.31. Found: C, 27.63; H, 8.90; N, 3.09.

$[HNEt_3]^+[Co(B_9C_2H_{11})_2]^-$. ^1H NMR: (acetone-d_6, 25 °C) δ 3.10 (br, s, 4H, anion C–H), 1.88 (q, $^3J_{H-H}$ = 7.1 Hz, 6H, CH_2), 0.38 (t, $^3J_{H-H}$ = 7.1 Hz, 9H, CH_3); (C_6D_6, 25 °C) δ 3.04 (br, s, 4H), 1.78 (m, 6H), 0.30 (t, $^3J_{H-H}$ = 7.2 Hz, 9H). Anal. Calcd for $C_{10}H_{38}B_{18}CoN$: C, 28.20; H, 8.99; N, 3.29. Found: C, 27.67; H, 8.91; N, 3.09.

$[Cp'_2ThCH_3]^+[Co(B_9C_2H_{11})_2]^-$ (1). $Cp'_2Th(CH_3)_2$ (0.196 g, 0.368 mmol) and $[HNEt_3]^+[Co(B_9C_2H_{11})_2]^-$ (0.149 g, 0.351 mmol) were loaded into a 50-mL reaction flask in the glovebox. Toluene (15 mL) was condensed onto the solids under vacuum at −78 °C. The mixture was then warmed to room temperature and stirred for 10 h. The solvent volume was reduced to about 5 mL, and the yellow solid was collected by filtration. It was then washed with a small amount of toluene and dried under vacuum. Yield: 70%.

^1H NMR (C_6D_6, 25 °C): δ 2.80 (br, s, 4H, anion C–H), 1.93 (s, 30H, Cp′–CH_3), 0.48 (s, 3H, Th–CH_3). ^{13}C NMR (C_6D_6, 25 °C): δ 61.56 (q, $^1J_{C-H}$ = 115.5 Hz, Th–CH_3), 53.53 (d, $^1J_{C-H}$ = 177.6 Hz, C–B), 11.77 (q, $^1J_{C-H}$ = 126.8 Hz, Cp′–CH_3). Anal. Calcd for $C_{25}H_{55}B_{18}CoTh$: C, 35.69; H, 6.89. Found: C, 35.81; H, 6.55.

$[Cp'_2ThCH_3]_2^{2+}[Fe(B_9C_2H_{11})_2]^{2-}$ (2). A 50-mL flask was charged with $Cp'_2Th(CH_3)_2$ (0.305 g, 0.573 mmol) and $[HNEt_3]^+$-$[Fe(B_9C_2H_{11})_2]^-$ (0.109 g, 0.258 mmol) in the glovebox. Then toluene and benzene (10 mL each) were condensed onto the above solids, and the mixture was stirred at room temperature for 2 days, during which time the solution turned from brown to purple. The solvent volume was reduced to 10 mL, and then 15 mL of pentane was added. The purple solid which precipitated was collected by filtration, washed twice with pentane, and dried under vacuum. Yield: 80%.

