

New class of metallocarboranes incorporating the η^7 -carboranyl ligand*

Zuowei Xie

Department of Chemistry, The Chinese University of Hong Kong, Shatin,
New Territories, Hong Kong, P. R. China

Abstract: This article provides an overview of our work on the synthesis, molecular structure, and bonding of a novel class of 13-vertex *closo*-metallocarboranes incorporating the η^7 -carboranyl ligand. This bonding mode can only be observed in the d^0/f^n transition-metal ions with the proper size.

INTRODUCTION

The chemistry of metallocarboranes has witnessed an explosive growth since the first metallocarborane was reported in 1965 [1]. A large number of metallocarboranes of s-, p-, d-, and f-block elements are known; however, the highest hapticity of carboranyl ligands in these compounds has been six [2]. We have recently discovered a brand new bonding mode for carborane molecules, and some recent findings in our laboratory are summarized here.

ACTINACARBORANES

Interaction between *o*-carborane and excess alkali metal in tetrahydrofuran (THF) followed by treatment with $AnCl_4$ gave $\{[(\eta^7-C_2B_{10}H_{12})(\eta^6-C_2B_{10}H_{12})An][M_2(THF)_5]\}_2$ [$M = Na, K; An = Th$ (**1**), U (**2**)]. **2** has been subjected to an X-ray diffraction study. As shown in Fig. 1, it is a centrosymmetric dimer with a bent sandwich structural motif. Each U atom is η^6 -bound to *nido*- $C_2B_{10}H_{12}^{2-}$, η^7 -bound to *arachno*- $C_2B_{10}H_{12}^{4-}$, and coordinated to two B–H bonds from the C_2B_5 bonding face of the neighboring *arachno*- $C_2B_{10}H_{12}^{4-}$ ligand, resulting in a highly distorted-tetrahedral geometry at U atom [3]. **2** represents not only the first metallocarborane containing a novel $\eta^7-C_2B_{10}H_{12}^{4-}$ ligand, but also the first organoactinide compound bearing a $\eta^6-C_2B_{10}H_{12}^{2-}$ ligand.

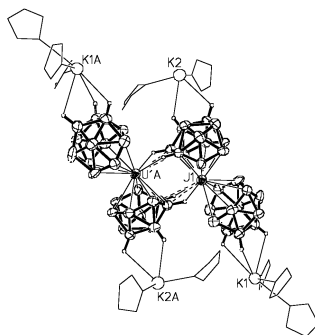


Fig. 1 Molecular structure of **2**.

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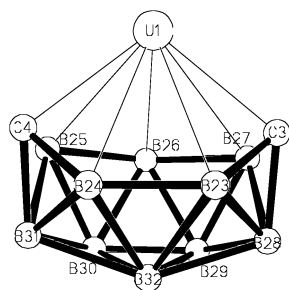
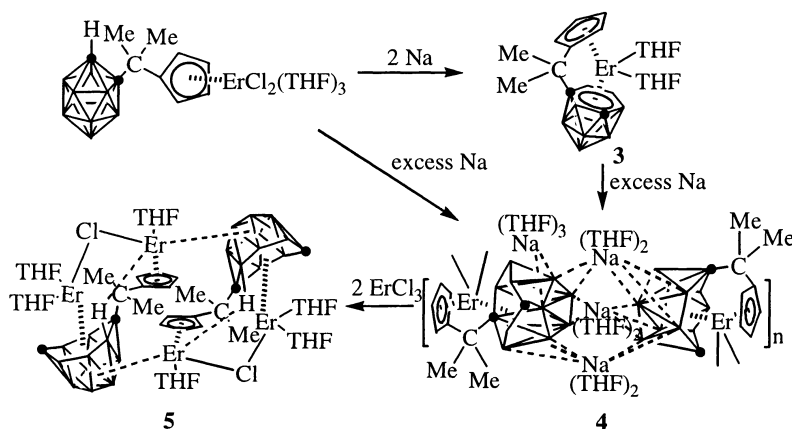


Fig. 2 Interaction between U and $C_2B_{10}H_{12}^{4-}$.

LANTHANACARBORANES

The above-mentioned results demonstrate a brand new bonding mode for carborane molecules, which encourages us to extend our research to lanthanide metals. Treatment of $[\eta^5\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{ErCl}_2(\text{THF})_3$ with 2 equiv or an excess amount of Na metal in THF afforded the mixed-sandwich compound $[\eta^5:\eta^6\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Er}(\text{THF})_2$ (**3**) or the novel lanthanacarborane $\{[\eta^5:\eta^7\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Er}\}_2\{\text{Na}_4(\text{THF})_9\}_n$ (**4**), respectively [4]. Reaction of **3** with excess Na metal also generated **4**. It is reasonable to suggest that **3** serves as an intermediate in the above reactions. The Na ions in **4** can be completely replaced by other metals. Treatment of **4** with 2 equiv of ErCl_3 in THF gave the novel tetranuclear lanthanacarborane $\{[\eta^5:\eta^7\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Er}_2(\mu\text{-Cl})(\text{THF})_3\}_2$ (**5**) (Scheme 1). Both **4** and **5** are extremely air- and moisture-sensitive, but remain stable for months at room temperature under an inert atmosphere. Traces of air immediately convert them to a white solid. They are soluble in THF, DME, and pyridine, sparingly soluble in toluene, and insoluble in hexane and decompose in CH_2Cl_2 .



