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Synthesis and Structural Characterization of New Carboranyl-Indenyl Ligands and Their Lanthanide Complexes

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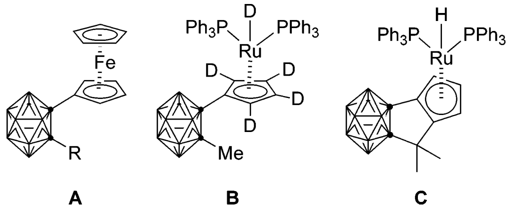
Two new directly attached carboranyl-indenyl compounds, 2-(*o*-carboranyl)indene (**2**) and 1-(*o*-carboranyl)indene (**4**), were synthesized, and their applications in lanthanide chemistry were explored. Reactions of 2-indanone or indene epoxide with $Li_2C_2B_{10}H_{10}$ followed by dehydration reactions gave **2** or **4**, respectively. Treatment of **2** with excess sodium metal afforded presumably $\{\eta^5:\eta^6\text{-}(2\text{-}C_9H_6)(C_2B_{10}H_{11})\}\{Na_3(THF)_n\}$, which reacted with $LnCl_3$ to produce dinuclear complexes $[\{\eta^5:\eta^6\text{-}(2\text{-}C_9H_6)(C_2B_{10}H_{11})Ln(THF)\}_2(\mu\text{-}Cl)][Na(THF)_6]$ (Ln = Y (**5a**), Er (**5b**)). Compound **4** reacted with excess sodium metal, yielding $[\{\eta^5:\eta^6\text{-}(1\text{-}C_9H_6)(C_2B_{10}H_{11})\}\{Na_3(THF)_5\}]_2$ (**6**), bearing a six-membered C_2B_4 open face and a five-membered C_5 bonding face. Reaction of **6** with $LnCl_3$ or $Ln(BH_4)_3(THF)_3$ gave $[\{\eta^5:\eta^6\text{-}(1\text{-}C_9H_6)(C_2B_{10}H_{11})Ln(THF)\}_2(\mu\text{-}Cl)][Na(THF)_3]$ (Ln = Y (**7a**), Nd (**7b**), Er (**7c**)) or $\{[\eta^5:\eta^6\text{-}(1\text{-}C_9H_6)(C_2B_{10}H_{11})Er(THF)]_2(\mu\text{-}BH_4)\}\{Na(THF)_2\}$ (**8**), respectively. Interaction of **8** with excess sodium metal generated $\{[\eta^5:\eta^7\text{-}(1\text{-}C_9H_6)(C_2B_{10}H_{11})Er(THF)]_2\}\{Na_4(THF)_8\}$ (**9**). These new complexes were characterized by various spectroscopic techniques and elemental analyses. The molecular structures of **1**−**4**, **5b**, **6**, **7a**, **7c**, **8**, and **9** were confirmed by single-crystal X-ray analyses. The results showed that these new ligands favored the formation of the "metal-bridged" type of dinuclear complexes due to the lack of the linkage between the indenyl and carboranyl units.

Introduction

Chart 1



Ligands are an essential part of organometallic compounds. They impose a dominant control over both the chemical and the physical properties of the resulting metal complexes. Therefore, ligand design has become a central theme in the development of the chemistry of organometallic compounds.[1] In this connection, a series of single-atom-bridged cyclopentadienyl-, indenyl-, and fluorenyl-carboranyl ligands, $A(C_5H_5)(C_2B_{10}H_{11})$ (A = Me_2C,[2] Me_2Si[3]), $A'(C_9H_7)(C_2B_{10}H_{11})$ (A′ = Me_2C,[4] Me_2Si,[5] Pr^i_2NB,[6] Pr^i_2NP[7]), and $A''(C_{13}H_9)(C_2B_{10}H_{11})$ (A″ = H_2C,[8] Me_2Si[9]), have been developed. These ligands are finding many applications in organometallic chemistry.[1−10] Experimental results show that the bridging atom significantly influences the chemical and physical properties of the resulting organometallic complexes.[10] It is anticipated that the interactions between a cyclic organic moiety and a carboranyl group would be largely enhanced if there is not any linkage between them, probably leading to a new class of ligands demanding highly constrained geometries.

Cyclopentadiene-substituted *o*-carboranes are known.[11] They are prepared from either the direct reaction of $LiC_2B_{10}H_{10}R$ with cyclopentenone followed by dehydration[11b] or the intramolecular cyclization of 1-Ph-2-$[CH(CH_2CH_2C_6H_5)_2]$-1,2-$C_2B_{10}H_{10}$.[11c] Organometallic complexes directly derived from these compounds have not appeared in the literature yet, although some sandwich/half-sandwich complexes were reported (**A**−**C**, in Chart 1).[2e,12] These species were prepared from the reaction of ethynylferrocene with decaborane[12a] or $(\eta^5\text{-}C_5D_5)RuCl(PPh_3)_2$ with 1-Li-2-Me-1,2-$C_2B_{10}H_{10}$[12b] or $RuCl_2(PPh_3)_3$ with $Li_2[Me_2C(C_5H_4)$-

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($C_2B_{10}H_{10}$)].[2e] The mechanisms for the formation of **B** and **C** were not clear. To investigate the properties of directly linked indenyl-carboranyl compounds and to compare them with the corresponding single-atom-bridged systems, we prepared 2-(*o*-carboranyl)indene and 1-(*o*-carboranyl)indene and investigated their applications in organolanthanide chemistry. These results are reported in this article.

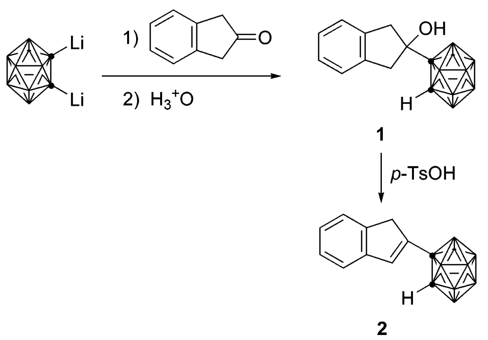
Results and Discussion

Ligands. Our objective was to directly connect the carboranyl moiety to the indenyl group with the cage CH available for further functionalization. Some indenyl derivatives were conveniently prepared from the reaction of indenyllithium with electrophiles. Unfortunately, 1-I-1,2-$C_2B_{10}H_{11}$ showed no reactivity toward indenyllithium. In view of the nucleophilicity of readily available $Li_2C_2B_{10}H_{10}$, several electrophilic compounds were examined. The results showed that the reaction of $Li_2C_2B_{10}H_{10}$ with secondary halides such as 3-bromoindene afforded very poor yields, probably due to the relatively low nucleophilicity of the carborane anion. After many attempts, it was found that very strong electrophiles of indanone and indene epoxide were suitable starting materials.

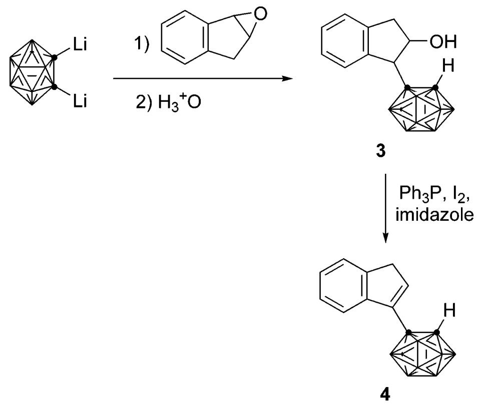
Treatment of 2-indanone with 1 equiv of $Li_2C_2B_{10}H_{10}$ at room temperature afforded, after column chromatographic separation, 2-(*o*-carboranyl)-2-indanol (**1**) and *o*-carborane in 31% and 56% yields, respectively. The ^{11}B NMR experiments indicated that only 40% of $Li_2C_2B_{10}H_{10}$ was consumed before quenching the reaction with a diluted HCl solution. The yield of **1** was not improved even under forced reaction conditions. A stronger electrophile was necessary to increase the efficiency of this nucleophilic reaction. Reaction of indene epoxide with 1 equiv of $Li_2C_2B_{10}H_{10}$ in diethyl ether gave 1-(*o*-carboranyl)-2-indanol (**3**) in 82% yield. Although the β-position is sterically more accessible, it is a much less reactive site than α-carbon toward nucleophiles due to the presence of the aromatic ring. Therefore, no other isomer was isolated.

