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Synthesis and Structural Characterization of Constrained-Geometry Organolanthanide Chlorides and Alkyls Incorporating the Ligand $[\eta^5:\sigma\text{-}(C_9H_6)C_2B_{10}H_{10}]^{2-}$

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Interaction of 1-indenyl-1,2-carborane (**1**) with 2 equiv of KH in refluxing THF gave the dipotassium salt $[K_2][(C_9H_6)C_2B_{10}H_{10}]$. Treatment of $[K_2][(C_9H_6)C_2B_{10}H_{10}]$ with 1 equiv of $LnCl_3$ in THF generated the ionic complex $[K(THF)_6][\{\eta^5:\sigma\text{-}(C_9H_6)C_2B_{10}H_{10}\}_2La(THF)]$ (**2**) for early lanthanide or organolanthanide chloride complexes $[\{\eta^5:\sigma\text{-}(C_9H_6)C_2B_{10}H_{10}\}Ln(THF)_2(\mu\text{-}Cl)_2K(THF)_2]_2$ (Ln = Y (**3a**), Gd (**3b**), Er (**3c**), Yb (**3d**)) for late lanthanides. Reaction of **3** with nucleophile NaCp or $KCH_2C_6H_4\text{-}o\text{-}NMe_2$ afforded the corresponding salt metathesis products $[\eta^5:\sigma\text{-}(C_9H_6)C_2B_{10}H_{10}]Ln(\eta^5\text{-}C_5H_5)(THF)_2$ (Ln = Y (**4a**), Gd (**4b**)) or $[\eta^5:\sigma\text{-}(C_9H_6)C_2B_{10}H_{10}]Ln(CH_2C_6H_4\text{-}o\text{-}NMe_2)(DME)$ (Ln = Y (**5a**), Er (**5c**)), respectively. Complexes **5** were also synthesized via the alkane elimination reaction of 1-indenyl-1,2-carborane with $Ln(CH_2C_6H_4\text{-}o\text{-}NMe_2)_3$. They represent the first examples of organolanthanide alkyl complexes incorporating a carboranyl ligand. These complexes were fully characterized by various spectroscopic techniques and elemental analyses. Some were further confirmed by single-crystal X-ray analyses.

Introduction

Ligands impose a dominant control over both chemical and physical properties of the resulting metal complexes.[1,2] Organometallics with constrained-geometry ligands have found wide interest in both academia and industry since 1990.[2,3] Catalytic systems based on such compounds give access to a large array of polymers with unique material properties and considerable commercial value.[2,4] However, constrained-geometry organolanthanides are relatively less studied,[2b,c,5] compared with their group 4 analogs.[2,6] In this connection, a series of single-atom-bridged indenyl-carboranyl ligands of the type $A(C_9H_7)(C_2B_{10}H_{11})$ (A = Me_2C,[7] Me_2Si, [8] *i*Pr_2NB, [9] *i*Pr_2NP[10]) have been developed to study the linkage effect (*ansa* effect) on the formation of organolanthanide chloride complexes.[7−11] The results show that only the $[{}^iPr_2NP(C_9H_6)C_2B_{10}H_{10}]^{2-}$ ligand can suppress the ligand redistribution reaction, leading to the formation of organolanthanide chlorides (Ln = Y, Er),[10] probably due to the joint effect of a tetrahedral geometry of the P atom and bulky ${}^iPr_2N$ substituent. As an ongoing project, we recently reported a directly linked indenyl-carboranyl compound, 1-indenyl-1,2-carborane.[12] Its tri-anion $[7\text{-}C_9H_6\text{-}7,9\text{-}nido\text{-}C_2B_{10}H_{11}]^{3-}$ and penta-anion $[7\text{-}C_9H_6\text{-}7,10\text{-}arachno\text{-}C_2B_{10}H_{11}]^{5-}$ have demonstrated a very similar coordination mode to that of $[C_6H_5(C_5H_4)]^-$ in lanthanide chemistry, which favors the formation of "metal-bridged" complexes.[12] In sharp contrast, $[Me_2E(C_9H_6)(nido\text{-}C_2B_{10}H_{11})]^{3-}$ and $[Me_2E(C_9H_6)(arachno\text{-}C_2B_{10}H_{11})]^{5-}$ (E = C, Si) prefer the formation of "chelating

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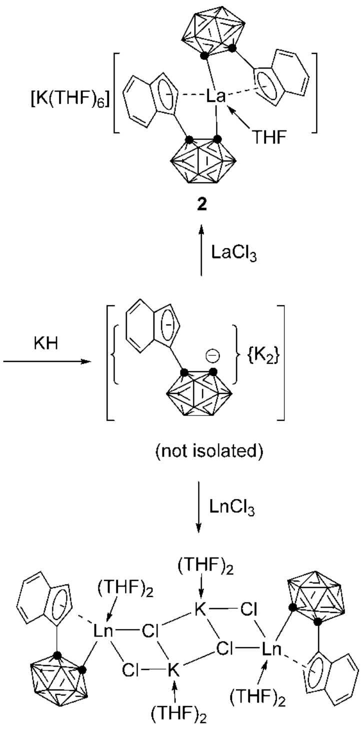
Scheme 1



Ln = Y (**3a**), Gd (**3b**), Er (**3c**), Yb (**3d**)

type" organolanthanides.[8,11,13] These results prompted us to investigate the coordination chemistry of the dianion $[1\text{-}C_9H_6\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10}]^{2-}$. It is found that this dianion can unexpectedly stabilize late organolanthanide chloride complexes, leading to the successful preparation of the first organolanthanide alkyl complexes incorporating a carboranyl ligand. These findings are reported in this article.

Results and Discussion

Organolanthanide Chlorides. Treatment of $1\text{-}C_9H_7\text{-}1,2\text{-}C_2B_{10}H_{11}$ (**1**) with 2 equiv of ^{n}BuLi in THF yielded presumably the dilithium salt $[Li_2][(C_9H_6)C_2B_{10}H_{10}]$. Reaction of this salt with various $LnCl_3$ in THF led to the formation of organolanthanide complexes that could not be isolated in the pure form probably due to the high solubility of LiCl in THF. Other group 1 metal salts were then examined. The ^{11}B NMR spectrum showed that NaH cannot convert **1** to the dianion. On the other hand, KH can react well with **1** to generate the corresponding dipotassium salt $[K_2][(C_9H_6)C_2B_{10}H_{10}]$. In the following experiments, $[K_2][(C_9H_6)C_2B_{10}H_{10}]$ was prepared *in situ* by heating a THF solution of **1** and 2 equiv of KH to reflux for 2 h until the completion of the reaction as monitored by the ^{11}B NMR spectrum. Treatment of $[K_2][(C_9H_6)C_2B_{10}H_{10}]$ with 1 equiv of anhydrous $LaCl_3$ in THF afforded, after recrystallization from THF/*n*-hexane, the ionic complex $[K(THF)_6][\{\eta^5{:}\sigma\text{-}(C_9H_6)C_2B_{10}H_{10}\}_2La(THF)]$ (**2**) in 60% isolated yield, as shown in Scheme 1. No organolanthanum chloride species was isolated, but it might serve as an intermediate that subsequently underwent ligand redistribution to give **2**.[14] The larger radius of the La atom could be responsible for such a ligand redistribution reaction. In contrast, reaction of $[K_2][(C_9H_6)C_2B_{10}H_{10}]$ with 1 equiv of late lanthanide trichloride $LnCl_3$ produced, after recrystallization from THF/*n*-hexane, organolanthanide chlorides $[\{\eta^5{:}\sigma\text{-}(C_9H_6)C_2B_{10}H_{10}\}Ln(THF)_2(\mu\text{-}Cl)_2K(THF)_2]_2$ (Ln = Y (**3a**), Gd (**3b**), Er (**3c**), Yb (**3d**)) in 42−62% isolated yields (Scheme 1). It is noteworthy that reactions of $LnCl_3$ with $[Me_2E(C_9H_6)(C_2B_{10}H_{10})]^{2-}$ (E = C, Si) always generated $\{Ln[\eta^5{:}\sigma\text{-}Me_2E(C_9H_6)(C_2B_{10}H_{10})]_2\}^-$ (E = C, Si) regardless of the sizes of the lanthanides.[7,11] The stability of complexes **3** may be ascribed to the high rigidity of the ligand. Complexes **2** and **3** are soluble in THF and pyridine, but insoluble in toluene and *n*-hexane.