Scheme 1

The polymeric nature of **4** has been confirmed by a single-crystal X-ray analysis. 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 $2e\text{-}3c$ bonds (Fig. 3). The asymmetrical units are then linked to each other via B–H–Er bonds to form an infinitive polymeric chain. An X-ray analysis reveals that **5** is a centrosymmetric tetranuclear lanthanacarborane 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 $2e\text{-}3c$ bonds (Fig. 4). Each of two Er(1) atoms is

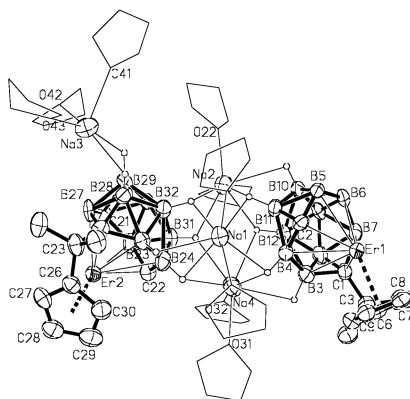


Fig. 3 Molecular structure of 4.

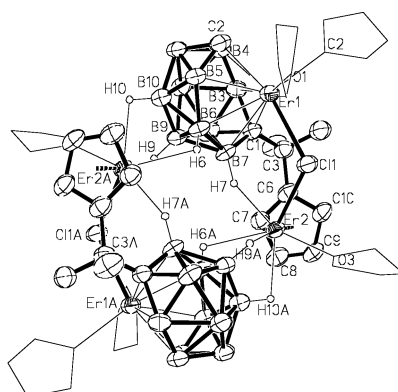
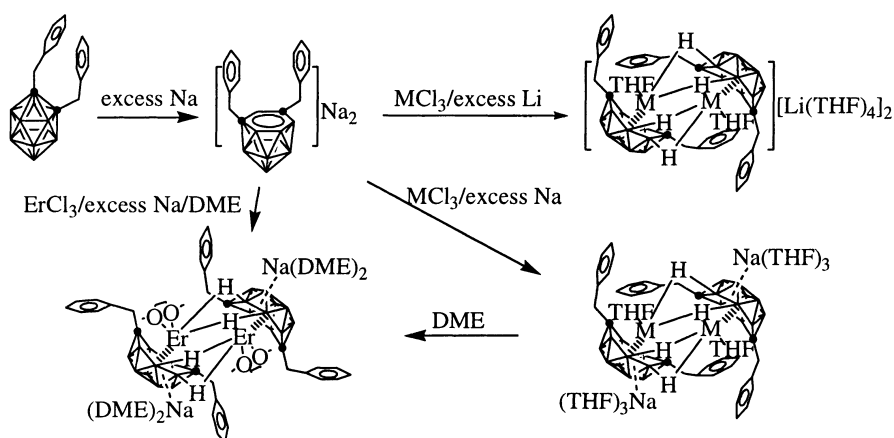


Fig. 4 Molecular structure of 5.

η^7 -bound to $[\text{arachno-C}_2\text{B}_{10}\text{H}_{11}]^{4-}$ and coordinated to two O atoms from THF molecules and one doubly bridging Cl atom in a distorted-tetrahedral geometry. Each of the other two Er(2) atoms is η^5 -bound to the cyclopentadienyl ring and coordinated to one O atom from THF molecule, one B–H bond from $[\text{arachno-C}_2\text{B}_{10}\text{H}_{11}]^{4-}$, one doubly bridging Cl atom, and three B–H bonds from the neighboring $[\text{arachno-C}_2\text{B}_{10}\text{H}_{11}]^{4-}$ in a distorted-pentagonal-bipyramidal geometry with the centroid of the cyclopentadienyl ring and H(9A) occupying the axial sites. It is interesting to note 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.

To eliminate the ambiguity and to definitely distinguish the cage carbon atoms from those boron atoms of the carborane molecule in X-ray diffraction studies, a carbon-substituted *o*-carborane, 1,2-($\text{C}_6\text{H}_5\text{CH}_2$)₂-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$, was chosen as a ligand. As shown in Scheme 2, reaction of 1,2-($\text{C}_6\text{H}_5\text{CH}_2$)₂-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ with excess Na metal in THF gave *closo-exo*- $[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_{10}\text{H}_{10}]\text{Na}_2(\text{THF})_4$ as a sole product. It, however, could react with 1 equiv of LnCl_3 in the presence of excess Na metal in THF afforded 13-vertex *closo*-metallacarboranes $\{[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_{10}\text{H}_{10}]\text{Ln}(\text{THF})\}_2\{\text{Na}(\text{THF})_3\}_2$ [$\text{Ln} = \text{Dy}$ (6), Er (7)]. These results indicate that the electron-accepting ability of *nido*-carborane is largely dependent upon the central metal ions. The coordinated THF molecules in the metallacarborane can be replaced by dimethoxyethane (DME) molecules giving $\{[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_{10}\text{H}_{10}]\text{Er}(\text{DME})\}_2\{\text{Na}(\text{DME})_2\}_2$ (8) if recrystallization of 7 from a DME solution. Molecular structures of 7 and 8 are shown in Figs. 5 and 6, respectively [5].