There are many methods to convert alcohols to olefins. Compound **1** is very stable in acidic media under normal reaction conditions. After many attempts, it was found that a very strong acid and high temperature were required to convert **1** into the corresponding indene derivative. Heating the mixture of **1** and *p*-TsOH in a molar ratio of 1:1 in a sealed Pyrex tube at 180 °C for 10 min gave, after workup, 2-(*o*-carboranyl)indene (**2**) in 84% yield (Scheme 1). On the other hand, compound **3** is surprisingly stable under various acidic conditions. Direct dehydration of **3** is not feasible. Alternative routes were then examined. Treatment of **3** with a mixture of triphenylphosphine, imidazole, and iodine in a molar ratio of 1:1.2:2:1.3 in refluxing toluene for 48 h generated, after workup, 1-(*o*-carboranyl)indene (**4**) in 78% yield (Scheme 2). The thermodynamically more stable compound **4** was the only isomer. No 3-(*o*-carboranyl)-indene was isolated. Compounds **1** and **3** are soluble in Et_2O, THF, and toluene and slightly soluble in *n*-hexane, whereas **2** and **4** are soluble in common organic solvents including *n*-hexane.

Scheme 1



Scheme 2



In addition to the aromatic protons, two doublets at 3.52 and 2.97 ppm with $^2J = 16.2$ Hz assignable to the axial and equatorial protons at the benzyl positions, one singlet at 4.29 ppm attributable to the cage C*H* proton, and one broad singlet at 2.42 ppm corresponding to the O*H* group were observed in the ^{1}H NMR spectrum of **1**. For **2**, the ^{1}H NMR spectrum showed three singlets at 7.02 (vinyl proton), 3.89 (cage C*H* proton), and 3.54 ppm (benzyl protons) besides the aromatic protons. Their ^{13}C NMR spectra were consistent with the ^{1}H NMR results. The ^{11}B NMR spectra exhibited a 2:2:2:4 splitting pattern for **1** and a 1:1:2:2:2:2 splitting pattern for **2**. The solid-state IR spectrum of **1** displayed a characteristic broad, strong absorption of OH at 3571 cm^{-1} and a very strong absorption of BH at ca. 2600 cm^{-1}. The characteristic OH absorption disappeared in the IR spectrum of **2**, but that of BH remained.

The ^3J coupling constants of *trans* protons are too small to be observed in the ^{1}H NMR spectrum of **3** since the dihedral angles between the *trans* protons are close to 90°.[13] Accordingly, a singlet at 3.88 ppm of the tertiary C*H* (benzyl) proton, a doublet at 4.77 ppm of the tertiary C*H*(OH) proton with $^3J = 5.1$ Hz, a doublet at 2.81 ppm of one methylene proton with $^2J = 17.1$ Hz, and a doublet of doublets at 3.45 ppm of another methylene proton with coupling constants of $^2J = 17.1$ and $^3J = 5.1$ Hz were observed in the ^{1}H NMR spectrum of **3**. A singlet at 3.58 ppm corresponding to the cage C*H* proton and a broad singlet at 1.72 ppm assignable to the O*H* proton were also observed. The latter disappeared after adding D_2O to the NMR solution, confirming that it was an O*H* proton. The ^{1}H NMR spectrum of **4** was relatively simple, showing a triplet at 6.84 ppm with $^3J = 2.1$ Hz of the vinyl proton, a doublet at 3.41 ppm with $^3J = 2.1$ Hz of the methylene protons, and a singlet at 4.14 ppm of the cage C*H* proton, in addition to the aromatic protons. The ^{11}B NMR spectra exhibited a 1:1:2:3:3 splitting pattern for **3** and 1:1:2:4:2 for **4**, respectively. Their solid-state IR spectra displayed a very strong characteristic peak of BH

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1−4

	1	**2**		**3**[a]	**4**
C(11)−C(12)	1.545(2)	1.387(2)	C(11)−C(12)	1.510(3) [1.518(3)]	1.485(3)
C(12)−C(13)	1.512(2)	1.474(2)	C(12)−C(17)	1.392(3) [1.381(3)]	1.403(3)
C(13)−C(18)	1.391(2)	1.383(2)	C(17)−C(18)	1.502(4) [1.490(4)]	1.493(4)
C(18)−C(19)	1.507(2)	1.496(2)	C(18)−C(19)	1.528(4) [1.537(4)]	1.483(3)
C(19)−C(11)	1.549(2)	1.450(2)	C(19)−C(11)	1.557(3) [1.546(3)]	1.338(4)
C(1)−C(11)	1.554(2)	1.489(2)	C(1)−C(11)	1.547(3) [1.545(3)]	1.492(3)
C(11)−O(1)	1.427(2)		C(19)−O(1)	1.420(3) [1.419(3)]	
C(1)−C(2)	1.653(2)	1.645(2)	C(1)−C(2)	1.672(3) [1.702(4)]	1.648(3)
∑∠C(11)	332.7(1)	360.0(1)	∑∠C(11)	329.3(2) [331.6(2)]	360.0(2)

[a] Distances and angles in brackets are those of a second molecule.

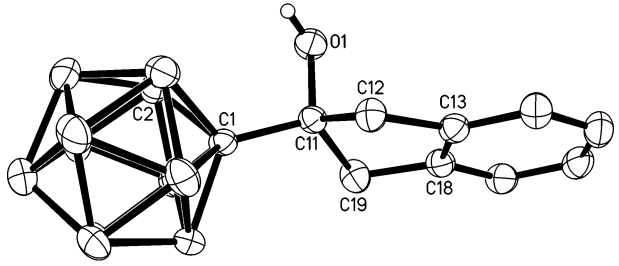


Figure 1. Molecular structure of 2-(*o*-carboranyl)-2-indanol (**1**).

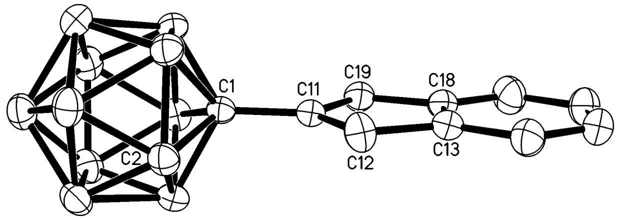


Figure 2. Molecular structure of 2-(*o*-carboranyl)indene (**2**).

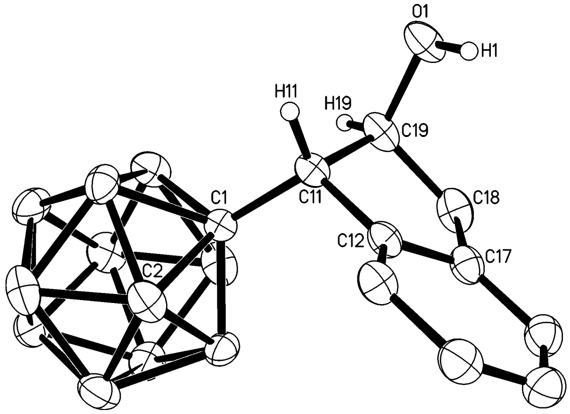


Figure 3. Molecular structure of 1-(*o*-carboranyl)-2-indanol (**3**).

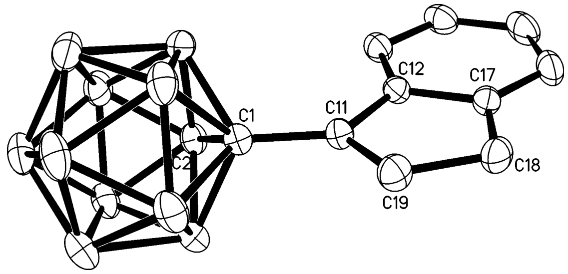
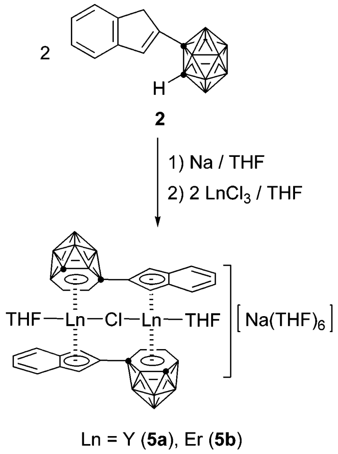


Figure 4. Molecular structure of 1-(*o*-carboranyl)indene (**4**).

Scheme 3



absorption at ca. 2600 cm^{-1}. A broad, strong absorption of an OH group at 3335 cm^{-1} was also observed in the IR spectrum of **3**.

The solid-state structures of **1**−**4** were further confirmed by single-crystal X-ray analyses. The selected bond distances and angles are listed in Table 1. The molecular structure of **1** (Figure 1) shows that both the cage and OH group are bonded to C(11). The bond distances and angles indicate that C(11), C(12), and C(19) are all sp^3-carbons, whereas C(13) and C(18) are sp^2-carbons. In the molecular structure of **2** (Figure 2), the C(11) and C(12) become sp^2-carbons with a bond distance of 1.387(2) Å. The C(11)−C(1) distance of 1.489(2) Å is much shorter than that of 1.554(2) Å observed in **1**, indicative of a certain degree of conjugation between the cage and indenyl group.