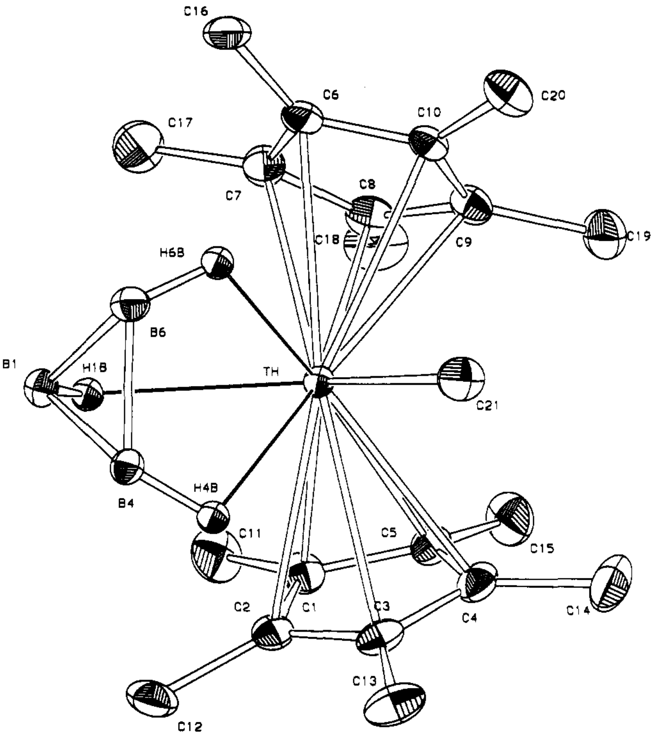

Figure 2. Close-up view of the Th cation–dicarbollide dianion coordination geometry in **2**.

^1H NMR (C_6D_6, 25 °C): δ 3.85 (br, s, 4H, anion C–H), 2.05 (s, 60H, Cp′–CH_3), 0.49 (s, 6H, Th–CH_3). $^{13}C\{^1H\}$ (C_6D_6, 25 °C): δ 59.16 (s, Th–CH_3), 12.46 (s, Cp′–CH_3). Anal. Calcd for $C_{46}H_{88}B_{18}Th_2Fe$: C, 40.75; H, 6.54. Found: C, 40.79; H, 6.30.

$[Cp'_2ThCH_2Si(CH_3)_3]^+[Co(B_9C_2H_{11})_2]^-$ (3). A 50-mL flask was charged with $Cp'_2Th[(CH_2Si(CH_3)_3)]_2$ (0.162 g, 0.239 mmol) and $[HNEt_3]^+[Co(B_9C_2H_{11})_2]^-$ (0.100 g, 0.235 mmol) in the glovebox. Toluene (15 mL) was transferred into the above flask, and the mixture was heated to 50 °C and stirred for 2 days. The solvent was next reduced to about 5 mL, and 10 mL of pentane was added. The resulting yellow solid was collected by filtration and dried under vacuum. Yield: 70%. Further purification by diffusing pentane into a toluene solution of this solid afforded yellow needlelike crystals. However, despite prolonged (more that 36 h) drying under high vacuum, the compound invariably