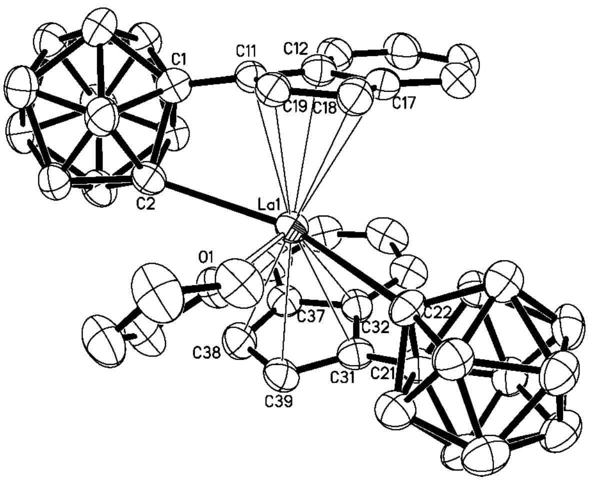


Figure 1. Molecular structure of the anion in $[K(THF)_6][\{\eta^5{:}\sigma\text{-}(C_9H_6)C_2B_{10}H_{10}\}_2La(THF)]$ (**2**) (thermal ellipsoids drawn at the 30% probability level).

The ^{1}H NMR spectrum of **2** clearly showed two sets of indenyl resonances in the range 8.0−6.3 ppm and the THF signals at 3.65 and 1.62 ppm. Its ^{13}C NMR spectrum was consistent with the ^{1}H NMR result. A 1:1:8 pattern was observed in its ^{11}B NMR spectrum. On the other hand, the ^{1}H NMR spectrum of the diamagnetic complex **3a** exhibited two doublets at 8.53 and 7.62 ppm with $J = 7.2$ Hz and two triplets at 7.19 and 7.09 ppm with $J = 7.2$ Hz for the protons on the six-membered ring, two doublets at 7.53 and 6.65 ppm with $J = 4.5$ Hz assignable to the two protons on the five-membered ring, and two THF resonances at 3.64 and 1.60 ppm. The ^{11}B NMR spectrum displayed a 1:4:4:1 pattern. The NMR spectra of **3b**,**c**,**d** displayed broad and unresolved resonances due to the paramagnetism. The compositions of **2** and **3** were further confirmed by elemental analyses.

Single-crystal X-ray diffraction study revealed that **2** has an ionic structure consisting of well-separated, alternating layers of octahedral cations $[K(THF)_6]^+$ and five-coordinated anions $[\{\eta^5{:}\sigma\text{-}(C_9H_6)C_2B_{10}H_{10}\}_2La(THF)]^-$. In the anion, the La atom is η^5-bound to two indenyl, σ-bound to two cage carbon atoms, and coordinated to a THF molecule in a highly distorted square-pyramidal geometry (Figure 1). For easy comparison, key

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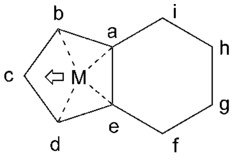
Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2, 3a, 3b, and 5a

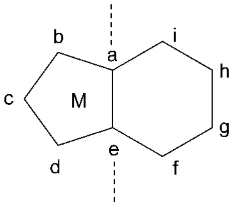
	2	**3a**	**3b**	**5a**[a]
(Ln)	(La)	(Y)	(Gd)	(Y)
$C_{cage}-C_{cage}$	1.76(1)	1.71(1)	1.719(7)	1.73(1)[1.71(1)]
$C_{cage}-C_{Ind}$[b]	1.53(1)	1.49(1)	1.495(6)	1.49(1)[1.51(1)]
$Ln-C_{cage}$	2.840(8)	2.641(8)	2.672(5)	2.63(1)[2.59(1)]
$Ln-C_5$[c]	3.055(8)	2.864(8)	2.860(5)	2.87(1)[2.90(1)]
	3.006(8)	2.835(8)	2.816(5)	2.79(1)[2.80(1)]
	2.946(8)	2.740(8)	2.773(5)	2.78(1)[2.81(1)]
	2.867(8)	2.636(8)	2.673(5)	2.65(1)[2.64(1)]
	2.812(8)	2.625(8)	2.646(5)	2.61(1)[2.62(1)]
av $Ln-C_5$[c]	2.936(8)	2.740(8)	2.754(5)	2.74(1)[2.75(1)]
Ln−Cent[d]	2.670	2.465	2.477	2.459[2.472]
$Ln-C_{alkyl}$				2.36(1)[2.40(1)]
Ln−Cl		2.605(2)	2.655(1)	
		2.624(2)	2.674(1)	
$C_{cage}-C_{cage}-Ln$	92.0(4)	92.2(4)	92.1(2)	90.6(5)[92.1(5)]
$C_{cage}-C_{cage}-C_{Ind}$[b]	111.0(6)	109.7(6)	109.7(4)	110.2(7)[109.6(7)]
$C_{cage}-Ln-Cent$[d]	83.5	86.8	86.5	87.6[88.0]
Δ_{M-C}[e]	0.092	0.167	0.129	0.125[0.145]
fold angle (FA)[e]	2.84	4.95	4.67	2.98[3.51]
hinge angle (HA)[e]	3.25	4.62	4.61	2.63[0.89]

[a] Distances and angles in brackets are those of the second molecule in the unit cell. [b] C_{Ind} = the carbon atom directly bonded to the cage. [c] C_5 = carbon atoms of the five-membered ring. [d] Cent = the centroid of the five-membered ring of indenyl. [e] See Chart.

