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A New Class of Metallacarboranes: Synthesis and Molecular Structure of the First Example of an Organolanthanide Compound Bearing an η^7-Carboranyl Ligand

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*Summary: The first organolanthanide compound containing an η^7-carboranyl ligand, $[\{[\eta^5:\eta^7\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]Er\}_2\{Na_4(THF)_9\}]_n$ (**3**), has been achieved by treatment of $[\eta^5\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]ErCl_2(THF)_3$ (**1**) or $[\eta^5:\eta^6\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]Er(THF)_2$ (**2**) with excess Na metal in THF. The Na^+ ions in **3** can be replaced by Er^{3+} ions, giving the novel tetranuclear cluster $[\{\eta^5:\eta^7\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})\}Er_2(\mu\text{-}Cl)(THF)_3]_2$ (**4**).*

The chemistry of metallacarboranes has witnessed an explosive growth since the discovery of the first metallacarborane in 1965.[1,2] However, the highest hapticity of carboranyl ligands in all of known metallacarboranes described in the literature is 6; that is, the largest bonding face that a carboranyl ligand can offer is a hexagonal face.[2] We have very recently reported the unprecedented uranium compound $[\{(\eta^7\text{-}C_2B_{10}H_{12})(\eta^6\text{-}C_2B_{10}H_{12})U\}\{K_2(THF)_5\}]_2$, in which the U atom is η^7-bound to one of the $C_2B_{10}H_{12}$ ligands.[3] We report here a new class of metallacarboranes derived from the versatile ligand $Me_2C(C_5H_5)(C_2B_{10}H_{11})$.

Treatment of $ErCl_3$ with 1 equiv of $[Me_2C(C_5H_4)(C_2B_{10}H_{11})]Na$[4] in THF gave $[\eta^5\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]ErCl_2(THF)_3$ (**1**) as a pink crystalline solid in 52% yield.[5] Interaction between **1** and 2 equiv of Na metal in THF at room temperature afforded the mixed-sandwich compound $[\eta^5:\eta^6\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]Er(THF)_2$ (**2**) as pink crystals in 48% yield.[5] A single-crystal X-ray diffraction study of this compound[6] reveals a monomeric structure with a distorted-tetrahedral coordination geometry around the Er metal similar to that of $[\eta^5:\eta^6\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{11})]Sm(THF)_2$.[7]

Reaction of **2** with excess Na metal in THF at room temperature generated, after workup, the novel metal-

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[1] Hawthorne, M. F.; Young, D. C.; Wegner, P. A. *J. Am. Chem. Soc.* **1965**, *87*, 1818.

[2] For recent reviews, see: (a) Grimes, R. N. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 1, p 371. (b) Saxena, A. K.; Hosmane, N. S. *Chem. Rev.* **1993**, *93*, 1081. (c) Saxena, A. K.; Maguire, J. A.; Hosmane, N. S. *Chem. Rev.* **1997**, *97*, 2421.

[3] Xie, Z.; Yan, C.; Yang, Q.; Mak, T. C. W. *Angew. Chem., Int. Ed.* **1999**, *38*, 1761.

[4] Hong, E.; Kim, Y.; Do, Y. *Organometallics* **1998**, *17*, 2933.

[5] Complete synthetic procedures and compound characterization data are given in the Supporting Information.

[6] Crystal data for **2** ($C_{18}H_{37}B_{10}ErO_2$; fw 560.8): monoclinic, space group $P2_1/c$, $a = 14.272(3)$ Å, $b = 17.056(3)$ Å, $c = 9.853(2)$ Å, $\beta = 90.22(3)°$, $V = 2398.4(8)$ Å^3, $d_{calcd} = 1.553$ g/cm^3, $Z = 4$, R1 = 0.075 ($I > 2.0\sigma(I)$), wR2 = 0.203 on F^2.

[7] Xie, Z.; Wang, S.; Zhou, Z.; Mak, T. C. W. *Organometallics* **1998**, *17*, 1907.