There are two crystallographically independent molecules in the unit cell of **3**. Figure 3 shows the representative structure. It is clear that the OH group and the cage are in *trans* arrangement. The C−C distances are very close to those observed in **1**. The C(11) and C(19) become the sp^2-carbons in **4** (Figure 4), as judged from the bond distances and angles listed in Table 1. The C(1)−C(11) distance of 1.493(3) Å is very close to that of 1.489(2) Å in **2** but is much shorter than the 1.545(3) [1.547(3)] Å in **3**, again suggestive of some conjugation between the indenyl and carboranyl units. These results clearly imply that the interactions between the indenyl and cage are stronger than those observed in single-atom-bridged systems.

Organolanthanide Complexes. Compounds **2** and **4** are isomers bearing two functional moieties that can be conveniently converted into π ligands. Treatment of **2** with excess finely cut sodium metal at room temperature in THF for 48 h generated, after removal of excess Na, presumably a $\{\eta^5:\eta^6\text{-}(2\text{-}C_9H_6)(C_2B_{10}H_{11})\}\{Na_3(THF)_n\}$ solution, followed by reaction with 1 equiv of LnCl$_3$ to give $[\{\eta^5:\eta^6\text{-}(2\text{-}C_9H_6)(C_2B_{10}H_{11})Ln(THF)\}_2(\mu\text{-}Cl)][Na(THF)_6]$ (Ln = Y (**5a**), Er (**5b**)) in about 70% isolated yield (Scheme 3). The same complexes were isolated even when the molar ratio of **2**:LnCl$_3$ was changed from 1:1 to 1:2. The diamagnetic yttrium complex **5a** offered useful NMR information. Its ^{1}H NMR indicated the presence of an indenyl group and THF and supported a molar ratio of four THF molecules per indenyl. The ^{11}B NMR spectrum showed a 1:2:4:2:1 splitting pattern. These data, however, do not offer any structural information on whether **5a** is a monomeric or dimeric species. An X-ray analysis is desired.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 5b, 7a, 7c, 8, and 9

	5b (Er)	**6** (Na)	**7a** (Y)	**7c** (Er)	**8** (Er)	**9** (Er)
av C(1)−C(11)	1.473(19)	1.470(6)	1.515(1)	1.495(2)	1.50(1)	1.492(9)
av M−C_5 ring	2.669(15)	2.831(6)	2.701(1)	2.677(2)	2.683(5)	2.716(7)
av M−C_2B_4 ring	2.715(16)	2.775(6)	2.765(5)	2.759(2)	2.770(7)	2.703(8)[b]
av M−O	2.374(9)	2.275(5)	2.377(1)	2.383(1)	2.353(2)	2.438(5)
av M−X[a]	2.633(4)		2.657 (1)	2.636(1)	2.656(5)	
∠M−X-M[a]	107.5(1)		106.3(1)	106.4(3)	107.2(2)	
av Cent6−M−Cent5	132.3		130.6	132.5	127.7	142.1

[a] For **5b**, **7a**, and **7c**, X = Cl; for **8**, X = B. [b] Average Er−cage B distance.

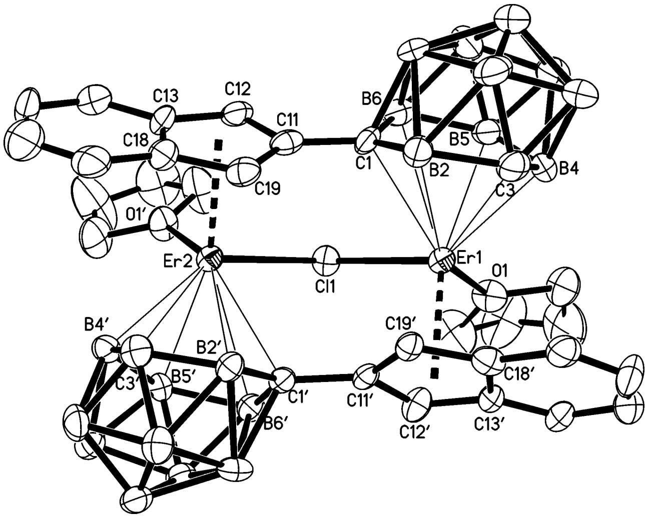


Figure 5. Molecular structure of the anion in $[\{\eta^5{:}\eta^6\text{-}(2\text{-}C_9H_6)(C_2B_{10}H_{11})Er(THF)\}_2(\mu\text{-}Cl)][Na(THF)_6]$ (**5b**).

A single-crystal X-ray diffraction study revealed that **5b** is a dinuclear molecule consisting of well-separated, alternating layers of discrete complex cations $[Na(THF)_6]^+$ and dinuclear anions $[\{\eta^5{:}\eta^6\text{-}(2\text{-}C_9H_6)(C_2B_{10}H_{11})Er(THF)\}_2(\mu\text{-}Cl)]^-$. In the anion, each Er atom is η^6-bound to the *nido*-carboranyl, η^5-bound to the indenyl, σ-bound to one doubly bridging Cl atom, and coordinated to one THF molecule in a distorted-tetrahedral geometry, as shown in Figure 5. The selected bond distances and angles are listed in Table 2. Thus **5a** and **5b** are metal-bridged type of complexes in which the same ligand bonds to two metal atoms due to the highly constrained system.[14] The dihedral angles between the five- and six-membered bonding faces in the same ligand are 13.8° and 14.8°, respectively.

The average Er−cage atom distance of 2.715(16) Å and Er−C_5 ring distance of 2.669(15) Å are comparable to the corresponding values of 2.680(3) and 2.602(5) Å in $[\eta^5{:}\eta^6\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]Er(THF)_2$[2b,15] and 2.773(12) and 2.675(15) Å in $[\{\eta^5{:}\eta^6\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})\}Er(THF)(\mu\text{-}Cl)Na(THF)_2]_n$.[5c] The Cent6−Er−Cent5 (Cent6 and Cent5 represent the centroids of the six- and five-membered bonding faces, respectively) angle of 132.3° is significantly larger than the chelating type of complexes,[14] for example, 118.4° in $[\eta^5{:}\eta^6\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]Er(THF)_2$[2b,15] and 126.1° in $[\{\eta^5{:}\eta^6\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})\}Er(THF)(\mu\text{-}Cl)Na(THF)_2]_n$.[5c,10a] The average Er−Cl distance of 2.633(4) Å is significantly shorter than that of 2.733(1) Å in $[\{\eta^5{:}\eta^7\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})\}Er_2(\mu\text{-}Cl)(THF)_3]_2$,[2b,15] but much longer than that of 2.545(1) Å in $[\{\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})\}\{\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})\}]Er(\mu\text{-}Cl)Na(THF)_3$[5b] and 2.563(4) Å in $[\{\eta^5{:}\eta^6\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})\}Er(THF)(\mu\text{-}Cl)Na(THF)_2]_n$.[5c] The C(1)−C(11)/C(1′)−C(11′) bond distances of 1.449(19)/1.497(18) Å in **5b** are close to that of 1.489(2) Å in **2**.

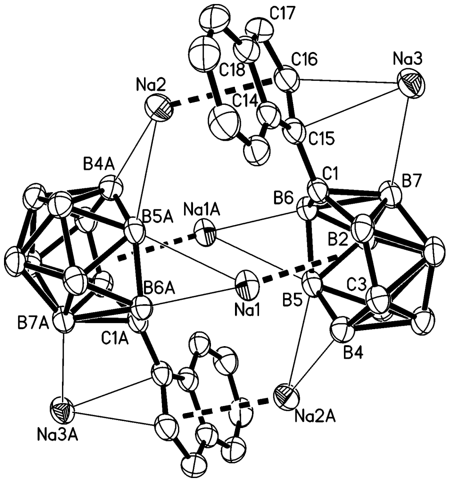


Figure 6. Molecular structure of $[\{\eta^5{:}\eta^6\text{-}(1\text{-}C_9H_6)(C_2B_{10}H_{11})\}\{Na_3(THF)_5\}]_2$ (**6**) (all coordinated THF molecules and H atoms are omitted for clarity).