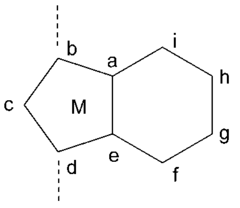
Chart 1



Δ_{M-C} = 0.5[M-a + M-e] - 0.5[M-b + M-d]



FA = fold angle, angle between [a,b,c,d,e] and [a,e,f,g,h,i]



HA = hinge angle, angle between [b,c,d] and [a,b,d,e]

structural data for **2**, **3**, and related single-atom-bridged organolanthanide complexes **Ia**−**Id**[7−10] and **IIa**−**IId**[9−11] are compiled in Tables 1−3. The La−C_5 distances in **2** vary from 2.812(8) to 3.055(8) Å with an average distance of 2.936(8) Å (Table 1), indicating a considerable distortion. Such distortions in metal-indenyl complexes can be described by three parameters (Chart 1):[15] (i) the slip parameter (Δ_{M-C}), which is defined as the difference between the average distance from the metal center to the two carbons shared by both five- and six-membered rings (a and e) and the average distance from the metal to the adjacent carbon atoms (b and d), (ii) the fold angle (FA), which is defined as the angle between the planes of the five- and six-membered rings, and (iii) the hinge angle (HA), which is defined as the angle between the planes of b,c,d and a,b,d,e. In general, indenyl complexes considered to be η^5 show values of HA and Δ_{M-C} less than 10° and 0.25 Å, respectively.[15b] In contrast, complexes considered to be η^3 show HA values of 20−30° while those of Δ_{M-C} are between 0.69 and 0.80 Å.[15b] Although complex **2** has large variations in La−C_5 distances, the indenyl is best described as an η^5-ligand on the basis of its HA value of 3.25° and Δ_{M-C} of 0.092 Å. On the other hand, the La−C_{cage} distance of 2.840(8) Å in **2** represents the longest La−C σ-bond reported thus far.[16] The average La−C_5 distance of 2.936(8) Å is much longer than those of 2.840(5) and 2.848(6) Å in $(C_4H_7OCH_2C_9H_6)_2LaCl$,[17] 2.832(5) and 2.853(5) Å in $(MeOCH_2CH_2C_9H_6)_2LaBH_4$,[18] and the corresponding values of 2.499(1)−2.606(3) Å in **Ia**−**Id**[7−10] (Table 2). The Cent−La−Cent/C_{cage}−La−C_{cage} angles of 151.9°/154.3(2)° are significantly larger than those of 112.6−136.1° and 99.7(1)−117.0(1)° observed in **Ia**−**Id**. However, the C_{cage}−C_{cage}−La/C_{cage}−La−Cent angles of 92.0(4)°/83.5° are much smaller than the corresponding values of 119.1(1)−120.5(1)° and 92.0−102.3° found in **Ia**−**Id**. These parameters clearly indicate a highly constrained geometry of complex **2**.

Complexes **3a**,**b** were also confirmed by single-crystal X-ray analyses. They are isostructural but not isomorphous. The representative structure of **3a** is shown in Figure 2. Each Ln metal is six-coordinated by two chloro groups, two THF molecules, one cage carbon atom, and an η^5-indenyl ligand in a distorted-octahedral geometry with O(1) and the centroid of the indenyl five-membered ring (Cent) at the axial positions. The average Y−C_5 distance of 2.740(8) Å in **3a** is longer than that of 2.632(5) Å in $[Me_2C(C_9H_6)_2]Y[1,3\text{-}(SiMe_3)_2C_3H_3]$,[19] 2.663(3) Å in *rac*-$[Me_2Si(2\text{-}Me\text{-}C_9H_5)_2]YN(SiHMe_2)_2$,[20] 2.675(5) Å in $[\eta^5\text{-}(CH_2)_2(C_9H_6)_2]YN(SiMe_3)_2$,[21] 2.701(1) Å in $[\{\eta^5{:}\eta^6\text{-}(C_9H_6)(C_2B_{10}H_{11})Y(THF)\}_2(\mu\text{-}Cl)][Na(THF)_3]$,[12] 2.68(1) Å in $[\eta^5{:}\eta^1{:}\sigma\text{-}Me_2Si(C_9H_6CH_2CH_2OMe)C_2B_{10}H_{10}]Y(NHC_6H_3\text{-}2,5\text{-}Bu^t{}_2)(\mu\text{-}Cl)Li(THF)_3$,[22] and 2.72(1) Å in $[\{[\eta^5{:}\sigma\text{-}{}^iPr_2NP(C_9H_6)C_2B_{10}H_{10}]YCl\}_2(\mu\text{-}Cl)_3Li(DME)][Li(DME)_3]_2$ (**IIc**).[10] The Ln−C_5 distances vary from 2.625(8) to 2.864(8) Å in **3a** and 2.646(5) to 2.860(5) Å in **3b**, showing HA values of 4.62° and 4.61° and Δ_{M-C} values of 0.167 and 0.129 Å in **3a** and **3b**, respectively (Table 1). Again, the indenyl ligand bonds to Ln in an η^5-fashion. The Y−Cl distances of 2.605(2)/2.624(2) Å in **3a** are comparable with those of 2.576(1) Å in $[CH(PPh_2NSiMe_3)_2]Y(\eta^5\text{-}C_5Me_5)Cl$,[23] 2.579(6)/2.776(5) Å in $Cp^*{}_2Y(\mu\text{-}Cl)YClCp^*{}_2$,[24] 2.5973(5) Å in $(CH_2{=}CHCH_2CH_2C_5Me_4)_2YCl(THF)$,[25] 2.6310(6)/2.6350(6) Å in $(CH_2{=}CHCH_2CH_2C_5Me_4)Cp^*Y(\mu\text{-}Cl)_2Na(OEt_2)_2$,[25] 2.657 (1) Å in $[\{\eta^5{:}\eta^6\text{-}$

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Table 2. Key Structural Data for Ia−Id and 2

Ia: A = Me_2Si; Ln = Sm; $M(S)_n$ = $Na(THF)_6$;
Ib: A = Me_2C; Ln = Nd; $M(S)_n$ = $Li(DME)_2$;
Ic: A = $^iPr_2NB$; Ln = Yb; $M(S)_n$ = $Li(THF)_4$;
Id: A = $^iPr_2NP$; Ln = Y; $M(S)_n$ = $Li(THF)(DME)_2$.

2

	Ln	Ln−C_{cage}	av Ln−C_5[a]	Ln−Cent[b]	Cent−Ln−Cent[b]	C_{cage}−C_{cage}−Ln	C_{cage}−Ln−Cent[b]	C_{cage}−C_{cage}−X[c]	C_{cage}−Ln−$C_{cage'}$
Ia	Sm	2.606(3)	2.757(2)	2.478	112.6	119.3(1)	102.3	116.7(2)	109.2(12)
Ib	Nd	2.576(3)	2.761(3)	2.483	127.6	119.1(1)	92.0	116.7(1)	117.0(1)
Ic	Yb	2.499(1)	2.643(2)	2.352	135.3	120.5(1)	98.3	112.5(1)	107.4(1)
Id	Y	2.538(3)	2.703(3)	2.418	136.1	119.2(3)	100.7	118.8(2)	99.7(1)
2	La	2.840(8)	2.936(8)	2.670	151.9	92.0(4)	83.5	111.0(6)	154.3(2)

[a] C_5 = carbon atoms of the five-membered ring. [b] Cent = centroid of the five-membered ring. [c] X = bridging atom (in **Ia**−**Id**) or the carbon atom directly bonded to the cage (in **2**).

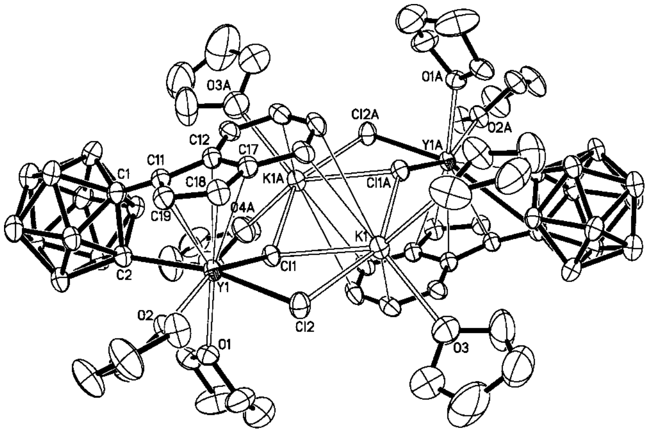

Figure 2. Molecular structure of $[\{\eta^5:\sigma\text{-}(C_9H_6)C_2B_{10}H_{10}\}Y(THF)_2(\mu\text{-}Cl)_2K(THF)_2]_2$ (**3a**) (thermal ellipsoids drawn at the 30% probability level).