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Table II. Positional Parameters for the Atoms of $[Cp'_2ThMe]_2^{2+}[Fe(B_9C_2H_{11})_2]^{2-}$ (2)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Th	0.90441(1)	0.34178(1)	0.239717(5)	H(5B)	0.379(4)	0.149(4)	0.438(2)
Fe	0.0000	0	0.5000	H(6B)	0.128(4)	0.282(4)	0.319(2)
C(1)	0.6382(3)	0.2812(3)	0.2093(2)	H(7B)	0.372(3)	0.027(3)	0.287(2)
C(2)	0.7480(3)	0.1494(3)	0.2044(2)	H(8B)	0.451(4)	−0.158(4)	0.438(2)
C(3)	0.8356(3)	0.1677(3)	0.1378(2)	H(9B)	0.253(4)	−0.213(4)	0.331(2)
C(4)	0.7788(3)	0.3101(3)	0.1003(2)	H(22)	0.268(3)	−0.030(3)	0.539(2)
C(5)	0.6545(3)	0.3789(3)	0.1436(2)	H(23)	0.205(3)	−0.219(4)	0.477(2)
C(6)	0.9755(4)	0.5506(3)	0.3192(2)	H(111)	0.445(6)	0.275(6)	0.257(3)
C(7)	0.8230(4)	0.5568(3)	0.3355(2)	H(112)	0.471(6)	0.402(6)	0.283(3)
C(8)	0.7403(3)	0.6148(3)	0.2658(2)	H(113)	0.543(5)	0.261(6)	0.321(3)
C(9)	0.8424(3)	0.6388(3)	0.2058(2)	H(121)	0.726(4)	0.023(4)	0.310(2)
C(10)	0.9876(3)	0.5990(3)	0.2393(2)	H(122)	0.845(5)	−0.057(5)	0.250(3)
C(11)	0.5161(4)	0.3044(4)	0.2696(2)	H(123)	0.678(6)	−0.034(5)	0.236(3)
C(12)	0.7498(4)	0.0096(4)	0.2532(2)	H(131)	0.913(4)	0.007(4)	0.070(2)
C(13)	0.9536(4)	0.0530(4)	0.1041(2)	H(132)	0.000(4)	−0.016(4)	0.141(2)
C(14)	0.8255(5)	0.3685(5)	0.0219(2)	H(133)	0.043(6)	0.085(5)	0.076(3)
C(15)	0.5356(4)	0.5126(4)	0.1125(2)	H(141)	0.928(6)	0.335(5)	0.011(3)
C(16)	0.0970(4)	0.5239(3)	0.3788(2)	H(142)	0.764(5)	0.347(5)	−0.020(3)
C(17)	0.7560(5)	0.5310(4)	0.4142(2)	H(143)	0.797(6)	0.474(6)	0.008(3)
C(18)	0.5722(4)	0.6763(4)	0.2639(2)	H(151)	0.469(5)	0.556(5)	0.152(3)
C(19)	0.8068(5)	0.7106(4)	0.1239(2)	H(152)	0.570(6)	0.583(6)	0.080(3)
C(20)	0.1263(4)	0.6273(4)	0.2005(2)	H(153)	0.470(6)	0.495(5)	0.078(3)
C(21)	0.1173(4)	0.3267(4)	0.1479(2)	H(161)	0.100(5)	0.616(5)	0.397(2)
C(22)	0.2221(3)	−0.0068(3)	0.4886(2)	H(162)	0.211(6)	0.489(5)	0.355(3)
C(23)	0.1778(3)	−0.1309(3)	0.4509(2)	H(163)	0.085(5)	0.466(5)	0.421(3)
C(24)	0.5248(8)	0.0967(6)	0.0423(5)	H(171)	0.665(5)	0.504(5)	0.412(3)
C(25)	0.5975(7)	0.0780(7)	−0.0268(6)	H(172)	0.818(6)	0.467(6)	0.444(3)
C(26)	0.4267(7)	0.0179(8)	0.0711(4)	H(173)	0.723(4)	0.617(5)	0.438(2)
B(1)	0.9851(3)	0.1245(3)	0.3887(2)	H(181)	0.528(3)	0.714(3)	0.207(2)
B(2)	0.0293(4)	−0.0639(3)	0.3897(2)	H(182)	0.518(4)	0.603(4)	0.276(2)
B(3)	0.1069(4)	0.1573(3)	0.4565(2)	H(183)	0.545(5)	0.744(5)	0.292(3)
B(4)	0.0989(3)	0.0438(3)	0.3133(2)	H(191)	0.866(8)	0.796(8)	0.113(4)
B(5)	0.2969(4)	0.0979(4)	0.4205(2)	H(192)	0.719(7)	0.730(6)	0.117(3)
B(6)	0.1480(4)	0.1784(3)	0.3545(2)	H(193)	0.854(6)	0.661(6)	0.089(3)
B(7)	0.2915(4)	0.0273(3)	0.3321(2)	H(201)	0.114(5)	0.630(5)	0.143(3)
B(8)	0.3422(4)	−0.0889(4)	0.4196(2)	H(202)	0.217(6)	0.560(5)	0.220(3)
B(9)	0.2192(4)	−0.1225(3)	0.3541(2)	H(203)	0.127(6)	0.726(6)	0.204(3)
H(1B)	0.873(4)	0.202(3)	0.368(2)	H(211)	0.202(5)	0.337(5)	0.175(3)
H(2B)	0.957(4)	−0.132(4)	0.377(2)	H(212)	0.139(5)	0.236(5)	0.137(3)
H(3B)	0.086(4)	0.248(4)	0.492(2)	H(213)	0.101(6)	0.399(6)	0.109(4)
H(4B)	0.062(4)	0.067(4)	0.253(2)				

contains small quantities (~0.02–0.05 equiv by ^{1}H NMR) of toluene (presumably incorporated in the crystal structure) which results in slightly high C, H analyses.