[8] Reaction of $(\eta^6\text{-}C_2B_{10}H_{12})Co(\eta^5\text{-}C_5H_5)$ with Na/naphthalene, followed by treatment with C_5H_5Na and $CoCl_2$, gave the 14-vertex *closo*-metallacarborane $(\eta^6:\eta^6\text{-}C_2B_{10}H_{12})[Co(\eta^5\text{-}C_5H_5)]_2$. The proposed geometry of the cage is a bicapped hexagonal antiprism. X-ray confirmation of this species has not been reported: Evans, W. J.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 38.

10.1021/om990554e CCC: $15.00

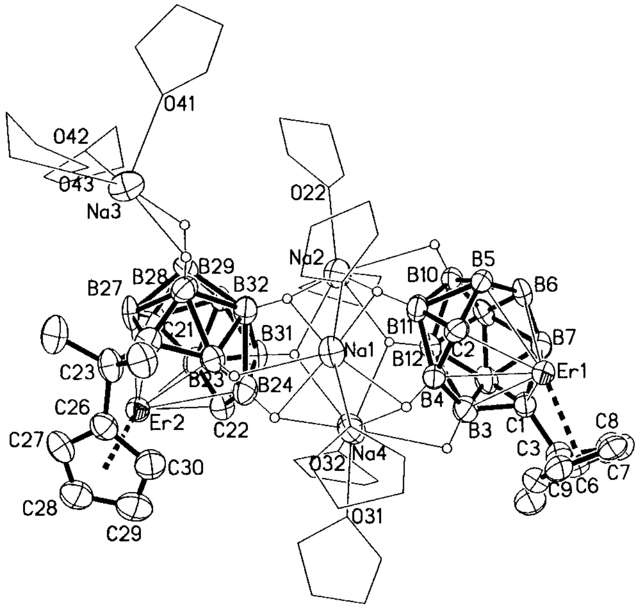

Figure 1. ORTEP illustration of **3** with thermal ellipsoids drawn at the 35% probability level, showing one asymmetrical unit of the infinite polymeric chain.

lacarborane $[\{[\eta^5{:}\eta^7\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Er}\}_2\{\text{Na}_4(\text{THF})_9\}]_n$ (**3**) as pink crystals in 76% yield.[5,8] Compound **3** is extremely air- and moisture-sensitive but remains stable for months at room temperature under an inert atmosphere. Traces of air immediately convert it to a white solid. **3** is soluble in THF, DME, and pyridine, sparingly soluble in toluene, and insoluble in hexane and decomposes in CH_2Cl_2.

The polymeric nature of **3** has been confirmed by a single-crystal X-ray analysis.[9] Each asymmetrical unit contains two $[\eta^5{:}\eta^7\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Er}^{2-}$ structural motifs that are connected by three Na atoms through several B−H−Na two-electron−three-center (2e−3c) bonds (Figure 1). The asymmetrical units are then linked to each other via B−H−Er bonds to form an infinitive polymeric chain (Figure 2). It is interesting to note that the $[arachno\text{-C}_2\text{B}_{10}\text{H}_{11}]^{4-}$ has a boatlike C_2B_5 bonding face in which the five B atoms are coplanar and the two C atoms are ca. 0.6 Å above this plane, resulting in the average Er−C(cage) distance being ca. 0.26 Å shorter than the average Er−B(cage) distance. In comparison with the Er−C σ bond distances of 2.528(2) Å in $[\{\eta^5{:}\sigma\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})\}_2\text{Er}][\text{Li}(\text{THF})_4]$,[10a] 2.44(2) Å in $[(\text{C}_5\text{H}_5)_2\text{Er}(\mu\text{-C}{\equiv}\text{CBu}^t)]_2$,[10b] 2.458(19) Å in $(\text{C}_5\text{H}_5)_2\text{Er}(\mu\text{-Me})_2\text{Li(tmed)}$,[10c] and 2.526(6) Å in $[(\text{C}_5\text{H}_5)_2\text{Er}(\eta^2\text{-CHNBu}^t)]_2$,[10d] it is suggested that the Er−C(cage) bonds (average 2.410(6) Å) may be best described as σ bonds, perhaps also indicating that the 5-coordinate C atoms bear more negative charge than the 6-coordinate B atoms in the C_2B_5 bonding face. As far as we are aware, **3** is the first organolanthanide compound containing an η^7-carboranyl ligand to be reported.

