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Synthesis of $[Li(THF)_4]_2[Th(\eta^5\text{-}C_2B_9H_{11})_2X_2]$ (X = Cl, Br, I): The First Dicarbollide Complexes of Thorium

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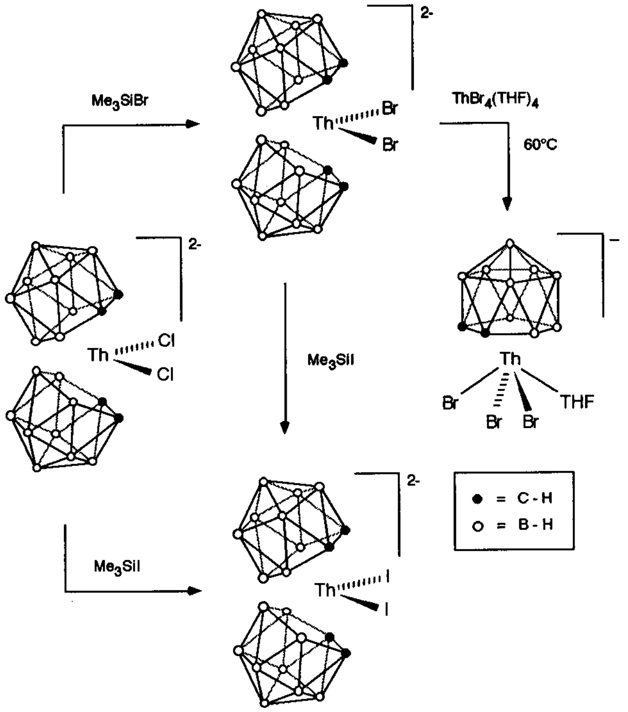
The first thorium complexes incorporating dicarbollide ligands, $[Li(THF)_4]_2[Th(\eta^5\text{-}C_2B_9H_{11})_2X_2]$ (X = Cl, Br, I) and $[Li(THF)_4][Th(\eta^5\text{-}C_2B_9H_{11})Br_3(THF)]$, have been prepared and characterized by a combination of spectroscopic and analytical techniques. The molecular structure of the dibromo derivative has been determined by single-crystal X-ray diffraction. $[Li(THF)_4]_2[Th(\eta^5\text{-}C_2B_9H_{11})_2Br_2]$ is monoclinic, *Cc* (No. 9), $a = 26.303$ (2) Å, $b = 11.143$ (2) Å, $c = 20.054$ (2) Å, $\beta = 103.263$ (7)°, $Z = 4$.

We reported recently the synthesis of a series of new anionic complexes of uranium containing dicarbollide ($\eta^5\text{-}C_2B_9H_{11}^{2-}$) ligands.[1,2] As an extension of these investigations, and not discouraged by an earlier report that no dicarbollide complexes were detected upon reacting $ThCl_4$ with $Na_2C_2B_9H_{11}$,[3] we set out to explore the synthesis of dicarbollide complexes of thorium. We have found that such complexes can indeed be prepared, and we describe herein the isolation and characterization of the first dicarbollide complexes of thorium.

A THF suspension of $ThCl_4$ or a THF solution of $ThCl_4(TMEDA)_2$,[4] reacted with 2 equiv of lithium dicarbollide ($Li_2C_2B_9H_{11}$)[5] to form the anionic bis(dicarbollide) complex $[Th(\eta^5\text{-}C_2B_9H_{11})_2Cl_2]^{2-}$ (eq 1), isolated by fractional crystallization in a moderate 39% yield as the lithium salt $[Li(THF)_4]_2[Th(\eta^5\text{-}C_2B_9H_{11})_2Cl_2]$.[6,7] Similarly, the dibromo complex $[Li(THF)_4]_2[Th(\eta^5\text{-}C_2B_9H_{11})_2Br_2]$[7] was isolated in 75% yield from the reaction of $ThBr_4(THF)_4$[8] and 2 equiv of $Li_2C_2B_9H_{11}$ in THF or, alternatively, by reacting the dichloro complex with Me_3SiBr. Likewise, the diiodo derivative $[Li(THF)_4]_2[Th(\eta^5\text{-}C_2B_9H_{11})_2I_2]$ was readily obtained by treating either the dichloro or the dibromo complex with a slight excess of trimethylsilyl iodide (Scheme 1).[7] The large difference in bond dissociation energies between the reagents Me_3SiX (X = Br, I) and the byproduct Me_3SiCl (≈36 kcal/mol)[9] is presumably the driving force for these reactions. It is also noteworthy that, despite trimethylsilyl reagents Me_3SiX (X = Br, I) having a variety of applications in organic synthesis,[10] their use for halide exchange reactions in coordination chemistry is virtually unexplored.[11]

$$ThCl_4 + 2Li_2C_2B_9H_{11} \xrightarrow[-2LiCl]{THF} [Li(THF)_4]_2[Th(\eta^5\text{-}C_2B_9H_{11})_2Cl_2] \quad (1)$$