Like **2**, reduction of **4** with excess Na metal in THF at room temperature for 24 h afforded $[\{\eta^5{:}\eta^6\text{-}(1\text{-}C_9H_6)(C_2B_{10}H_{11})\}\{Na_3(THF)_5\}]_2$ (**6**) in 92% yield. Its ^{11}B NMR spectrum displayed a 3:4:3 splitting pattern, which was significantly different from that of **4**. Therefore, this reduction reaction was closely followed by the ^{11}B NMR. Its ^1H NMR spectrum showed the presence of the ligand and supported a molar ratio of five THF molecules per indenyl group. The solid-state structure of **6** was further confirmed by single-crystal X-ray analysis and is shown in Figure 6. It has a centrosymmetrical structure, in which the trianionic ligand is bonded to two Na atoms via the six- and five-membered rings in η^6- and η^5-fashion and to the third Na atom through one Na···B−H and one Na−(η^2-C(15)=C(16)) interaction, respectively. The average Na(1)−cage atom distance of 2.775(6) Å is very close to that of 2.776(2) Å in *closo-exo*-$[(C_6H_5CH_2)_2C_2B_{10}H_{10}]Na_2(THF)_4$,[16] but is much shorter than that of 2.854(4) Å in $[\{\mu\text{-}1,2\text{-}[o\text{-}C_6H_4\text{-}(CH_2)_2)]\text{-}1,2\text{-}C_2B_{10}H_{10}\}_2Na_4(THF)_6]_n$[17a] and 2.848(7) Å in $[\{\eta^6\text{-}[(CH_3OCH_2CH_2)_2C_2B_{10}H_{10}]Na\}\{Na(THF)\}]_n$.[17b] The average Na(2)−C_5 ring distance of 2.831(6) Å is much shorter than that of 2.934(3) Å in $[\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Yb(THF)[(\mu\text{-}\eta^5){:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Na(THF)_3$[5a] and 2.877(1) Å in $[NaC_9H_7(15\text{-crown-}5)]$.[18]

Interaction of **6** with 2 or 4 equiv of $LnCl_3$ in THF at room temperature afforded $[\{\eta^5{:}\eta^6\text{-}(1\text{-}C_9H_6)(C_2B_{10}H_{11})Ln(THF)\}_2(\mu\text{-}Cl)][Na(THF)_3]$ (Ln = Y (**7a**), Nd (**7b**), Er (**7c**)) in 75−83% yields (Scheme 4). The ^1H NMR spectrum of the diamagnetic

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(14) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865.

(15) Xie, Z.; Chui, K.; Yang, Q.; Mak, T. C. W. *Organometallics* **1999**, *18*, 3947.

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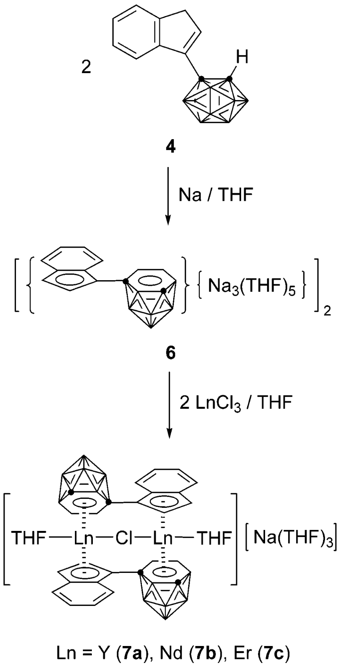
(18) Kähler, T.; Behrens, U.; Neander, S.; Olbrich, F. *J. Organomet. Chem.* **2002**, *649*, 50.

Scheme 4



complex **7a** showed four doublets and two triplets in the aromatic region, a singlet at 4.26 ppm corresponding to the two cage C*H* protons, and two multiplets at 3.64 and 1.60 ppm attributable to the THF protons, and supported a molar ratio of 2.5 THF molecules per ligand. Its ^{11}B NMR spectrum exhibited a 1:1:2:2:1:1:1:1 splitting pattern, which is quite different from that of **6**. Again, this reaction was closely monitored by ^{11}B NMR spectroscopy.

Single-crystal X-ray analyses revealed that **7a** and **7c** are isomorphous and isostructural, consisting of well-separated, alternating layers of discrete complex cations $[Na(THF)_3]^+$ and anions $[\{\eta^5:\eta^6\text{-}(1\text{-}C_9H_6)(C_2B_{10}H_{11})Ln(THF)\}_2(\mu\text{-}Cl)]^-$. The representative structure of **7c** is shown in Figure 7. The anion is a metal-bridged[14] centrosymmetrical dinuclear complex with a coordination environment and geometry very similar to that observed in **5b**. These results indicate that both **2** and **4** form the same type of metal complexes. The dihedral angles between the six- and five-membered bonding faces of 25.5° in **7a** and 26.6° in **7c** are significantly larger than the corresponding values of 13.8° and 14.8° found in **5b**. Consequently, the C(1)−C(11) distances of 1.515(1) Å in **7a** and 1.495(2) Å in **7c** are statistically longer than those of 1.497(18) and 1.449(19) Å in **5b**, which might reflect some differences in conjugation between the two π systems.

Organolanthanide chloride complexes are generally useful starting materials for the synthesis of the corresponding complexes containing Ln−X (X = H, C, N, O, S, P, BH_4) bonds.[14,19] We examined the chemical properties of **5a** and **7a**. They were surprisingly inert toward nucleophiles such as $NaBH_4$, CH_3COONa, $Na[CH_3COCHCOCH_3]$, and $KOBu^t$ and toward chlorine-abstracting reagents such as AgOTf and $AgNO_3$. To help understand these results, the space-filling drawing of the anion in **7c** was generated using X-ray data (Figure 7). The figure clearly shows that the coordination sphere of the lanthanide ion is fully occupied by the surrounding ligands, which prevents the metal ion from any attack of nucleophiles.

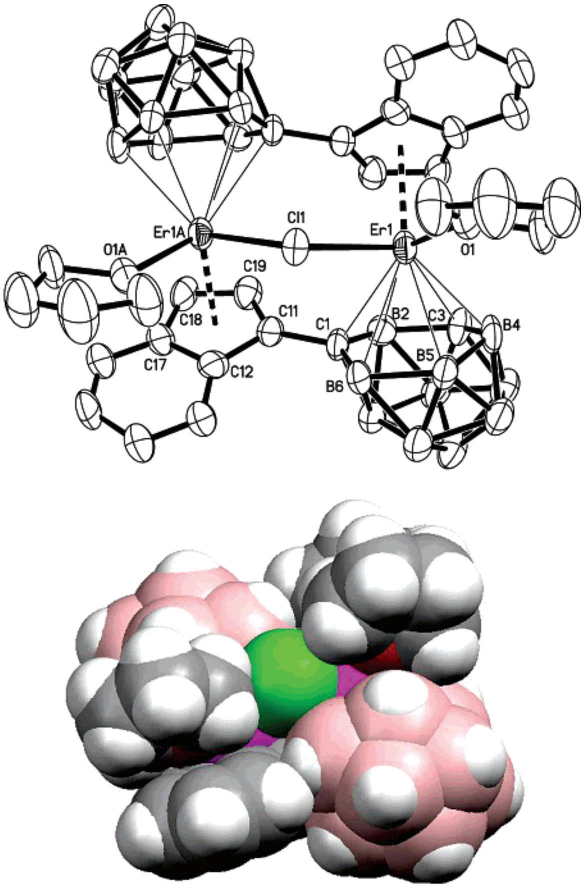


Figure 7. Top: Molecular structure of the anion in $[\{\eta^5:\eta^6\text{-}(1\text{-}C_9H_6)(C_2B_{10}H_{11})Er(THF)\}_2(\mu\text{-}Cl)][Na(THF)_3]$ (**7c**). Bottom: Space-filling drawing of the anion.

On the other hand, although the bridging Cl atom is accessible by Ag^+, such interactions may not be strong enough to break the Ln−Cl−Ln bonds.

To prepare derivatives of **7c**, an alternate synthetic route was desired. Reaction of **6** with $Er(BH_4)_3(THF)_3$ in a molar ratio of 1:2 in THF at room temperature gave the BH_4^--bridged dinuclear complex $\{[\eta^5:\eta^6\text{-}(1\text{-}C_9H_6)(C_2B_{10}H_{11})Er(THF)]_2(\mu\text{-}BH_4)\}\{Na(THF)_2\}$ (**8**) in 74% yield. Treatment of **8** with excess sodium metal in THF at room temperature afforded the BH_4^--free dinuclear complex $\{[\eta^5:\eta^7\text{-}(1\text{-}C_9H_6)(C_2B_{10}H_{11})Er(THF)]_2\}\text{-}\{Na_4(THF)_8\}$ (**9**) in 68% yield, as shown in Scheme 5. The formation of the insoluble $NaBH_4$ in THF facilitated the purification of **9**. Both **8** and **9** are paramagnetic complexes and do not provide interpretable NMR spectra. Their structures were, however, ultimately established by single-crystal X-ray diffraction studies.