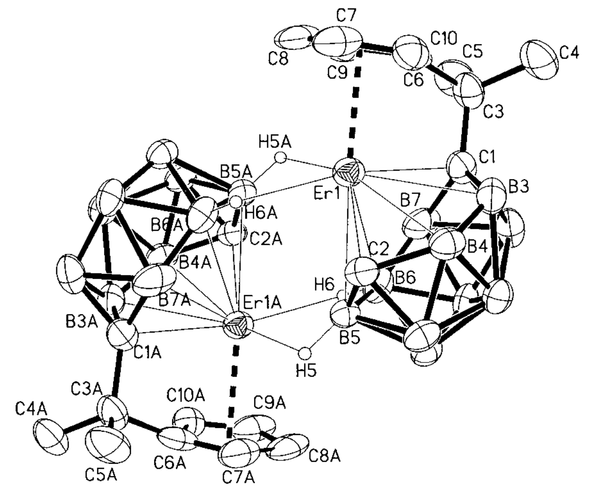

Figure 2. Closer view of the interactions of the Er metal with the neighboring carboranes in **3**.

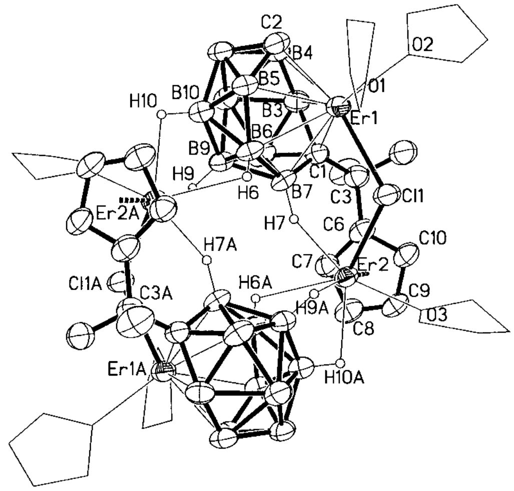

Figure 3. ORTEP illustration of **4** with thermal ellipsoids drawn at the 35% probability level.

The Na atoms in **3** can be completely replaced by other metals. Treatment of **3** with 2 equiv of ErCl_3 in THF at room temperature gave the novel tetranuclear metallacarborane $[\{\eta^5{:}\eta^7\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})\}\text{Er}_2(\mu\text{-Cl})(\text{THF})_3]_2$ (**4**) as pink crystals in 60% yield.[5] It is noteworthy that the added Er atoms not only replace the Na atoms but also compete with the existing Er atoms for the coordination sites, resulting in a new structural motif, which offers an opportunity to prepare heteronuclear metallacarboranes.

An X-ray analysis[11] reveals that **4** is a centrosymmetric tetranuclear metallacarborane cluster with two $\{[\eta^5{:}\eta^7\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Er}_2(\mu\text{-Cl})(\text{THF})_3\}$ units that are connected by two sets of three B−H−Er 2e−3c bonds (Figure 3). Each of the two Er(1) atoms is η^7-bound to $[arachno\text{-C}_2\text{B}_{10}\text{H}_{11}]^{4-}$ and coordinated to two O atoms from THF molecules and one doubly bridging Cl atom in a distorted-tetrahedral geometry. The average Er-

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[9] Crystal data for **3** ($\text{C}_{56}\text{H}_{114}\text{B}_{20}\text{Er}_2\text{Na}_4\text{O}_9$; fw 1574.2): monoclinic, space group $P2_1/n$, $a = 13.076(1)$ Å, $b = 26.212(2)$ Å, $c = 23.061(1)$ Å, $\beta = 104.84(1)°$, $V = 7640.5(8)$ Å^3, $d_{\text{calcd}} = 1.368$ g/cm^3, $Z = 4$, R1 = 0.077 ($I > 2.0\sigma(I)$), wR2 = 0.182 on F^2.