Scheme 1. Synthesis of Thorium Dicarbollide Complexes



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(6) A suspension of $ThCl_4$ (0.28 g, 0.75 mmol) and $Li_2C_2B_9H_{11}$ (0.22 g, 1.50 mmol) in THF (20 mL) was stirred at room temperature for 3 h. The solution was then filtered and its volume reduced *in vacuo* to 10 mL. The concentrated solution was layered with pentane (*ca.* 1 mL) and cooled at −30 °C overnight to form a white microcrystalline solid, which was isolated by filtration and dried under vacuum for 10 min (0.34 g, 39%). ^{11}B NMR data for $[Li(THF)_4]_2[Th(\eta^5\text{-}C_2B_9H_{11})_2Cl_2]$ (in CD_3CN): δ 4.9 (d, $^1J_{B-H} = 103$ Hz, 2 B), −2.9 (d, $^1J_{B-H} = 103$ Hz, 4 B), −3.8 (d, $^1J_{B-H} = 132$ Hz, 4 B), −12.5 (d, $^1J_{B-H} = 151$ Hz, 6 B), −24.3 (d, $^1J_{B-H} = 137$ Hz, 2 B). Anal. Calcd for $C_{36}H_{86}B_{18}Cl_2Li_2O_8Th$: C, 37.3; H, 7.5. Found: C, 37.2; H, 7.4.

(7) All new compounds have been characterized spectroscopically and analytically (see Supporting Information).

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The lithium salts $[Li(THF)_4]_2[Th(\eta^5\text{-}C_2B_9H_{11})_2X_2]$ (X = Cl, Br, I) are white, diamagnetic, air- and moisture-sensitive compounds, moderately (X = Cl) or only slightly (X = Br, I) soluble in THF, but very soluble in acetonitrile. The tetrahalides $ThCl_4$ or $ThBr_4(THF)_4$ also react with the dicarbollide reagents $M_2C_2B_9H_{11}$ (M = Na, K) and $[(Ph_3P)_2N](TlC_2B_9H_{11})$ to form the same anionic bis(dicarbollide) complexes, as verified by $^{11}B\{^1H\}$ NMR spectroscopy, but isolation of these salts was not pursued.

Although no intermediates were observed by $^{11}B\{^1H\}$ NMR spectroscopy in the formation of $[Th(\eta^5\text{-}C_2B_9H_{11})_2Br_2]^{2-}$ from $ThBr_4(THF)_4$ and 2 equiv of $Li_2C_2B_9H_{11}$ at room temperature, a mono(dicarbollide) complex $[Li(THF)_4][Th(\eta^5\text{-}C_2B_9H_{11})Br_3(THF)]$[7] was obtained from the reaction (60 °C, 1 day) of equimolar amounts of $ThBr_4(THF)_4$ and $[Li(THF)_4]_2[Th(\eta^5\text{-}C_2B_9H_{11})_2Br_2]$ in THF (Scheme 1).[12] Interestingly, no such ligand redistribution reaction was observed for the analogous uranium system. Instead, significant decomposition of the uranium bis(dicarbollide) complex $[U(\eta^5\text{-}C_2B_9H_{11})_2Br_2]^{2-}$ to $C_2B_9H_{12}^-$ and other unidentified species occurred at temperatures above 60 °C.