$(C_9H_6)(C_2B_{10}H_{11})Y(THF)\}_2(\mu\text{-}Cl)][Na(THF)_3]$,[12] 2.728(3) Å in $[\eta^5:\eta^1:\sigma\text{-}Me_2Si(C_9H_6CH_2CH_2OMe)C_2B_{10}H_{10}]Y(NHC_6H_3\text{-}2,5\text{-}Bu^t_2)(\mu\text{-}Cl)Li(THF)_3$,[22] and 2.625(3) Å in **IIc**.[10] The Ln−C_{cage} distances of 2.641(8) Å in **3a** and 2.672(5) Å in **3b** are significantly longer than those of 2.479(13)−2.598(3) Å observed in complexes **IIa**−**IId**[9−11] (Table 3) and probably present the longest Ln−C σ-bond distances for Y and Gd elements, respectively.[16] The C_{cage}−C_{cage}−Ln angles of 92.2(4)° in **3a** and 92.1(2)° in **3b** are much smaller than those of around 120° found in **IIa**−**IId**[9−11] (Table 3). The C_{cage}−Ln−Cent angles of 93.2−108.5° in **IIa**−**IId**[9−11] are considerably reduced to 86.8°/86.5° in **3a**/**b** (Table 3). The rigidity of the ligand $[(C_9H_6)C_2B_{10}H_{10}]^{2-}$ results in the formation of the highly constrained structural motif $\{Ln[\eta^5:\sigma\text{-}(C_9H_6)C_2B_{10}H_{10}]\}^-$, as evidenced by the above structural data.

Organolanthanide Alkyls. Organolanthanide chloride complexes are generally useful starting materials for the synthesis of the corresponding complexes containing a Ln−X (X = H, C, N, O, S, P, BH_4, etc.) bond.[5a,26] To the best of our knowledge, an organolanthanide alkyl complex incorporating a carboranyl ligand has never been isolated before, although many attempts were made.[10,22,27] We examined the reactions of the diamagnetic complex **3a** with various carbon nucleophiles such as MeLi, ^nBuLi, PhLi, MeMgBr, C_3H_5MgCl, PhMgBr, Me_3SiCH_2MgCl, and $PhCH_2K$. No pure products were isolated from the above reactions. Both ^1H and ^{11}B NMR spectra suggested that the products were inseparable mixtures, which might result from the decomposition of organolanthanide alkyls. Because organolanthanide complexes can usually be stabilized by multidentate ligands,[5a,26,28] the cyclopentadienyl (Cp) and $(CH_2C_6H_4\text{-}o\text{-}NMe_2)^-$ nucleophiles were attempted. The interaction of **3a**,**b** with 2 equiv of NaCp in THF gave, after recrystallization from THF/toluene solution, complexes $[\eta^5:\sigma\text{-}(C_9H_6)C_2B_{10}H_{10}]Ln(\eta^5\text{-}C_5H_5)(THF)_2$ (Ln = Y (**4a**), Gd (**4b**)) in 37−39% isolated yields (Scheme 2). Treatment of **3a**,**c** with 2 equiv of $KCH_2C_6H_4\text{-}o\text{-}NMe_2$ in THF afforded, after recrystallization from toluene/DME solution, complexes $[\eta^5:\sigma\text{-}(C_9H_6)C_2B_{10}H_{10}]Ln(CH_2C_6H_4\text{-}o\text{-}NMe_2)(DME)$ (Ln = Y (**5a**), Er (**5c**)) in 27−29% isolated yields, as shown in Scheme 2.

As the salt metathesis offered low yields, the alkane elimination method was then examined. The homoleptic complexes $Ln(CH_2C_6H_4\text{-}o\text{-}NMe_2)_3$ (Ln = Y, La) were reported to be synthesized via salt metathesis of $LnCl_3$ and $KCH_2C_6H_4\text{-}o\text{-}NMe_2$, generated from $LiCH_2C_6H_4\text{-}o\text{-}NMe_2$ and potassium alkoxide, in THF at low temperature in 41−59% yields.[29] We found that $Ln(CH_2C_6H_4\text{-}o\text{-}NMe_2)_3$ (Ln = Y (**6a**), Er (**6c**)) can be prepared in 55−81% yields directly using $LiCH_2C_6H_4\text{-}o\text{-}NMe_2$ in toluene/diethyl ether at room temperature. Conversion of the lithium salt to the potassium one is thus not necessary.

Interaction of proligand **1** with homoleptic complexes **6** in THF at room temperature led to the isolation of $[\eta^5:\sigma\text{-}(C_9H_6)C_2B_{10}H_{10}]Ln(CH_2C_6H_4\text{-}o\text{-}NMe_2)(THF)_2$ (Ln = Y (**5a′**), Er (**5c′**)) in 82−87% yields. They were conveniently converted to **5a**,**c** by recrystallization from DME. The above reactions are outlined in Scheme 2. Complexes **4** and **5** are slightly soluble in toluene and soluble in DME, THF, and pyridine.

In the ^1H NMR spectrum of the diamagnetic complex **4a**, six resonances in the range 8.6−6.6 ppm for indenyl protons, a singlet at 6.04 ppm for Cp protons, and two multiplets at 3.66 and 1.64 ppm for THF were observed, supporting a molar ratio of one Cp and two THF molecules per indenyl. Its ^{13}C NMR

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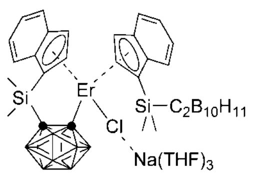
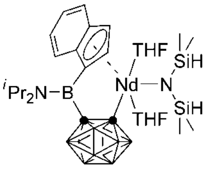
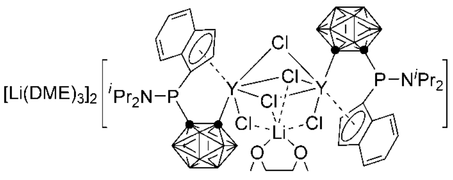
Table 3. Key Structural Data for IIa–IId, 3a,b, and 5a