^{1}H NMR (toluene-d_8, 25 °C): δ 2.84 (br, s, 4H, anion C–*H*), 2.01 (s, 30H, Cp′–C*H*$_3$), 0.33 (s, 9H, Si(C*H*$_3$)$_3$), 0.29 (s, 2H, C*H*$_2$). Anal. Calcd for $C_{28}H_{63}B_{18}SiThCo$: C, 36.82; H, 6.95. Found: C, 37.80; H, 6.81.

$[Cp'_2ThH]^+[Co(B_9C_2H_{11})_2]^-$ (4). A solution of **3** (0.220 g, 0.241 mmol) in toluene (10 mL) was exposed to 1 atm of H_2. A yellow solid began to precipitate after the solution was stirred at room temperature for 20 min. The mixture was then stirred for an additional 10 h and filtered. The yellow solid product was washed twice with a small amount of toluene and dried under vacuum. Yield: 40%. This solid contains ca. 10–15% of an unidentified thorium-containing species as revealed by ^{1}H NMR spectroscopy (δ 1.89–1.91). The low solubility of **4** has hampered further purification.

^{1}H NMR (C_6D_6, 25 °C): δ 2.06 (s, 30H, Cp′–C*H*$_3$), 2.80 (s, 4H, anion C–*H*), 19.04 (s, 1H, Th–*H*). Anal. Calcd for $C_{24}H_{53}B_{18}CoTh$: C, 34.85; H, 4.46. Found: C, 35.81; H, 6.28.

X-ray Crystallographic Study of 2. Purple, transparent crystals suitable for X-ray diffraction study were grown from a benzene solution over a period of 1 day from a mixture of $Cp'_2Th(CH_3)_2$ and $[HNEt_3]^+[Fe(B_9C_2H_{11})_2]^-$ (with $Cp'_2Th(CH_3)_2$ in excess) at room temperature. They were sealed in glass capillaries under an inert atmosphere (N_2) in the glovebox and then mounted on the diffractometer. Intensity data were collected at −120 °C. The structure was solved by direct methods (SHELXS). The correct thorium and iron positions were deduced from an electron density map. Subsequent least-squares difference Fourier calculations revealed atomic positions for the remaining atoms. In the final cycle of least squares, the non-hydrogen atoms were refined with anisotropic thermal coefficients, while the hydrogen atoms were refined with common isotropic thermal parameters. Crystallographic details are compiled in Table I.

Results and Discussion

Reaction of Cp'_2ThR_2 compounds ($Cp' = \eta^5$-$(CH_3)_5C_5$) with the triethylammonium salts[10] of the bis(dicarbollide) anions in hydrocarbon solvents affords cationic thorium alkyl complexes in high yields (eqs 1 and 2). These new

$$Cp'_2ThR_2 + [HNEt_3]^+[Co(B_9C_2H_{11})_2]^- \xrightarrow{\text{toluene}} \underset{\substack{1,\ R\,=\,CH_3 \\ 3,\ R\,=\,CH_2Si(CH_3)_3}}{[Cp'_2ThR]^+[Co(B_9C_2H_{11})_2]^-} + NEt_3 + H\text{–}R \quad (1)$$

$$2Cp'_2Th(CH_3)_2 + HNEt_3{}^+[Fe(B_9C_2H_{11})_2]^- \xrightarrow{\text{toluene or benzene}} \underset{\mathbf{2}}{[Cp'_2ThCH_3]_2{}^{2+}[Fe(B_9C_2H_{11})_2]^{2-}} + NEt_3 + CH_4 + {}^1/{}_2C_2H_6 \quad (2)$$

complexes were characterized by standard analytical and spectroscopic techniques. While the course of the cobalt

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[10] (a) Lin, Z.; LeMarechal, J. F.; Marks, T. J. *Abstracts of Papers*, 193rd National Meeting of the American Chemical Society, Denver, CO, 1987; American Chemical Society: Washington, DC, 1987; INOR314. (b) Lin, Z.; Marechal, J.-F.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 4127–4129.