The molecular structure of $[Li(THF)_4]_2[Th(\eta^5\text{-}C_2B_9H_{11})_2Br_2]$ was determined by single-crystal X-ray diffraction (Figure 1).[13] The anionic complex $[Th(\eta^5\text{-}C_2B_9H_{11})_2Br_2]^{2-}$ is isostructural with its uranium analogue[1] and displays a "bent-metallocene" structure, similar to those observed for other bis(dicarbollide) complexes.[3,14] More importantly, the centroid−Th−centroid angle in $[Th(\eta^5\text{-}C_2B_9H_{11})_2Br_2]^{2-}$ (142.4°) is larger than that in the bis(pentamethylcyclopentadienyl) analogue $Cp^*_2ThBr_2$ (137.1°),[15] implying that the dicarbollide ligand has a slightly larger cone angle than Cp*.[16] This observation may be a consequence of the relatively short Th−centroid distances in $[Th(\eta^5\text{-}C_2B_9H_{11})_2Br_2]^{2-}$ (average 2.39 Å, *versus* 2.51 Å in $Cp^*_2ThBr_2$), whereby the effective cone angle of the dicarbollide ligands is increased.[17] The Th−Br bond lengths in $[Th(\eta^5\text{-}C_2B_9H_{11})_2Br_2]^{2-}$ [2.863(1) Å and 2.874(1) Å] are similar to those reported for other complexes containing terminal Th−Br bonds,[8,18] and the rest of the interatomic distances also appear to be normal.

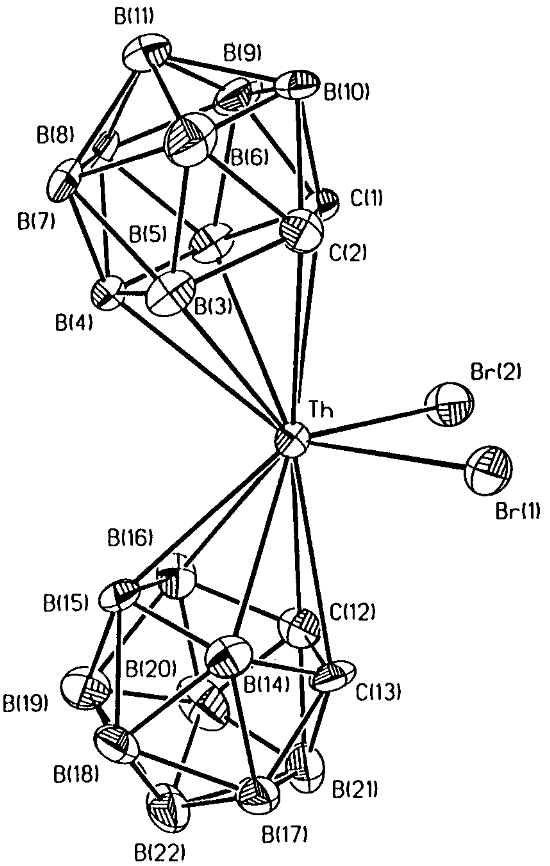

Figure 1. Molecular structure of $[Th(\eta^5\text{-}C_2B_9H_{11})_2Br_2]^{2-}$ (thermal ellipsoids at 35% probability level).

In summary, we have verified that $ThCl_4$ reacts with different alkali dicarbollide salts $M_2C_2B_9H_{11}$ (M = Li, Na, K) to form the bis(dicarbollide) complex $[Th(\eta^5\text{-}C_2B_9H_{11})_2Cl_2]^{2-}$. Together with the corresponding dibromo and diiodo analogues, and the mono(dicarbollide) species $[Th(\eta^5\text{-}C_2B_9H_{11})Br_3(THF)]^-$, these derivatives constitute the first dicarbollide complexes of thorium.

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Supporting Information Available: Table of spectroscopic and analytical data for all new compounds and tables of crystal data collection, atomic coordinates, bond lengths, bond angles, anisotropic displacement parameters, and hydrogen atom coordinates and ORTEP drawings for $[Li(THF)_4]_2[Th(\eta^5\text{-}C_2B_9H_{11})_2Br_2]$ (19 pages). Ordering information is given on any current masthead page.

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(12) A similar approach has been used to prepare mono(cyclooctatetraenyl) complexes of thorium. See: (a) Le Vanda, C.; Solar, J. P.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 2128−2129. (b) Gilbert, T. M.; Ryan, R. R.; Sattelberger, A. P. *Organometallics* **1988**, *7*, 2514−2518.

(13) Crystal data (at −90 °C): monoclinic space group *Cc* (No. 9), a = 26.303(2) Å, b = 11.143(2) Å, c = 20.054(2) Å, β = 103.263(7)°, d_{calcd} = 1.448 g/cm^3, Z = 4, $R1$= 0.0398, $R2_w$ = 0.0766.

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