[10] (a) Xie, Z.; Wang, S.; Zhou, Z.; Mak, T. C. W. *Organometallics* **1999**, *18*, 1641. (b) Atwood, J. L.; Hunter, W. E.; Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1981**, *20*, 4115. (c) Schumann, H.; Lauke, H.; Hahn, E. F.; Heeg, M. J.; van der Helm, D. *Organometallics* **1985**, *4*, 321. (d) Evans, W. J.; Hanusa, T. P.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1987**, *6*, 295.

[11] Crystal data for **4** ($\text{C}_{44}\text{H}_{90}\text{B}_{20}\text{Cl}_2\text{Er}_4\text{O}_6$; fw 1671.3): trigonal, space group $R\bar{3}$, $a = 18.033(2)$ Å, $\beta = 84.36(1)°$, $V = 5784(1)$ Å^3, $d_{\text{calcd}} = 1.439$ g/cm^3, $Z = 3$, R1 = 0.063 ($I > 2.0\sigma(I)$), wR2 = 0.152 on F^2.

(1)−C(cage) and Er(1)−B(cage) distances of 2.385(4) and 2.656(5) Å are close to the corresponding values in **3**. Each of the other two Er(2) atoms is η^5-bound to the cyclopentadienyl ring and coordinated to one O atom from the THF molecule, one B−H bond from [*arachno*-$C_2B_{10}H_{11}$],$^{4-}$ one doubly bridging Cl atom, and three B−H bonds from the neighboring [*arachno*-$C_2B_{10}H_{11}$]$^{4-}$ in a distorted-pentagonal-bipyramidal geometry with the centroid of the cyclopentadienyl ring and H(9A) occupying the axial sites. The average Er(2)−C(C_5 ring) distance of 2.597(4) Å is comparable to those in **2** and **3**. The average Er⋯B distance of 2.787(4) Å is longer than that of 2.644(12) Å in $[\{(Me_3Si)_2C_2B_4H_4\}_2Er]_2[Li(TMEDA)_2]_2$.[12]

All of the above-mentioned reactions are summarized in Scheme 1. Attempts to convert $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ directly into $[Me_2C(C_5H_4)(C_2B_{10}H_{11})]^{5-}$ by treatment with excess Na or K metal in THF failed, and only $[Me_2C(C_5H_4)(C_2B_{10}H_{11})]^{3-}$ was detected, indicating that **2** serves as an intermediate in the formation of **3**. It seems to be a general method that reduction of 13-vertex *closo*-metallacarboranes gives a new class of metallacarboranes containing an η^7-carboranyl ligand.

Acknowledgment. We thank the Hong Kong Research Grants Council (Earmarked Grant CUHK 4183/97P) for financial support.

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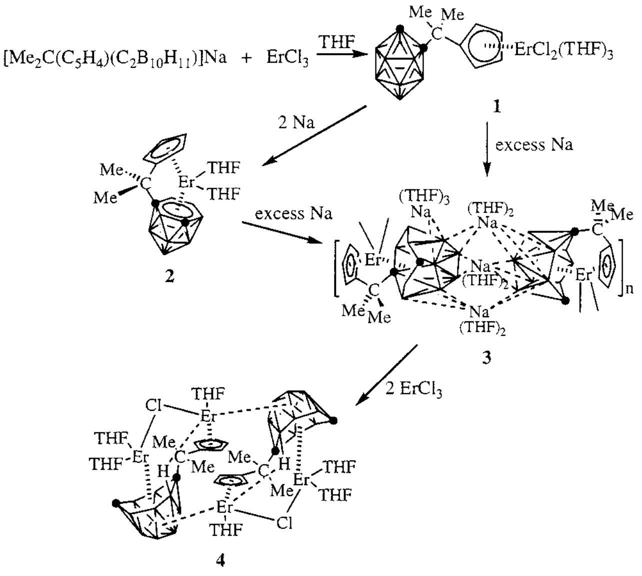
[12] Hosmane, N. S.; Wang, Y.; Zhang, H.; Oki, A. R.; Maguire, J. A.; Waldhör, E.; Kaim, W.; Binder, H.; Kremer, R. K. *Organometallics* **1995**, *14*, 1101.

Scheme 1



Supporting Information Available: Tables of crystallographic data and data collection details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates and figures containing the atom-numbering schemes for **2**−**4** and text giving experimental procedures and compound characterization data. Crystal data are also available as files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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