Complex **8** adopts the polymeric structure in which the Na^+ ions serve as linkages to connect the dinuclear complex anions $[\{\eta^5:\eta^6\text{-}(1\text{-}C_9H_6)(C_2B_{10}H_{11})Er(THF)\}_2(\mu\text{-}BH_4)]^-$ to form zigzag infinite polymeric chains. Overall, the structure of the anion is similar to that observed in **7c** except for the bridging BH_4^- unit, as shown in Figure 8. The hydrogen atoms of the BH_4^- group cannot be located from X-ray data, which prevents the precise assignment of the coordination mode of the BH_4^- group. Since B(41) is almost located at the middle of the two Er atoms (Table 2), it is reasonable to suggest that the BH_4^- moiety bonds to the two Er atoms in the same coordination mode, which may be determined according to the Er−B distances. For η^2-BH_4^-, the Ln−B distances are normally in the range 2.65−2.78

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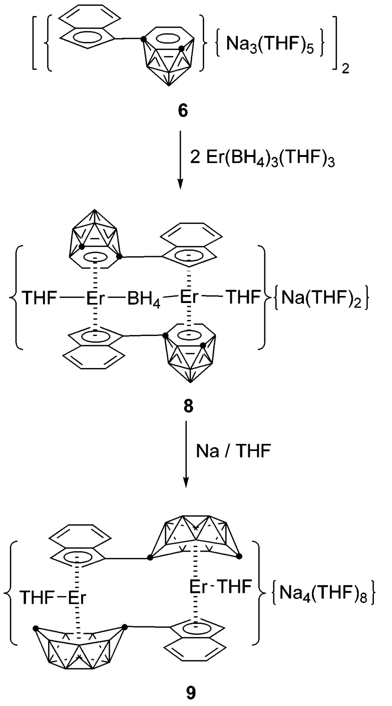
[19] (a) Edelmann, F. T.; Freckmann, D. M. M.; Schumann, H. *Chem. Rev.* **2002**, *102*, 1851. (b) Arndt, S.; Okuda, J. *Chem. Rev.* **2002**, *102*, 1953. (c) Marques, N.; Sella, A.; Takats, J. *Chem. Rev.* **2002**, *102*, 2137.

Scheme 5



Å.[7a,17a,20] In view of the Er−B(41) distances of 2.645(5) and 2.667(5) Å, it is best suggested that the BH_4^- group is η^2-bonded to two Er atoms to form a Er(μ-H)$_2$B(μ-H)$_2$Er unit.

The average Er−cage atom distance of 2.770(7) Å and Er−C_5 ring distance of 2.683(5) Å are very close to the corresponding values of 2.759(2) and 2.677(2) Å in **7c** (Table 2). The Cent6−Er−Cent5 angles of 128.0° and 127.4° are smaller than that of 132.5° in **7c**. The dihedral angles between the two bonding faces are 26.9° and 27.2°, which is almost the same as that of 26.6° observed in **7c**. As a result, the C(1)−C(11) distances of 1.513(7) and 1.490(7) Å are close to that of 1.495(2) Å found in **7c**.

An X-ray analysis revealed that **9** is a coordination polymer in which the Na^+ ions act as linkages to connect the complex anions $[\eta^5{:}\eta^7\text{-}(1\text{-}C_9H_6)(C_2B_{10}H_{11})Er(THF)]_2^{4-}$ to generate two-dimensional coordination sheets. The anion is a centrosymmetrical dinuclear complex, shown in Figure 9. Each Er atom is η^7-bound to the *arachno*-carboranyl, η^5-bound to the indenyl unit of the other ligand, and coordinated to one THF molecule in an almost trigonal planar geometry. Such an arrangement has not been observed before in lanthanacarboranes incorporating an *arachno*-carboranyl ligand.[1,10] The average Er−C_5 ring distance of 2.716(7) Å compares to that of 2.683(5) Å in **8** and 2.758(5) Å in $[\{\eta^5{:}\eta^7\text{-}[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Er\}_2\{Na_4(THF)_8\}]_n$.[5c] The Er−C(1,4) distances of 2.375(6) and 2.364(8) Å and the average Er−cage B distance of 2.703(8) Å are comparable to those of 2.386(5) and 2.655(7) Å in $[\{\eta^5{:}\eta^7\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})\}Er_2(\mu\text{-}Cl)(THF)_3]_2$,[2b,15] 2.410(6) and 2.671(7) Å in $[\{[\eta^5{:}\eta^7\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]Er\}_2\{Na_4(THF)_9\}]_n$,[5c] and 2.421(5) and 2.739(5) Å in $[\{\eta^5{:}\eta^7\text{-}[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Er\}_2\{Na_4(THF)_8\}]_n$.[2b,15]

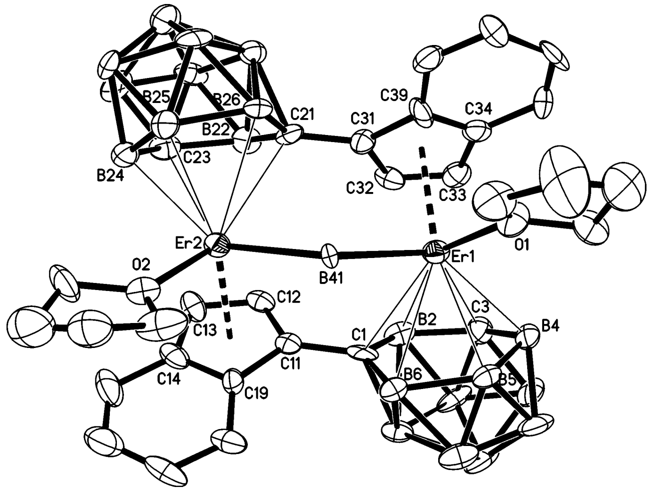


Figure 8. Molecular structure of the anion in $\{[\eta^5{:}\eta^6\text{-}(1\text{-}C_9H_6)(C_2B_{10}H_{11})Er(THF)]_2(\mu\text{-}BH_4)\}\{Na(THF)_2\}$ (**8**).

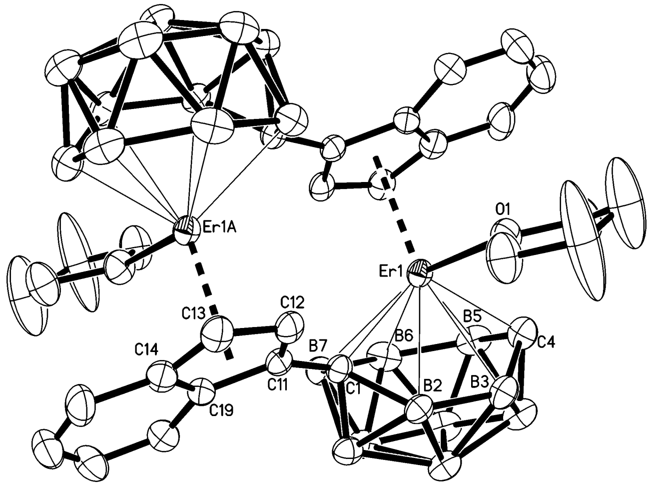


Figure 9. Molecular structure of the anion in $\{[\eta^5{:}\eta^7\text{-}(1\text{-}C_9H_6)(C_2B_{10}H_{11})Er(THF)]_2\}\{Na_4(THF)_8\}$ (**9**).

Conclusion

Two new directly attached carboranyl-indenyl ligands were synthesized and structurally characterized. They were readily converted into the trianions bearing an open six-membered C_2B_4 face and a C_5 ring that are directly connected to each other. The lack of the linkage between the two bonding faces makes these trianions highly constrained, favoring the formation of metal-bridged dinuclear complexes with lanthanides, for example, $[\{\eta^5{:}\eta^6\text{-}(C_9H_6)(C_2B_{10}H_{11})Ln(THF)\}_2(\mu\text{-}X)][Na(THF)_n]$. The *nido*-$C_2B_{10}H_{11}$ unit in these complexes was able to be further reduced to the *arachno*-$C_2B_{10}H_{11}$ ligand by Na metal. Accordingly, another type of metal-bridged dinuclear complex, $\{[\eta^5{:}\eta^7\text{-}(1\text{-}C_9H_6)(C_2B_{10}H_{11})Er(THF)]_2\}\{Na_4(THF)_8\}$, was prepared and structurally characterized. These results indicate that the coordination mode exhibited by the new ligands $[(C_9H_6)C_2B_{10}H_{11}]^{3-}$ is similar to that of the $[(C_5H_4)C_6H_5]^-$ ligand,[21] but is different from the single-atom-bridged systems $[A(C_9H_6)(C_2B_{10}H_{11})]^{3-}$ (A = Me_2C, Me_2Si).[1,10] The reactivity of $(C_9H_7)C_2B_{10}H_{11}$ is, however, very similar to that of $A(C_9H_6)(C_2B_{10}H_{11})$.[1,10]

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Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry nitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. $Li_2C_2B_{10}H_{10}$,[22] 2-indanone,[23] indene epoxide,[24] anhydrous $LnCl_3$,[25] and $Ln(BH_4)_3(THF)_3$[26] were prepared according to the literature methods. All other chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets prepared in the glovebox on a Perkin-Elmer 1600 Fourier transform spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300.13 and 75.47 MHz, respectively. ^{11}B NMR spectra were recorded on a Varian Inova 400 spectrometer at 128.32 MHz. All chemical shifts were reported in δ units with reference to the residual protons of the deuterated solvents for proton and carbon chemical shifts and to external $BF_3{\cdot}OEt_2$ (0.00 ppm) for boron chemical shifts. Elemental analyses were performed by MEDAC Ltd. Brunel University, Middlesex, U.K., or Shanghai Institute of Organic Chemistry, CAS, China.