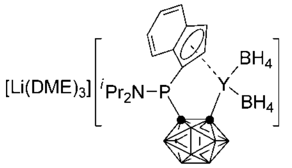
IIa



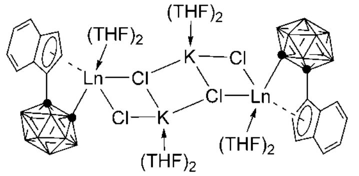
IIb



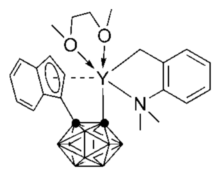
IIc



IId



3a: Ln = Y; **3b**: Ln = Gd

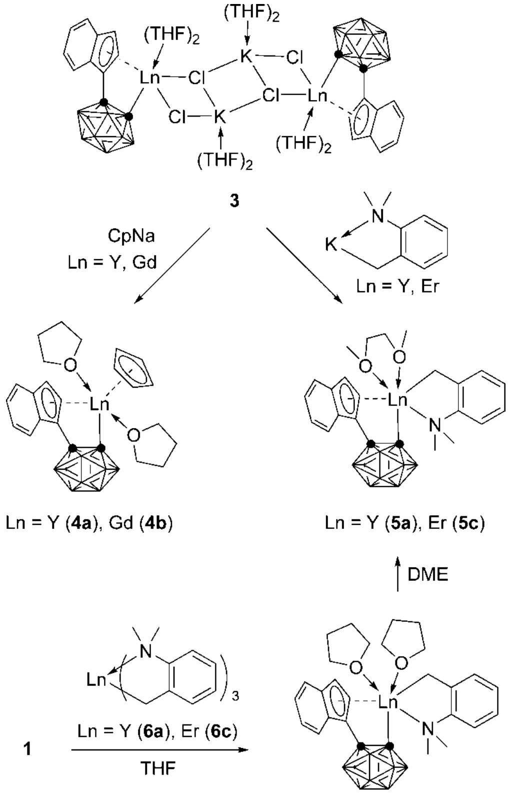


5a

	Ln	Ln–C$_{cage}$	C$_{cage}$–C$_{cage}$	av Ln–C$_5$[a]	Ln–Cent[b]	C$_{cage}$–X[c]	C$_{cage}$–C$_{cage}$–Ln	C$_{cage}$–Ln–Cent[b]	C$_{cage}$–C$_{cage}$–X[c]
IIa	Er	2.520(3)	1.738(3)[d]	2.671(3)[d]	2.391[d]	1.882(3)[d]	118.6(7)	108.5	117.6(7)[d]
IIb	Nd	2.598(3)	1.736(4)	2.760(4)	2.481	1.608(4)	123.5(2)	93.2	112.2(2)
IIc	Y	2.545(10)	1.707(9)	2.719(10)	2.437	1.893(9)	121.0(5)	99.3	117.6(5)
IId	Y	2.479(13)	1.70(2)	2.663(18)	2.375	1.89(2)	119.9(2)	101.0	117.0(1)
3a	Y	2.641(8)	1.71(1)	2.740(8)	2.465	1.49(1)	92.2(4)	86.8	109.7(6)
3b	Gd	2.672(5)	1.719(7)	2.754(5)	2.477	1.495(6)	92.1(2)	86.5	109.7(4)
5a	Y	2.61(1)	1.72(1)	2.74(1)	2.466	1.50(1)	91.4(5)	87.8	109.9(7)

[a] C$_5$ = carbon atoms of the five-membered ring. [b] Cent = centroid of the five-membered ring. [c] X = bridging atom (in **IIa–IId**) or the carbon atom directly bonded to the cage (in **3** and **5a**). [d] Values of the divalent ligand.

Scheme 2



spectrum was consistent with the ^{1}H NMR. The ^{11}B NMR spectrum exhibited a 1:1:6:2 pattern, which is different from that of **3a**. In addition to the coordinated solvent resonances, the ^{1}H NMR spectra of **5a**,**a′** in pyridine-d_5 showed four doublets at 7.91, 7.77, 6.89, and 6.62 ppm, three triplets at 7.03, 6.95, and 6.74 ppm, and a multiplet at 6.68 ppm assignable to aromatic protons, a singlet at ~2.46 ppm corresponding to N(CH_3)$_2$ protons, and two characteristic doublets of doublets at 1.84 and 1.71 ppm with $^2J_{H-H} = 9.6$ Hz and $^2J_{H-Y} = 1.8$ or 2.4 Hz attributable to Y-CH_2 protons.[29] A doublet at ~49.2 ppm with $^1J_{C-Y} = 33.6$ Hz for a Y-CH$_2$ carbon[29] was also observed in their ^{13}C NMR spectra. The ^{11}B NMR spectra of **5a**,**a′** showed a 1:1:8 pattern. The compositions of **4** and **5** were further confirmed by elemental analyses.

Single-crystal X-ray analyses of **5a** revealed that there are two crystallographically independent molecules in the unit cell and showed two THF of solvation. The Y atom is σ-bound to both the benzylic carbon and cage carbon, η^5-bound to the indenyl, and coordinated to one N and two O atoms in a highly distorted octahedral geometry with N(1) and the Cent of indenyl at the axial positions (Figure 3). As indicated in Table 1, the HA values of 2.63°/0.89° and Δ_{M-C} values of 0.125/0.145 Å suggest the η^5-bonding interactions between the indenyl and Y atom. The Y–C$_{alkyl}$ distances of 2.36(1)/2.40(1) Å are slightly shorter than that of 2.472(3) Å in Y(CH$_2$C$_6$H$_4$-*o*-NMe$_2$)$_3$,[29] 2.409(3) Å in (9-*t*-BuNSiMe$_2$-fluorenyl)Y(CH$_2$C$_6$H$_4$-*o*-NMe$_2$)(THF),[29] 2.445(4) Å in (2,5-di-*t*-Bu-3,4-dimethylphospholide)Y(CH$_2$C$_6$H$_4$-*o*-NMe$_2$)$_2$,[30] 2.426(4) Å in [*N*,*N*′-bis(2,6-di-^{i}Pr-C$_6$H$_3$)-benzamidinate]Y(CH$_2$-C$_6$H$_4$-*o*-NMe$_2$)$_2$,[31] 2.445(2)/2.456(2) Å in [(CH$_3$OCH$_2$CH$_2$)$_2$NCH$_2$-C$_6$H$_2$-3,5-(CMe$_3$)$_2$-2-O]Y(CH$_2$SiMe$_2$Ph)$_2$,[32] and 2.425(5)/2.430(5) Å in [(Et$_2$NCH$_2$CH$_2$)$_2$NCH$_2$-C$_6$H$_2$-3,5-(CMe$_3$)$_2$-2-O]Y-(CH$_2$SiMe$_2$Ph)$_2$.[32] Complex **5a** represents the first structurally characterized example of a rare earth metal alkyl complex bearing a carboranyl ligand.

Conclusion

The directly linked indenyl-carboranyl ligand [(C$_9$H$_6$)C$_2$-B$_{10}$H$_{10}$]$^{2-}$ can suppress the ligand redistribution reaction and

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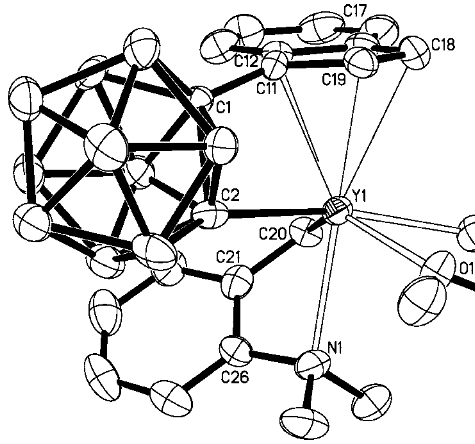

Figure 3. Molecular structure of $[\eta^5:\sigma\text{-}(C_9H_6)C_2B_{10}H_{10}]Y(CH_2C_6H_4\text{-}o\text{-}NMe_2)(DME)$ (**5a**) (thermal ellipsoids drawn at the 30% probability level).

stabilize late organolanthanide chloride complexes **3**, which is significantly different from the single-atom-bridged analogues $[A(C_9H_6)(C_2B_{10}H_{10})]^{2-}$ (A = Me_2C, Me_2Si, $^iPr_2NB$). This may be ascribed to the high rigidity of the $[(C_9H_6)C_2B_{10}H_{10}]^{2-}$ ligand. The chloro group in **3** can be substituted by a carbon nucleophile $(CH_2C_6H_4\text{-}o\text{-}NMe_2)^-$, resulting in the isolation of the first examples of organolanthanide alkyl complexes incorporating a carboranyl ligand $[\eta^5:\sigma\text{-}(C_9H_6)C_2B_{10}H_{10}]Ln(CH_2C_6H_4\text{-}o\text{-}NMe_2)(DME)$. They can also be prepared in much higher yields via alkane elimination reaction of $1\text{-}C_9H_7\text{-}1,2\text{-}C_2B_{10}H_{11}$ with $Ln(CH_2C_6H_4\text{-}o\text{-}NMe_2)_3$. X-ray analyses confirm that the structural motif $[\eta^5:\sigma\text{-}(C_9H_6)C_2B_{10}H_{10}]Ln$ has a highly constrained geometry with significantly longer $Ln{-}C_{cage}$ distances and much smaller $C_{cage}{-}C_{cage}{-}Ln$ angles as compared to the corresponding values observed in the analogues shown in Tables 2 and 3.