Table III. Selected Bond Distances (Å) and Angles (deg) for $[Cp'_2ThMe]_2^{2+}[Fe(B_9C_2H_{11})_2]^{2-}$ (2)

	Bond Lengths		
Th–C1	2.782(3)	Th–C2	2.828(3)
Th–C3	2.838(3)	Th–C4	2.824(3)
Th–C5	2.820(3)	Th–C6	2.865(3)
Th–C7	2.800(3)	Th–C8	2.782(3)
Th–C9	2.792(3)	Th–C10	2.842(3)
C1–C2	1.418(4)	C1–C5	1.417(4)
C2–C3	1.411(5)	C3–C4	1.418(5)
C4–C5	1.414(4)	C1–C11	1.507(5)
C2–C12	1.504(5)	C3–C13	1.505(5)
C4–C14	1.501(5)	C5–C15	1.505(4)
C6–C7	1.419(5)	C6–C10	1.415(4)
C7–C8	1.418(5)	C8–C9	1.423(5)
C9–C10	1.416(4)	C6–C16	1.503(4)
C7–C17	1.502(5)	C8–C18	1.506(4)
C9–C19	1.502(5)	C10–C20	1.507(4)
Th–C21	2.479(3)	C21–H21a	0.97(5)
C21–H21b	0.90(5)	C21–H21c	0.89(6)
Th–H6B	2.42(3)	Th–H1B	2.50(3)
Th–H4B	2.67(4)	Th–B6	3.011(3)
Th–B1	3.086(3)	Th–B4	3.101(3)
F3–C22	2.046(3)	Fe–C23	2.032(3)
Fe–B1	2.125(3)	Fe–B2	2.091(3)
Fe–B3	2.101(3)	B1–B3	1.785(5)
B1–B4	1.788(4)	B1–B6	1.791(5)
B2–B4	1.795(5)	B2–B9	1.809(5)
B3–B6	1.799(5)	B3–B5	1.813(5)
B4–B6	1.763(5)	B4–B7	1.786(4)
B4–B9	1.768(4)	B5–B8	1.768(5)
B5–B6	1.761(5)	B5–B7	1.785(5)
B6–B7	1.775(4)	B7–B8	1.761(5)
B7–B9	1.771(5)	B8–B9	1.768(5)
C22–B3	1.696(4)	C22–B5	1.713(4)
C22–B8	1.736(4)	C23–B2	1.693(4)
C23–B9	1.710(4)	C23–B8	1.737(4)
C24–C25	1.37(1)	B1–B2	1.780(5)
C24–C26	1.39(1)	C25–C26	1.37(1)
C22–C23	1.620(4)	C22–H22	0.967
C23–H23	0.89(3)	B1–H1B	1.14(3)
B2–H2B	1.12(3)	B3–H3B	1.13(4)
B4–H4B	1.09(4)	B5–H5B	1.10(3)
B6–H6B	1.10(8)	B7–H7B	1.06(3)
B8–H8B	1.07(4)	B9–H9B	1.00(4)
	Angles		
C2–C1–C5	107.9(3)	C2–C1–C11	124.7(3)
C5–C1–C11	127.1(3)	C1–C2–C12	124.9(3)
C3–C2–C1	107.9(3)	C3–C2–C12	126.3(3)
C2–C3–C4	108.2(3)	C2–C3–C13	126.8(3)
C4–C3–C13	124.4(3)	C5–C4–C3	107.8(3)
C5–C4–C14	125.8(3)	C3–C4–C14	125.6(3)
C4–C5–C1	108.1(3)	C4–C5–C15	124.4(3)
C1–C5–C15	125.1(3)	C10–C6–C7	108.2(3)
C10–C6–C16	125.4(3)	C7–C6–C16	125.5(3)
C6–C7–C8	107.5(3)	C6–C7–C17	126.4(3)
C8–C7–C17	125.3(3)	C7–C8–C9	108.4(3)
C7–C8–C18	123.1(3)	C9–C8–C18	126.5(3)
C10–C9–C8	107.4(3)	C10–C9–C19	124.0(3)
C8–C9–C19	128.1(3)	C6–C10–C9	108.4(3)
C6–C10–C20	125.0(3)	C9–C10–C20	125.8(3)
H6B–Th–C21	74.0(8)	H6B–Th–H1B	68(1)
H6B–Th–H4B	66(1)	C21–Th–H1B	133.0(7)
C21–Th–H4B	73.4(8)	H1B–Th–H4B	66(1)