Preparation of 2-(*o*-Carboranyl)-2-indanol (1). A 1.6 M solution of *n*-BuLi in *n*-hexane (13.0 mL, 20.8 mmol) was slowly added to a stirring solution of *o*-carborane (1.50 g, 10.4 mmol) in toluene/diethyl ether (2:1, 30 mL) at 0 °C, and the mixture was stirred at room temperature for 2 h. The resulting $Li_2C_2B_{10}H_{10}$ solution was then cooled to -78 °C, to which was added 2-indanone (1.37 g, 10.4 mmol) in one portion. The reaction mixture was stirred at -78 °C for 1 h, at -30 °C for 2 h, and then at room temperature overnight. This solution was quenched by adding 2 M hydrochloric acid (15 mL). The organic layer was separated and washed by water (15 mL), saturated $NaHCO_3$ aqueous solution (15 mL), and brine (15 mL) and then dried with anhydrous Na_2SO_4. After removal of the solvent, column chromatographic separation (silicon gel, 230−400 mesh) using hexane/acetone (5:1 in v/v) as eluent afforded **1** (890 mg, 31%) and *o*-carborane (840 mg, 56%) all as a white solid. Recrystallization from *n*-hexane/diethyl ether gave X-ray-quality crystals of **1**, mp 110−111 °C. ^1H NMR ($CDCl_3$): δ 7.26 (m, 4H) (aromatic), 4.29 (s, 1H) (C*H* of cage), 3.52 (d, $^2J = 16.2$ Hz, 2H) (C*H*$_2$), 2.97 (d, $^2J = 16.2$ Hz, 2H) (C*H*$_2$), 2.42 (brs, 1H) (O*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 139.0, 127.5, 125.0 (aromatic *H*), 81.8, 80.1 (cage *C*), 59.4 (*C*-OH), 48.8 (*C*H$_2$). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ -3.8 (2B), -9.3 (2B), -11.9 (2B), -13.7 (4B). IR (KBr, cm^{-1}): ν 3571 (brs), 3065 (s), 2627 (vs), 2579 (vs), 2549 (vs), 1479 (m), 1223 (m), 1184 (m), 1092 (m), 1049 (m), 748 (vs), 723 (s). Anal. Calcd for $C_{11}H_{20}B_{10}O$ (**1**): C, 47.80; H, 7.29. Found: C, 47.44; H, 7.31.

Preparation of 2-(*o*-Carboranyl)indene (2). Compound **1** (552 mg, 2.0 mmol) and *p*-TsOH (344 mg, 2.0 mmol) were mixed in a glass tube. The tube was sealed and heated at 180 °C for 10 min. The resulting black residue was dissolved in diethyl ether (10 mL). The solution was washed with water (15 mL), saturated $NaHCO_3$ aqueous solution (15 mL), and brine (15 mL) and then dried with anhydrous Na_2SO_4. Removal of the solvent afforded a pale brown solid. Column chromatographic separation (silicon gel, 230−400 mesh) using hexane as eluent afforded **2** as a white solid (433 mg, 84%). Recrystallization from *n*-hexane gave X-ray-quality crystals of **2**, mp 116−117 °C. ^1H NMR ($CDCl_3$): δ 7.41 (m, 2H), 7.31 (m, 2H) (aromatic), 7.02 (s, 1H) (vinyl), 3.89 (s, 1H) (C*H* of cage), 3.54 (s, 2H) (C*H*$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.5, 142.3, 139.9, 133.9, 127.2, 126.6, 123.8, 122.0 (aromatic and vinyl), 73.6 (cage *C*), 61.4 (cage *C*H), 42.0 (*C*H$_2$). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ -3.1 (1B), -5.6 (1B), -10.1 (2B), -11.9 (2B), -12.4 (2B), -13.9 (2B). IR (KBr, cm^{-1}): ν 3057 (s), 2607 (vs), 1457 (m), 1385 (m), 1065 (m), 1014 (m), 916 (m), 868 (m), 727 (s). Anal. Calcd for $C_{11}H_{18}B_{10}$ (**2**): C, 51.14; H, 7.02. Found: C, 51.23; H 7.11.

Preparation of 1-(*o*-Carboranyl)-2-indanol (3). A 1.6 M solution of *n*-BuLi in *n*-hexane (13.0 mL, 20.8 mmol) was slowly added to a stirring solution of *o*-carborane (1.50 g, 10.4 mmol) in diethyl ether (30 mL) at 0 °C, and the reaction mixture was stirred at room temperature for 2 h. The resulting $Li_2C_2B_{10}H_{10}$ solution was then cooled to -78 °C, to which was added indene epoxide (1.37 g, 10.4 mmol) in one portion. The reaction mixture was stirred overnight at room temperature and then quenched by adding 2 M hydrochloric acid (15 mL). The organic layer was separated and washed by water (15 mL), saturated $NaHCO_3$ aqueous solution (15 mL), and brine (15 mL) and then dried with anhydrous Na_2SO_4. After removal of the solvent, column chromatographic separation (silicon gel, 230−400 mesh) using hexane/acetone (5:1 v/v) as eluent afforded **3** as a white solid (2.35 g, 82%). Recrystallization from *n*-hexane/diethyl ether gave X-ray-quality crystals of **3**, mp 165−167 °C. ^1H NMR ($CDCl_3$): δ 7.31 (m, 4H) (aromatic), 4.77 (d, $^3J = 5.1$ Hz, 1H) (C*H*OH), 3.88 (s, 1H) (C*H*), 3.58 (s, 1H) (C*H* of cage), 3.45 (dd, $^2J = 17.1$ and $^3J = 5.1$ Hz, 1H) (C*H*$_2$), 2.81 (d, $^2J = 17.1$ Hz, 1H) (C*H*$_2$), 1.72 (s, 1H) (O*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 141.6, 138.5, 129.4, 127.3, 126.4, 126.3 (aromatic), 78.4 (cage *C*H), 75.9 (cage *C*), 60.0 (*C*H), 59.8 (*C*H), 41.2 (*C*H$_2$). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ -2.2 (1B), -4.1 (1B), -8.6 (2B), -11.0 (3B), -13.2 (3B). IR (KBr, cm^{-1}): ν 3335 (brs), 2585 (vs), 1620 (m), 1439 (m), 1038 (m), 927 (m), 737 (m), 517 (m). Anal. Calcd for $C_{11}H_{20}B_{10}O$ (**3**): C, 47.80; H, 7.29. Found: C, 47.83; H, 7.21.

Preparation of 1-(*o*-Carboranyl)indene (4). Compound **3** (1.38 g, 5.0 mmol) was dissolved in 20 mL of toluene, to which was added triphenylphosphine (1.57 g, 6.0 mmol) and imidazole (680 mg, 10.0 mmol). The suspension was stirred at room temperature until a clear solution was obtained. Iodine powder (1.65 g, 6.5 mmol) was then added in several portions. The reaction mixture was stirred at room temperature for 1 h and heated to reflux for 48 h. The resulting solid was removed by filtration. The clear filtrate was washed with 5% H_2O_2 (15 mL), water (15 mL), 2 M hydrochloric acid (15 mL), water (15 mL), saturated $Na_2S_2O_3$ aqueous solution (15 mL), saturated $NaHCO_3$ aqueous solution (15 mL), and brine (15 mL), respectively, and dried with anhydrous Na_2SO_4. Removal of the solvent afforded a brown oil. Column chromatographic separation (silicon gel, 230−400 mesh) using *n*-hexane as eluent produced **4** as a white solid (1.01 g, 78%). Recrystallization from *n*-hexane gave X-ray-quality crystals of **4**, mp 136−137 °C. ^1H NMR ($CDCl_3$): δ 7.76 (d, $^3J = 7.8$ Hz, 1H), 7.48 (d, $^3J = 7.8$ Hz, 1H), 7.33 (m, 2H) (aromatic), 6.84 (t, $^3J = 2.1$ Hz, 1H) (vinyl), 4.14 (s, 1H) (C*H* of cage), 3.41 (d, $^3J = 2.1$ Hz, 2H) (C*H*$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 144.2, 140.8, 137.3, 137.0, 126.5, 125.8, 124.4, 121.1 (aromatic and vinyl), 72.2 (cage *C*), 60.7 (cage *C*H), 37.6 (*C*H$_2$). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ -2.2 (1B), -3.6 (1B), -9.0 (2B), -10.9 (4B), -13.0 (2B). IR (KBr, cm^{-1}): ν 3077 (m), 2578 (vs), 1452 (m), 1370 (m), 1068 (m), 1008 (m), 927 (m), 814 (m), 734 (s). Anal. Calcd for $C_{11}H_{18}B_{10}$ (**4**): C, 51.14; H, 7.02. Found: C, 50.98; H, 7.17.