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. $LiCH_2C_6H_4\text{-}o\text{-}NMe_2$,[33] $KCH_2C_6H_4\text{-}o\text{-}NMe_2$,[34] anhydrous $LnCl_3$,[35] and 1-indenyl-1,2-carborane (**1**)[12] were prepared according to 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 NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300.0 MHz. ^{13}C NMR spectra were recorded on a Bruker DPX 300.0 at 75.5 MHz or a Varian Inova 400 spectrometer at 100.7 MHz. ^{11}B NMR spectra were recorded on a Varian Inova 400 spectrometer at 128.0 MHz. All chemical shifts were reported in δ units with reference to the residual protons and carbons 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., U.K., or Shanghai Institute of Organic Chemistry, CAS, China.

Preparation of $[K(THF)_6][\{\eta^5:\sigma\text{-}(C_9H_6)C_2B_{10}H_{10}\}_2La(THF)]$ (2). KH powder (42 mg, 1.05 mmol) was added to a THF solution (10 mL) of 1-indenyl-1,2-carborane (**1**) (129 mg, 0.5 mmol), and the suspension was heated to reflux for 2 h until a clear yellow solution was obtained. The resultant solution was cooled to room temperature and slowly added to a THF suspension (5 mL) of $LaCl_3$ (124 mg, 0.5 mmol). The yellow suspension was stirred at room temperature for 24 h. The precipitate was removed by filtration. The clear solution was concentrated to 5 mL before adding *n*-hexane (5 mL). Complex **2** was obtained as colorless crystals after this solution stood at room temperature for 48 h (179 mg, 60%). ^1H NMR (pyridine-d_5): δ 7.99 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.39 (brs, 1H), 7.02 (t, J = 8.4 Hz, 1H), 6.83 (t, J = 8.4 Hz, 1H), 6.76 (d, J = 3.0 Hz, 1H), 6.66 (m, 2H), 6.37 (brs, 1H), 6.32 (d, J = 3.0 Hz, 1H), 3.65 (m, 28H), 1.62 (m, 28H) (THF). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 130.2, 128.1, 127.7, 124.7, 124.2, 122.3, 120.0, 119.9, 119.8, 119.4, 119.2, 104.6, 102.6, 102.2, 101.2, 100.6 (indenyl), 80.9, 65.1 (cage *C*), 67.2, 25.1 (THF). $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ −0.2 (2B), −3.6 (2B), −7.9 (16B). IR (KBr, cm^{-1}): ν 2559 (vs) (B−H). Anal. Calcd for $C_{38}H_{64}B_{20}KLaO_4$ (**2** − 3THF): C, 46.61; H, 6.59. Found: C, 47.09; H, 6.90.

Preparation of $[\{\eta^5:\sigma\text{-}(C_9H_6)C_2B_{10}H_{10}\}Y(THF)_2(\mu\text{-}Cl)_2K(THF)_2]_2$ (3a). This complex was prepared from **1** (129 mg, 0.5 mmol), KH (42 mg, 1.05 mmol), and YCl_3 (98 mg, 0.5 mmol) using procedures identical to those reported for **2**. Complex **3a** was obtained as orange crystals from THF/*n*-hexane (230 mg, 62%). ^1H NMR (pyridine-d_5): δ 8.53 (d, J = 7.2 Hz, 2H), 7.62 (d, J = 7.2 Hz, 2H), 7.53 (d, J = 4.5 Hz, 2H), 7.19 (t, J = 7.2 Hz, 2H), 7.09 (t, J = 7.2 Hz, 2H), 6.65 (d, J = 4.5 Hz, 2H) (indenyl), 3.64 (m, 32H), 1.60 (m, 32H) (THF). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 137.3, 128.7, 121.8, 121.4, 119.7, 119.6, 119.4, 119.3, 111.0 (indenyl), 67.2, 25.2 (THF), the cage carbons were not observed. $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ 0.6 (2B), −9.6 (14B), −16.8 (4B). IR (KBr, cm^{-1}): ν 2537 (vs) (B−H). Anal. Calcd for $C_{54}H_{96}B_{20}Cl_4K_2O_8Y_2$ (**3a**): C, 43.61; H, 6.51. Found: C, 44.05; H, 6.88.

Preparation of $[\{\eta^5:\sigma\text{-}(C_9H_6)C_2B_{10}H_{10}\}Gd(THF)_2(\mu\text{-}Cl)_2K(THF)_2]_2$ (3b). This complex was prepared from **1** (129 mg, 0.5 mmol), KH (42 mg, 1.05 mmol), and $GdCl_3$ (132 mg, 0.5 mmol) using procedures identical to those reported for **2**. Complex **3b** was obtained as yellow crystals from THF/*n*-hexane (195 mg, 48%). ^1H NMR (pyridine-d_5): δ 3.76 (brs), 1.73 (brs) (THF), and many unresolved peaks. $^{11}B\{^1H\}$ NMR (pyridine-d_5): many broad, unresolved resonances. IR (KBr, cm^{-1}): ν 2556 (vs) (B−H). Anal. Calcd for $C_{50}H_{88}B_{20}Cl_4Gd_2K_2O_7$ (**3b** − THF): C, 38.70; H, 5.72. Found: C, 38.39; H, 5.89.

Preparation of $[\{\eta^5:\sigma\text{-}(C_9H_6)C_2B_{10}H_{10}\}Er(THF)_2(\mu\text{-}Cl)_2K(THF)_2]_2$ (3c). This complex was prepared from **1** (129 mg, 0.5 mmol), KH (42 mg, 1.05 mmol), and $ErCl_3$ (137 mg, 0.5 mmol) using procedures identical to those reported for **2**. Complex **3c** was obtained as a pink solid from THF/*n*-hexane (193 mg, 47%). ^1H NMR (pyridine-d_5): δ 3.50 (brs), 1.41 (brs) (THF), and many unresolved peaks. $^{11}B\{^1H\}$ NMR (pyridine-d_5): many broad, unresolved resonances. IR (KBr, cm^{-1}): ν 2553 (vs) (B−H). Anal. Calcd for $C_{46}H_{80}B_{20}Cl_4Er_2K_2O_6$ (**3c** − 2THF): C, 36.84; H, 5.38. Found: C, 36.77; H, 5.39.