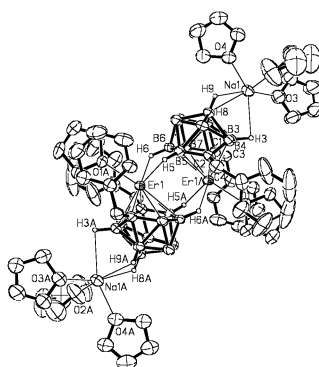


Scheme 2

METALLACARBORANES OF d^0 METAL ION

To facilitate the theoretical calculations and benefit NMR measurements, we have extended our research to d^0 transition-metal ion. Yttrium was chosen because its properties are similar to those of lanthanide series in terms of the ionic radius, oxidation state, and chemical reactions. As expected, $\{[(C_6H_5CH_2)_2C_2B_{10}H_{10}]Y(THF)_2\}_2\{Na(THF)_3\}_2$ was isolated in the same manner as **7**. They are isostructural and isomorphous.

Careful examination of the molecular structures of this novel class of 13-vertex metallacarboranes indicates that (1) the arrangement of the cage atoms in these metallacarboranes is the same regardless of the substituents on the cage carbons and of d^0/f^n transition-metal ions, (2) the $[arachno-R_2C_2B_{10}H_{10}]^{4-}$ 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 a significantly short M-C(cage) distances (Fig. 2), and (3) the unique arrangement of the cage atoms leads to three different types of coordination environment for cage atoms: 5-coordinate carbon, 6-coordinate boron, and 7-coordinate boron, respectively.

Fig. 5 Molecular structure of **7**.

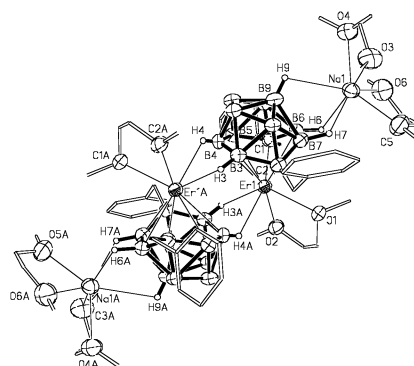


Fig. 6 Molecular structure of **8**.

BONDING

To understand the bonding interactions between the metal ion and *arachno*-carboranyl ligand, molecular orbital calculations have been performed. The results show that the $[\textit{arachno}\text{-C}_2\text{B}_{10}\text{H}_{12}]^{4-}$ tetraanion contributes five pairs of electrons to the five d orbitals of the metal ion to form metal-cage bonds in η^7 -fashion, and the metal-cage interaction is extensively delocalized. The natural bond order (NBO) analysis of $[\textit{arachno}\text{-C}_2\text{B}_{10}\text{H}_{12}]^{4-}$ shows that in the boatlike C_2B_5 bonding face the natural atomic charges of carbons (av -0.85) are significantly higher than those of borons (av -0.16), and the bond orders are much higher for the Y–C bonds (av 0.28) than those for the Y–B bonds (av 0.14), which is consistent with experimental data [5]. It is anticipated that only d^0 and f-block transition-metal ions with proper size can have such bonding interactions with the $[\textit{arachno}\text{-C}_2\text{B}_{10}\text{H}_{12}]^{4-}$ ligand. It is further anticipated that only f-block transition-metal ions could form full-sandwich metallacarboranes with two *arachno*-carboranyl ligands.

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REFERENCES

1. M. F. Hawthorne, D. C. Young, P. A. Wegner. *J. Am. Chem. Soc.* **87**, 1818 (1965).
2. (a) R. N. Grimes. In *Comprehensive Organometallic Chemistry II*, E. W. Abel, F. G. A. Stone, G. Wilkinson (Eds.), Vol. 1, Ch. 9, Pergamon, Oxford (1995); (b) A. K. Saxena and N. S. Hosmane. *Chem. Rev.* **93**, 1081 (1993).
3. Z. Xie, C. Yan, Q. Yang, T. C. W. Mak. *Angew. Chem., Int. Ed.* **38**, 1761 (1999).
4. (a) Z. Xie, K. Chui, Q. Yang, T. C. W. Mak. *Organometallics* **18**, 3947 (1999); (b) K. Chui, Q. Yang, T. C. W. Mak, Z. Xie. *Organometallics* **19**, 1391 (2000).
5. K. Chui, Q. Yang, T. C. W. Mak, W. H. Lam, Z. Lin, Z. Xie. *J. Am. Chem. Soc.* **122**, 5758 (2000).