Preparation of $[\{\eta^5{:}\eta^6\text{-}(2\text{-}C_9H_6)(C_2B_{10}H_{11})Y(THF)\}_2(\mu\text{-}Cl)][Na(THF)_6]$ (5a). A suspension of **2** (129 mg, 0.5 mmol) and finely cut sodium metal (115 mg, 5.0 mmol) in THF (5 mL) was stirred at room temperature for 24 h. After removal of excess Na metal, the clear solution was added dropwise to a suspension of YCl_3 (98 mg, 0.5 mmol) in THF (3 mL). The mixture was then stirred at room temperature for 2 days. After removal of the precipitate, the resulting clear solution was concentrated to ca. 3 mL, to which was added *n*-hexane (1 mL). Complex **5a** was collected as yellow crystals after this solution stood at room temperature for a week

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Table 3. Crystal Data and Summary of Data Collection and Refinement for 1−4 and 6

	1	**2**	**3**	**4**	**6**
formula	$C_{11}H_{20}B_{10}O$	$C_{11}H_{18}B_{10}$	$C_{11}H_{20}B_{10}O$	$C_{11}H_{18}B_{10}$	$C_{62}H_{114}B_{20}Na_6O_{10}$
cryst size (mm)	0.30 × 0.20 × 0.10	1.30 × 0.80 × 0.20	0.20 × 0.15 × 0.10	0.10 × 0.08 × 0.05	0.30 × 0.20 × 0.10
fw	276.37	258.35	276.37	258.35	1373.67
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	*Pbca*	*C*2/*c*	$P2_1/c$	$P\bar{1}$
a, Å	7.885(1)	12.864(1)	22.706(1)	7.171(1)	10.677(2)
b, Å	12.196(1)	12.908(1)	13.057(1)	19.546(1)	13.460(3)
c, Å	16.717(1)	18.120(1)	21.107(1)	10.775(1)	15.145(3)
α, deg	90	90	90	90	100.01(3)
β, deg	102.45(1)	90	90.13(1)	98.13 (1)	108.77(3)
γ, deg	90	90	90	90	100.24(3)
V, Å^3	1569.9(2)	3008.8(2)	6257.9(5)	1494.9(2)	1964.7(7)
Z	4	8	16	4	1
D_{calcd}, Mg/m^3	1.169	1.141	1.173	1.148	1.161
radiation (*λ*), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2*θ* range, deg	4.2 to 56.0	4.5 to 56.0	3.6 to 50.0	4.2 to 50.0	2.9 to 48.0
μ, mm^{-1}	0.061	0.054	0.061	0.055	0.099
F(000)	576	1072	2304	536	732
no. of obsd reflns	3774	3615	5508	2639	4556
no. of params refnd	200	190	397	190	491
goodness of fit	1.023	1.039	1.091	1.049	1.115
R1	0.060	0.058	0.063	0.062	0.099
wR2	0.174	0.163	0.180	0.159	0.263

Table 4. Crystal Data and Summary of Data Collection and Refinement for 5b·0.5THF, 7a, 7c, 8·C_7H_8, and 9

	5b·0.5THF	**7a**	**7c**	**8**·C_7H_8	**9**
formula	$C_{56}H_{102}B_{20}ClEr_2NaO_{8.5}$	$C_{42}H_{74}B_{20}ClNaO_5Y_2$	$C_{42}H_{74}B_{20}ClEr_2NaO_5$	$C_{45}H_{78}B_{21}Er_2NaO_4$	$C_{62}H_{114}B_{20}Er_2Na_4O_{10}$
cryst size (mm)	0.50 × 0.45 × 0.30	0.30 × 0.20 × 0.10	0.30 × 0.20 × 0.10	0.20 × 0.15 × 0.10	0.40 × 0.30 × 0.20
fw	1520.54	1111.47	1268.17	1267.59	1662.21
cryst syst	monoclinic	orthorhombic	orthorhombic	orthorhombic	monoclinic
space group	*C*2/*c*	*Fddd*	*Fddd*	*Fdd*2	$P2_1/n$
a, Å	45.890(4)	17.493(8)	17.547(8)	33.105(6)	16.917(2)
b, Å	10.949(1)	34.279(1)	34.651(2)	40.435(7)	13.113(2)
c, Å	35.572(3)	46.193(2)	46.269(2)	17.226(3)	17.237(2)
β, deg	121.65(1)	90	90	90	101.29(1)
V, Å^3	15216(2)	27699(2)	28133(2)	23059(7)	3749.7(9)
Z	8	16	16	16	2
D_{calcd}, Mg/m^3	1.328	1.066	1.198	1.461	1.472
radiation (*λ*), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2*θ* range, deg	2.1 to 54.0	3.7 to 48.0	2.7 to 50.0	2.8 to 50.0	3.1 to 50.0
μ, mm^{-1}	2.277	1.745	2.447	2.939	2.299
F(000)	6160	9152	10 080	10 112	1692
no. of obsd reflns	13 357	5439	6208	10 117	6603
no. of params refnd	725	313	313	658	465
goodness of fit	1.024	0.946	0.978	1.044	1.098
R1	0.083	0.087	0.072	0.067	0.039
wR2	0.242	0.275	0.232	0.153	0.105

(232 mg, 66%), mp 82 °C (dec). ^{1}H NMR (pyridine-d_5): δ 8.12 (s, 2H), 7.96 (d, $^3J = 8.1$ Hz, 2H), 7.03 (t, $^3J = 8.1$ Hz, 2H), 6.97 (s, 2H), 6.73 (t, $^3J = 8.1$ Hz, 2H), 6.24 (d, $^3J = 8.1$ Hz, 2H) (indenyl), 4.07 (s, 2H) (C*H* of cage), 3.64 (s, 32H), 1.61 (s, 32H) (THF). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 145.2, 133.3, 129.0, 126.1, 124.3, 122.1, 121.5, 103.5, 98.5 (indenyl), 54.4 (cage *C*H), 67.2, 25.1 (THF). ^{11}B{^{1}H} NMR (pyridine-d_5): δ 9.1 (2B), 2.0 (4B), −4.7 (8B), −8.3 (4B), −12.9 (2B). IR (KBr, cm^{-1}): ν 2965 (s), 2876 (s), 2525 (vs), 1454 (m), 1351 (m), 1105 (m), 1046 (s), 865 (m), 813 (m), 744 (m), 627 (m). Anal. Calcd for $C_{44}H_{78}B_{20}ClNaO_{5.5}Y_2$ (**5a** − 2.5THF): C, 46.05; H, 6.85. Found: C, 45.59; H, 7.20.

Preparation of [{η^5:η^6-(2-C_9H_6)($C_2B_{10}H_{11}$)Er(THF)}$_2$(μ-Cl)][Na(THF)$_6$]·0.5THF (5b·0.5THF). This complex was prepared as red crystals from $ErCl_3$ (137 mg, 0.5 mmol) and **2** (129 mg, 0.5 mmol) using procedures identical to those used in the synthesis of **5a** (273 mg 72%), mp 106 °C (dec). ^{1}H NMR (pyridine-d_5): δ 3.61 (s), 1.50 (s) (THF), and many other unresolved peaks. ^{11}B{^{1}H} NMR (pyridine-d_5): many broad, unresolved resonances. IR (KBr, cm^{-1}): ν 2966 (s), 2877 (s), 2527 (vs), 1455 (m), 1351 (m), 1108 (m), 1042 (s), 857 (m), 816 (m), 744 (m), 627 (m). Anal. Calcd for $C_{38}H_{66}B_{20}ClEr_2NaO_4$ (**5b** − 4THF): C, 38.16; H, 5.56. Found: C, 37.86; H, 5.99.