dicarbollide chemistry is via straightforward protonolysis[9,10] of the Th–C bonds (eq 1), that of the iron dicarbollide is more complex (eq 2). The reaction involves reduction of the high potential Fe(III) center ($E_{1/2}$ = −0.42 V for $Fe(B_9C_2H_{11})_2^-$ vs −1.42V for $Co(B_9C_2H_{11})_2^-$),[8] cleavage of $Th–CH_3$ bonds,[11] and ultimate coordination of two cationic thorium units per bis(dicarbollide) dianion (eq 2).[12] The identity of product 2 was further elucidated by X-ray diffraction (*vide infra*). The formation of the byproducts NEt_3, CH_4, and C_2H_6 was confirmed by ^1H NMR spectroscopy, with the measured CH_4:C_2H_6 mole ratio of 1.0:0.6 close to the expected 1.0:0.5.

Crystal Structure of $[Cp'_2ThCH_3]_2^{2+}[Fe(C_2B_9H_{11})_2]^{2-}$ (2). The solid state structure of this diamagnetic complex is in complete agreement with the spectroscopic and analytical data (Figures 1 and 2). Atomic coordinates as well as important bond distances and angles are compiled in Tables II and III, respectively.

The cationic thorium center adopts a normal "bent-sandwich" geometry (Figure 1) with $Th–CH_3$ = 2.479(3) Å and $Th–C_{ring}$(av) = 2.817(3) Å. These parameters are similar to those in $[Cp'_2Th(CH_3)(THF)_2]^+BPh_4^-$ (2.49(1) and 2.80(1) Å, respectively)[10b] but significantly longer than the corresponding distances in $[Cp'_2ThCH_3]^+B(C_6F_5)_4^-$ (2.349(8) and 2.754(3) Å, respectively).[4b] From structural trends we have previously observed in both $[Cp'_2ThCH_3]^+X^-$ and $[L_2ZrCH_3]^+X^-$ (L = Cp or substituted Cp ligands)[4b,c] complexes, we interpret the contraction in $Th–CH_3$ and in $Th–C_{ring}$(av) as reflecting the degree of electron deficiency/coordinative unsaturation at the cationic center. Interestingly, $\delta(Th–^{13}CH_3)$, $\delta(Zr–^{13}CH_3)$, and chemical reactivity (hydrogenolysis and olefin insertion—*vide infra*) also correlate qualitatively with these trends.[4b]

The high quality of the diffraction data also allow location of all the hydrogen atoms in the crystal structure of 2. Metal–hydride distances should of course be interpreted with the usual caveats for X-ray data.[13] It can be seen that each thorium center is coordinated to three B–H units, with Th···H–B distances ranging from 2.42(3) to 2.67(4) Å. Correcting for differences in Th^{4+} and Zr^{4+} ionic radii (0.94 vs 0.72 Å),[14] shortest Th···H contact is nearly identical to the Zr···H–B distance reported for $[(EtMe_4C_5)_2ZrCH_3]^+[B_9C_2H_{12}]^-$ (Zr–H = 2.12(4) Å).[2k] The present Th···H distances can be compared to terminal and bridging Th···H distances of 2.27(6) and 2.73(1) Å, respectively, in $[Th(H_3BCH_3)_4{\cdot}THF]_2$[15] and 2.03(1) and 2.29(3) Å, respectively, in the neutron diffraction structure of $Cp'_2(H)Th(\mu\text{-}H)_2Th(H)Cp'_2$.[16] The present B–H···Th distances are statistically indistinguishable from the other B–H distances in 2. Interestingly, the location of the three coordinating B–H groups in 2 involves that portion of the carborane cage which is believed to be most nucleophilic/electron-rich.[17]