Preparation of $[\{\eta^5:\sigma\text{-}(C_9H_6)C_2B_{10}H_{10}\}Yb(THF)_2(\mu\text{-}Cl)_2K(THF)_2]_2$ (3d). This complex was prepared from **1** (129 mg, 0.5 mmol), KH (42 mg, 1.05 mmol), and $YbCl_3$ (140 mg, 0.5 mmol) using procedures identical to those reported for **2**. Complex **3d** was obtained as a brown solid from THF/*n*-hexane (174 mg, 42%). ^1H NMR (pyridine-d_5): δ 3.56 (brs), 1.52 (brs) (THF), and many unresolved peaks. $^{11}B\{^1H\}$ NMR (pyridine-d_5): many broad, unresolved resonances. IR (KBr, cm^{-1}): ν 2580 (vs) (B−H). Anal. Calcd for $C_{50}H_{88}B_{20}Cl_4K_2O_7Yb_2$ (**3d** − THF): C, 37.92; H, 5.60. Found: C, 37.44; H, 6.02.

Preparation of $[\eta^5:\sigma\text{-}(C_9H_6)C_2B_{10}H_{10}]Y(\eta^5\text{-}C_5H_5)(THF)_2$ (4a). A THF solution (5 mL) of NaCp (53 mg, 0.6 mmol) was slowly added to a THF solution (5 mL) of complex **3a** (372 mg, 0.25 mmol). The mixture was stirred at room temperature for 24 h before

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Table 4. Crystal Data and Summary of Data Collection and Refinement for 2, 3a, 3b, and 5a·THF

	2	3a	3b	5a·THF
formula	$C_{50}H_{88}B_{20}KLaO_7$	$C_{54}H_{96}B_{20}Cl_4K_2O_8Y_2$	$C_{54}H_{96}B_{20}Cl_4Gd_2K_2O_8$	$C_{28}H_{46}B_{10}NO_3Y$
cryst size, mm	0.50 × 0.40 × 0.20	0.40 × 0.30 × 0.20	0.50 × 0.50 × 0.45	0.20 × 0.10 × 0.10
fw	1195.4	1487.3	1642.0	641.7
cryst syst	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a, Å	10.950(2)	10.312(1)	15.967(2)	16.422(2)
b, Å	17.141(3)	15.477(1)	10.634(1)	17.215(1)
c, Å	20.219(4)	16.037(1)	22.436(2)	28.682(2)
α, deg	69.65(3)	61.72(1)	90	90
β, deg	84.14(3)	76.49(1)	103.32(1)	120.51(1)
γ, deg	82.15(3)	73.44(1)	90	90
V, Å^3	3519(1)	2145.6(3)	3707.0(7)	6986(1)
Z	2	1	2	8
D_{calcd}, Mg/m^3	1.128	1.151	1.455	1.220
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	2.2 to 50.4	4.1 to 50.0	3.7 to 54.0	2.9 to 50.2
μ, mm^{-1}	0.707	1.607	2.076	1.699
F(000)	1240	768	1636	2672
no. of obsd reflns	9275	7472	8008	12 447
no. of params refnd	712	406	406	776
goodness of fit	1.073	1.085	0.974	0.948
R1	0.092	0.082	0.045	0.084
wR2	0.251	0.271	0.089	0.191

being heated to reflux for 30 min. The precipitate was removed by hot filtration. The clear solution was concentrated to ca. 5 mL, to which was added toluene (5 mL). Complex **4a** was collected as orange crystals from THF/toluene after 1 week (108 mg, 39%). ^{1}H NMR (pyridine-d_5): δ 8.56 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.59 (d, J = 4.2 Hz, 1H), 7.16 (t, J = 7.8 Hz, 1H), 7.07 (t, J = 7.8 Hz, 1H), 6.66 (d, J = 4.2 Hz, 1H) (indenyl), 6.04 (s, 5H) (Cp), 3.66 (m, 8H), 1.64 (m, 8H) (THF). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 136.2, 133.7, 127.4, 119.4, 118.2, 117.5, 116.2, 107.2, 104.0 (indenyl), 110.3 (Cp), 90.8, 84.4 (cage *C*), 67.2, 25.1 (THF). ^{11}B{^{1}H} NMR (pyridine-d_5): δ −0.9 (1B), −4.5 (1B), −8.3 (6B), −13.7 (2B). IR (KBr, cm^{-1}): ν 2554 (vs) (B−H). Anal. Calcd for $C_{24}H_{37}B_{10}O_2Y$ (**4a**): C, 51.98; H, 6.72. Found: C, 51.80; H, 6.50.

Preparation of [η^5:σ-(C_9H_6)$C_2B_{10}H_{10}$]Gd(η^5-C_5H_5)(THF)$_2$ (4b). This complex was prepared from **3b** (406 mg, 0.25 mmol) and NaCp (53 mg, 0.6 mmol) using procedures identical to those reported for **4a**. Complex **4b** was obtained as orange crystals from THF/toluene (115 mg, 37%). ^{1}H NMR (pyridine-d_5): δ 3.66 (brs), 1.62 (brs) (THF), and many unresolved peaks. ^{11}B{^{1}H} NMR (pyridine-d_5): many broad, unresolved resonances. IR (KBr, cm^{-1}): ν 2553 (vs) (B−H). Anal. Calcd for $C_{24}H_{37}B_{10}GdO_2$ (**4b**): C, 46.28; H, 5.99. Found: C, 46.09; H, 5.71.

Preparation of [η^5:σ-(C_9H_6)$C_2B_{10}H_{10}$]Y($CH_2C_6H_4$-*o*-NMe_2)(DME)·THF (5a·THF). A THF solution (5 mL) of $KCH_2C_6H_4$-*o*-NMe_2 (87 mg, 0.5 mmol) was slowly added to a THF solution (5 mL) of **3a** (372 mg, 0.25 mmol), and the mixture was stirred at room temperature for 24 h. Removal of the precipitate and solvent gave a red residue, which was extracted with hot toluene/DME (5:1 in v/v, 6 mL × 2). The combined solution was concentrated to ca. 5 mL. Complex **5a**·THF was collected as yellow crystals after this solution stood at room temperature for 2 days (93 mg, 29%). ^{1}H NMR (pyridine-d_5): δ 7.91 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.03 (t, J = 8.4 Hz, 2H), 6.95 (t, J = 8.4 Hz, 1H), 6.89 (d, J = 3.6 Hz, 1H), 6.74 (t, J = 8.4 Hz, 1H), 6.68 (m, 2H), 6.62 (d, J = 3.6 Hz, 1H) (aromatic), 3.64 (m, 4H) (THF), 3.48 (s, 4H), 3.25 (s, 6H) (DME), 2.46 (s, 6H) (N(CH_3)$_2$), 1.84 (dd, $^2J_{H-H}$ = 9.6 Hz, $^2J_{H-Y}$ = 1.8 Hz, 1H) (Y−C*H*H), 1.71 (dd, $^2J_{H-H}$ = 9.6 Hz, $^2J_{H-Y}$ = 1.8 Hz, 1H) (Y−CH*H*), 1.63 (m, 4H) (THF). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 148.2, 145.7, 129.6, 126.8, 126.0, 124.8, 123.5, 122.3, 121.6, 121.5, 118.2, 117.6, 102.7, 99.1 (aromatic), 80.1 (cage *C*), 71.4 (DME), 67.2 (THF), 57.9 (DME), 49.2 (d, $^1J_{C-Y}$ = 33.6 Hz, *C*H$_2$−Y), 44.8 (N(*C*H$_3$)$_2$), 25.1 (THF). ^{11}B{^{1}H} NMR (pyridine-d_5): δ 0.8 (1B), −3.8 (1B), −8.4 (8B). IR (KBr, cm^{-1}): ν 2564 (vs) (B−H). Anal. Calcd for $C_{26}H_{42}B_{10}NO_{2.5}Y$ (**5a** + 0.5THF): C, 51.56; H, 6.99; N, 2.31. Found: C, 51.38; H, 7.42; N, 1.99.