Preparation of [{η^5:η^6-(1-C_9H_6)($C_2B_{10}H_{11}$)}{Na_3(THF)$_5$}]$_2$ (6). A suspension of **4** (129 mg, 0.5 mmol) and finely cut sodium metal (115 mg, 5.0 mmol) in THF (5 mL) was stirred at room temperature for 24 h. After removal of excess Na metal, the clear solution was concentrated to ca. 5 mL, to which was added *n*-hexane (2 mL). Complex **6** was obtained as yellow-green crystals after this solution stood at room temperature for a week (316 mg, 92%), mp 76 °C (dec). ^{1}H NMR (pyridine-d_5): δ 8.94 (d, $^3J = 7.8$ Hz, 2H), 7.85 (d, $^3J = 7.8$ Hz, 2H), 7.81 (d, $^3J = 3.3$ Hz, 2H), 6.95 (t, $^3J = 6.9$ Hz, 2H), 6.82 (t, $^3J = 6.9$ Hz, 2H), 6.55 (d, $^3J = 3.3$ Hz, 2H) (indenyl), 3.68 (m, 40H) (THF), 2.70 (s, 2H) (C*H* of cage), 1.63 (m, 40H) (THF). ^{13}C NMR (pyridine-d_5): δ 131.8, 127.3, 124.3, 120.6, 120.1, 118.6, 112.9, 112.7, 94.4 (indenyl), 67.2 (THF), 42.5 (cage *C*H), 25.1 (THF). ^{11}B NMR (pyridine-d_5): δ −2.5 (6B), −10.3 (8B), −20.8 (6B). IR (KBr, cm^{-1}): ν 2968 (m), 2867 (m), 2522 (vs), 1431 (m), 1048 (vs), 907 (m), 736 (m). Anal. Calcd for $C_{58}H_{106}B_{20}Na_6O_9$ (**6** − THF): C, 53.52; H, 8.21. Found: C, 53.18; H 8.37.

Preparation of [{η^5:η^6-(1-C_9H_6)($C_2B_{10}H_{11}$)Y(THF)}$_2$(μ-Cl)][Na(THF)$_3$] (7a). A solution of **6** (343 mg, 0.25 mmol) in THF (5 mL) was added dropwise to a suspension of YCl_3 (98 mg, 0.5 mmol) in THF (3 mL). The mixture was then stirred at room temperature for 2 days. After removal of the precipitate, the resulting clear solution was concentrated to ca. 3 mL, to which was added *n*-hexane (1 mL). Complex **7a** was collected as yellow crystals after this solution stood at room temperature for 2 days (208 mg, 75%), mp 158 °C (dec). ^{1}H NMR (pyridine-d_5): δ 8.61 (d, $^3J = 8.4$ Hz, 2H), 8.53 (d, $^3J = 3.3$ Hz, 2H), 7.25 (d, $^3J = 8.4$ Hz, 2H), 7.06 (d, $^3J = 3.3$ Hz, 2H), 6.30 (t, $^3J = 7.2$ Hz, 2H), 6.19 (t, $^3J = 7.2$ Hz, 2H) (indenyl), 4.26 (s, 2H) (C*H* of cage), 3.64 (m, 20H), 1.60 (m, 20H) (THF). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 130.6, 129.4, 128.7, 128.0, 127.0, 125.5, 118.7, 100.3 (indenyl), 54.0 (cage *C*H), 67.2, 25.1 (THF). ^{11}B{^{1}H} NMR (pyridine-d_5): δ 2.0 (2B), −0.8 (2B), −4.7 (4B), −7.0 (4B), −9.7 (2B), −12.9 (2B), −15.6 (2B), −17.9 (2B). IR (KBr, cm^{-1}): ν 2951 (s), 2528 (vs), 1439 (m), 1035 (s), 878 (m), 756 (m). Anal. Calcd for $C_{42}H_{74}B_{20}ClNaO_5Y_2$ (**7a**): C, 45.39; H, 6.71. Found: C, 45.44; H, 7.06.

Preparation of [{η^5:η^6-(1-C_9H_6)($C_2B_{10}H_{11}$)Nd(THF)}$_2$(μ-Cl)]-[Na(THF)$_3$] (7b). This complex was prepared as orange crystals from $NdCl_3$ (125 mg, 0.5 mmol) and **6** (343 mg, 0.25 mmol) using procedures identical to those used in the synthesis of **7a** (247 mg 81%), mp 148 °C (dec). ^{1}H NMR (pyridine-d_5): δ 3.66 (s), 1.62 (s) (THF), and many other unresolved peaks. ^{11}B{^{1}H} NMR (pyridine-d_5): many broad, unresolved resonances. IR (KBr, cm^{-1}): ν 2954 (s), 2881 (s), 2528 (vs), 1434 (m), 1037 (s), 877 (m), 753 (m). Anal. Calcd for $C_{42}H_{74}B_{20}ClNaNd_2O_5$ (**7b**): C, 41.28; H, 6.10. Found: C, 41.50; H, 6.34.

Preparation of [{η^5:η^6-(1-C_9H_6)($C_2B_{10}H_{11}$)Er(THF)}$_2$(μ-Cl)]-[Na(THF)$_3$] (7c). This complex was prepared as red crystals from $ErCl_3$ (137 mg, 0.5 mmol) and **6** (343 mg, 0.25 mmol) using procedures identical to those used in the synthesis of **7a** (263 mg 83%), mp 166 °C (dec). ^{1}H NMR (pyridine-d_5): δ 3.63 (s), 1.50 (s) (THF), and many other unresolved peaks. ^{11}B{^{1}H} NMR (pyridine-d_5): many broad, unresolved resonances. IR (KBr, cm^{-1}): ν 2945 (s), 2525 (vs), 1447 (m), 1029 (s), 875 (m), 752 (m). Anal. Calcd for $C_{40}H_{70}B_{20}ClEr_2NaO_{4.5}$ (**7c** − 0.5THF): C, 38.99; H, 5.73. Found: C, 39.21; H, 5.78.

Preparation of {[η^5:η^6-(1-C_9H_6)($C_2B_{10}H_{11}$)Er(THF)]$_2$(μ-BH_4)}-{Na(THF)$_2$}·C_7H_8 (8·C_7H_8). This complex was prepared as yellow crystals from $Er(BH_4)_3(THF)_3$ (214 mg, 0.5 mmol) and **6** (343 mg, 0.25 mmol) using procedures identical to those used in the synthesis of **7a** (234 mg 74%), mp 115 °C (dec). ^{1}H NMR (pyridine-d_5): δ 3.62 (s), 1.52 (s) (THF), and many other unresolved peaks. ^{11}B-{^{1}H} NMR (pyridine-d_5): many broad, unresolved resonances. IR (KBr, cm^{-1}): ν 2966 (s), 2876 (s), 2533 (vs), 2440 (s), 1439 (s), 1375 (m), 1219 (m), 1139 (m), 1045 (s), 1003 (s), 904 (m), 852 (s), 750 (s), 680 (m). Anal. Calcd for $C_{32}H_{58}B_{21}Er_2NaO_{2.5}$ (**8** − 1.5THF): C, 36.01; H, 5.48. Found: C, 35.57; H, 5.82.

Preparation of {[η^5:η^7-(1-C_9H_6)($C_2B_{10}H_{11}$)Er(THF)]$_2$}{Na_4-(THF)$_8$} (9). A suspension of **8**·C_7H_8 (158 mg, 0.13 mmol) and finely cut sodium metal (46 mg, 2.0 mmol) in THF (5 mL) was stirred at room temperature for 2 days. After removal of excess Na metal, the clear solution was concentrated to ca. 3 mL, to which was added *n*-hexane (1 mL). Complex **9** was obtained as yellow crystals after this solution stood at room temperature for 2 days (141 mg, 68%), mp 162 °C (dec). ^{1}H NMR (pyridine-d_5): δ 3.84 (s), 1.82 (s) (THF), and many other unresolved peaks. ^{11}B{^{1}H} NMR (pyridine-d_5): many broad, unresolved resonances. IR (KBr, cm^{-1}): ν 2962 (s), 2870 (s), 2407 (vs), 1454 (m), 1326 (m), 1199 (m), 1123 (m), 1048 (s), 901 (s), 741 (s). Anal. Calcd for $C_{46}H_{82}B_{20}$-$Er_2Na_4O_6$ (**9** − 4THF): C, 40.22; H, 6.02. Found: C, 39.89; H, 6.10.

X-ray Structure Determination. All single crystals were immersed in Paraton-N oil and sealed under nitrogen in thin-walled glass capillaries. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation. An empirical absorption correction was applied using the SADABS program.[27] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares on F^2 using the SHELXTL program package.[28] All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements are given in Tables 3 and 4, respectively. Further details are included in the Supporting Information.

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Supporting Information Available: Crystallographic data in CIF format for **1**−**4**, **5b**, **6**, **7a**, **7c**, **8**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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