In terms of chemical reactivity, bis(dicarbollide) methyl cations 1 and 2 display surprising inertness. Thus, while hydrogenolysis is rapid for cationic complexes of structure I, X^- = BPh_4^-, $B(C_6F_5)_4^-$,[4b] and measurable for neutral complexes of the type $Cp'_2Th(CH_3)_2$, $Cp'_2Th(CH_3)$(halide), and $Cp'_2Th(CH_3)OR$,[18] no reaction is detected between 1 or 2 and H_2 (1 atm) over a period of many days at 25 °C. Not surprisingly, 1 and 2 also fail to undergo reaction with

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(11) For analogous Ag^+-induced cleavage processes, see: (a) Hitchcock, P. B.; Lappert, M. F.; Taylor, R. G. *J. Chem. Soc., Chem. Commun.* **1984**, 1082–1083. (b) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111–4113.

(12) When Cp'_2ThMe_2 is reacted with $[HNEt_3]^+[Fe(C_9C_2H_{11})_2]^-$ in a 1:1 molar ratio, ^1H NMR suggests that the compound $[Cp'_2Th]^{2+}[Fe(B_9C_2H_{11})_2]^{2-}$ is formed (C_6D_6, RT): δ 2.80 (s, 4H, anion C–*H*), 2.00 (s, 30H, Cp′–CH_3).

(13) (a) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263–293. (b) Teller, R. G.; Bau, R. *Struct. Bonding* **1981**, *44*, 1–82.

(14) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751–767.

(15) DeBoer, B. G.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1968**, *7*, 2288.

(16) Broach, R.; Schulz, A. J.; Williams, J. M.; Brown, G. M.; Manriquez, H. M.; Fagan, T. J.; Marks, T. J. *Science* **1979**, *203*, 172–174.

(17) (a) Grimes, R. N. *Carboranes*, Academic Press: New York, 1970; Chapters 6, 7. (b) Goursot, A.; Penigault, E.; Chermette, H.; Fripiat, J. G. *Can. J. Chem.* **1986**, *64*, 1752–1757.

(18) Lin, Z.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 7979–7985.

ethylene under conditions in which the BPh^-_4 and $B(C_6F_5)^-_4$ complexes undergo ~0.011 and 36 insertions s^{-1}, respectively (25 °C, 1 atm of pressure).[4b] The reasons appear to be a combination of electronic and steric factors involving both an increase in charge density donated to the thorium center as well as the steric bulk of what appears to be a relatively immobile anion. Possible confirmation of the latter situation is provided by hydrogenolysis involving a more sterically demanding hydrocarbyl group (eq 3). Here hydrogenolysis is complete within several

$$[Cp'_2ThCH_2Si(CH_3)_3]^+[Co(B_9C_2H_{11})_2]^- + H_2 \rightarrow [Cp'_2ThH]^+\underset{\mathbf{4}}{[Co(B_9C_2H_{11})_2]^-} + Si(CH_3)_4 \quad (3)$$

hours at room temperature. The formation of a Th–H linkage is confirmed by the characteristic[9,17] ^1H resonance at δ 19.04; however the exact structure of **4** awaits further elucidation.

The present results show that the nature of the ion-pairing in structures **I** reflects a subtle interplay of steric and electronic factors and that highly electron-deficient counterions can interact rather strongly with the hard, electrophilic metal centers. These interactions can have profound consequences for reactivity. Recent results from Hlatky, Eckman, and Turner on $[Cp_2Zr(CH_3)]^+[M(B_9C_2H_{11})_2]^-$ (M = Fe, Co, Ni)[7a] complexes suggest similar types of cation–anion interactions, although they appear to be somewhat weaker than those in **1** and **2**, perhaps a consequence of the more constricted zirconium coordination sphere.

Acknowledgment. This research was supported by the U.S. Department of Energy (Grant DE-FG02-86ER13511). X.Y. thanks Akzo Chemicals for a postdoctoral fellowship.

Supplementary Material Available: X-ray experimental details including tables of positional and anisotropic displacement parameters (4 pages). Ordering information is given on any current masthead page.

OM930308H