Alternative Method. Complex **5a′** (312 mg, 0.5 mmol) was dissolved in DME (15 mL). After this solution was stirred at room temperature for 6 h, it was concentrated to ca. 3 mL. Addition of *n*-hexane (5 mL) gave **5a** as a pale yellow solid (216 mg, 76%).

Preparation of [η^5:σ-(C_9H_6)$C_2B_{10}H_{10}$]Er($CH_2C_6H_4$-*o*-NMe_2)(DME) (5c). This complex was prepared from **3c** (411 mg, 0.25 mmol) and $KCH_2C_6H_4$-*o*-NMe_2 (87 mg, 0.5 mmol) in THF (10 mL) using procedures identical to those reported for **5a**. Complex **5c** was obtained as orange crystals from DME/toluene (87 mg, 27%). ^{1}H NMR (pyridine-d_5): δ 3.42 (brs), 3.20 (brs) (DME), and many other unresolved peaks. ^{11}B{^{1}H} NMR (pyridine-d_5): many broad, unresolved resonances. IR (KBr, cm^{-1}): ν 2560 (vs) (B−H). Anal. Calcd for $C_{24}H_{38}B_{10}ErNO_2$ (**5c**): C, 44.49; H, 5.91; N, 2.16. Found: C, 44.16; H, 5.84; N, 1.75.

Alternative Method. Complex **5c** was also prepared as an orange solid from **5c′** (351 mg, 0.5 mmol) and DME (15 mL) using the above procedures: yield 249 mg (77%).

Modified Method for Preparation of Y($CH_2C_6H_4$-*o*-NMe_2)$_3$ (6a). To a suspension of $LiCH_2C_6H_4$-*o*-NMe_2 (8.61 g, 61.0 mmol) in toluene/diethyl ether (300 mL, 2/1, v/v) was slowly added YCl_3 powder (3.91 g, 20.0 mmol). The reaction mixture was stirred at room temperature for 3 days to give a yellow suspension. After filtration, the residue was extracted with hot toluene (30 mL × 3). The combined filtrate was concentrated to 20 mL. Complex **6a** was collected as a yellow crystalline solid after this solution stood at room temperature for 2 days (7.96 g, 81%). ^{1}H NMR (benzene-d_6): δ 7.07 (d, J = 7.8 Hz, 3H), 6.98, (t, J = 7.8 Hz, 3H), 6.83 (d, J = 7.8 Hz, 3H), 6.66 (t, J = 7.2 Hz, 3H) (aromatic), 2.09 (s, 18H) ((N(C*H*$_3$)$_2$), 1.64 (s, 6H) (C*H*$_2$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 142.1, 135.4, 129.1, 127.6, 120.3, 117.5 (aromatic), 45.5 (d, $^1J_{C-Y}$ = 20.9 Hz) (*C*H$_2$), 44.0 (N(*C*H$_3$)$_2$). These data were identical with those reported in the literature.[29]

Preparation of Er($CH_2C_6H_4$-*o*-NMe_2)$_3$ (6c). This complex was prepared from $LiCH_2C_6H_4$-*o*-NMe_2 (8.61 g, 61.0 mmol) and $ErCl_3$ (5.47 g, 20.0 mmol) using procedures identical to those reported for **6a**. Complex **6c** was obtained as a deep red crystalline solid (6.27 g, 55%). Anal. Calcd for $C_{27}H_{36}N_3Er$ (**6c**): C, 56.91; H, 6.37; N, 7.37. Found: C, 56.99; H, 6.12; N, 7.19.

Preparation of [η^5:σ-(C_9H_6)$C_2B_{10}H_{10}$]Y($CH_2C_6H_4$-*o*-NMe_2)($THF)_2$ (5a′). A THF solution (5 mL) of **1** (129 mg, 0.5 mmol) was slowly added to a THF solution (5 mL) of Y($CH_2C_6H_4$-*o*-$NMe_2)_3$ (**6a**; 246 mg, 0.5 mmol), and the reaction mixture was stirred at room temperature for 24 h. The clear solution was concentrated to 3 mL, to which was added *n*-hexane (15 mL). Complex **5a′** was obtained as a pale yellow solid after this solution stood at room temperature overnight (271 mg, 87%).^{1}H NMR (pyridine-d_5): δ 7.91 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.03 (t, J = 8.4 Hz, 2H), 6.95 (t, J = 8.4 Hz, 1H), 6.89 (d, J = 3.6 Hz, 1H), 6.74 (t, J = 8.4 Hz, 1H), 6.68 (m, 2H), 6.62 (d, J = 3.6 Hz, 1H) (aromatic), 3.64 (m, 8H) (THF), 2.45 (s, 6H) (N(C$H_3)_2$), 1.84 (dd, $^2J_{H-H}$ = 9.6 Hz, $^2J_{H-Y}$ = 2.4 Hz, 1H) (Y−C*H*H), 1.71 (dd, $^2J_{H-H}$ = 9.6 Hz, $^2J_{H-Y}$ = 2.4 Hz, 1H) (Y−CH*H*), 1.59 (m, 8H) (THF). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 148.1, 145.7, 129.6, 126.8, 126.0, 124.9, 123.5, 122.1, 121.6, 121.5, 118.3, 117.5, 102.7, 99.1 (aromatic), 80.1 (cage *C*), 67.2 (THF), 49.1 (d, $^1J_{C-Y}$ = 33.6 Hz, *C*H_2−Y), 44.9 (N(*C*$H_3)_2$), 25.1 (THF). ^{11}B{^{1}H} NMR (pyridine-d_5): δ 0.6 (1B), −3.4 (1B), −7.3 (8B). IR (KBr, cm^{-1}): ν 2559 (vs) (B−H). Anal. Calcd for $C_{24}H_{36}B_{10}NOY$ (**5a′** − THF): C, 52.26; H, 6.58; N, 2.54. Found: C, 52.55; H, 7.01; N, 2.31.

Preparation of [η^5:σ-(C_9H_6)$C_2B_{10}H_{10}$]Er($CH_2C_6H_4$-*o*-NMe_2)($THF)_2$ (5c′). This complex was prepared from Er($CH_2C_6H_4$-*o*-$NMe_2)_3$ (**6c**; 285 mg, 0.5 mmol) and **1** (129 mg, 0.5 mmol) using procedures identical to those reported for **5a′**. Complex **5c′** was obtained as an orange crystalline solid (287 mg, 82%). ^{1}H NMR (pyridine-d_5): δ 3.53 (brs), 1.43 (brs) (THF), and many other unresolved peaks. ^{13}C{^{1}H} NMR (pyridine-d_5): δ 66.6, 24.5 (THF). ^{11}B{^{1}H} NMR (pyridine-d_5): many broad, unresolved resonances. IR (KBr, cm^{-1}): ν 2561 (vs) (B−H). Anal. Calcd for $C_{28}H_{44}B_{10}NO_2Er$ (**5c′**): C, 47.91; H, 6.32; N, 2.00. Found: C, 48.07; H, 6.60; N, 1.83.

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.[36] 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.[37] All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements are given in Table 4. Further details are included in the Supporting Information.

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Supporting Information Available: Crystallographic data in CIF format for **2**, **3a**, **3b**, and **5a**·THF. This material is available free of charge via the Internet at http://pubs.acs.org.

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