Synthesis, Structural Characterization, and Reactivity of 13-Vertex Lanthanacarboranes Bearing η^7-*arachno*-Carboranyl Ligands

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Treatment of 1-$Me_2NCH_2CH_2$-1,2-$C_2B_{10}H_{11}$ (**1**) with $LnCl_3$ in the presence of excess Na metal gave, after recrystallization from a combination of different solvents, 13-vertex *closo*-lanthanacarboranes $[\{\eta^1:\eta^7\text{-}[(Me_2NCH_2CH_2)C_2B_{10}H_{11}]Er(THF)\}\{Na(THF)_3\}]_2$ (**2**), $[\{\eta^1:\eta^7\text{-}[(Me_2NCH_2CH_2)C_2B_{10}H_{11}]Y(MeCN)\}\{Na(MeCN)_3\}]_2$ (**3**), or $[\{\eta^1:\eta^7\text{-}[(Me_2NCH_2CH_2)C_2B_{10}H_{11}]Y(THF)\}\{Na(THF)_2\}]_n$ (**4**), respectively. $[\{\eta^1:\eta^1:\eta^7\text{-}[(Me_2NCH_2CH_2)_2C_2B_{10}H_{10}]Y\}\{Na(MeCN)_2\}]_n$ (**6**), $[\{\eta^1:\eta^1:\eta^7\text{-}[(Me_2NCH_2CH_2)(MeOCH_2CH_2)C_2B_{10}H_{10}]Y\}\{Na(MeCN)\}]_n$ (**8**), and $[\{\eta^1:\eta^1:\eta^7\text{-}[(Me_2NCH_2CH_2)(MeOCH_2CH_2)C_2B_{10}H_{10}]Er\}\{Na(MeCN)(THF)\}]_n$ (**9**) were prepared in a similar manner from 1,2-$(Me_2NCH_2CH_2)_2$-1,2-$C_2B_{10}H_{10}$ (**5**) or 1-$Me_2NCH_2CH_2$-2-$MeOCH_2CH_2$-1,2-$C_2B_{10}H_{10}$ (**7**) and $LnCl_3$ in the presence of excess Na metal in THF. These complexes underwent cation exchange reactions. Complex **2** reacted with KBr in the presence of 18-crown-6 ether or $MgCl_2$ to afford $[\{\eta^1:\eta^7\text{-}[(Me_2NCH_2CH_2)C_2B_{10}H_{11}]Er(MeCN)\}\{K(18\text{-crown-}6)\}]_2$ (**10**) or $[\eta^1:\eta^7\text{-}\{(Me_2NCH_2CH_2)C_2B_{10}H_{11}\}Er(MeCN)]_2[Mg(MeCN)_6]$ (**11**), respectively. Complex **2** did not undergo carboranyl ligand exchange reactions and showed no reactivities toward $LnCl_3$ and $ZrCl_4$. Complex **4** reacted with $AgBPh_4$ or Me_2SiCl_2 to give **1** or $[YCl_2(THF)_5][YCl_4(THF)_2]$, respectively. The molecular structures of **2**−**4**, **6**, and **8**−**11** were confirmed by single-crystal X-ray diffraction studies.

Introduction

Cyclopentadienyl or indenyl ligands with Lewis base functionalities have found many applications in rare earth chemistry.[1,2] Our recent work shows that an ether or amine substituent on the five-membered ring of the indenyl unit in linked carboranyl−indenyl hybrid ligands has significant effects on the stability and reactivity of the resulting organo-rare-earth complexes via temporarily and reversibly coordinating to the metal ion.[3] The results indicate that steric effects imposed by the coordination of NMe_2 to the central metal ion are greater than those resulting from the coordination of OMe, usually leading to the decrease in the coordination number of the central metal ions and the isolation of kinetic products and monomeric neutral species, although the difference in steric hindrance between NMe_2 and OMe is just one methyl group. A question arises as to whether such differences in coordination chemistry would be observed in Lewis base-appended carboranyl ligands.

Although a number of metal complexes containing $[(Me_2NCH_2)RC_2B_9H_9]^{2-}$ (R = H, Me, Me_2NCH_2),[4] $[(HNCH_2)C_2B_9H_{10}]^{3-}$,[5] $[(RN)Me_2SiC_2B_{10}H_{11}]^{3-}$ (R = aryl),[6] $[(MeOCH_2)_2C_2B_9H_9]^{2-}$,[7] or $[(MeOCH_2CH_2)RC_2B_{10}H_{10}]^{4-}$ (R = H, $MeOCH_2CH_2$)[8] ligands have been reported, no direct comparative studies on the substituent effects have been carried out yet. We have recently developed a method to prepare $(Me_2NCH_2CH_2)RC_2B_{10}H_{10}$ (R = H, $Me_2NCH_2CH_2$, $MeOCH_2CH_2$),[9] which makes the comparisons possible among a series of closely related metallacarboranes. In this article, we report the synthesis and structural characterization of several 13-vertex *closo*-lanthanacarboranes incorporating the $[\eta^7\text{-}arachno\text{-}(Me_2NCH_2CH_2)RC_2B_{10}H_{10}]^{4-}$ ligands and describe the similarities and differences among $[(Me_2NCH_2CH_2)C_2B_{10}H_{11}]^{4-}$, $[(Me_2NCH_2CH_2)_2C_2B_{10}H_{10}]^{4-}$, $[(Me_2NCH_2CH_2)(MeOCH_2CH_2)C_2B_{10}H_{10}]^{4-}$, and $[(MeOCH_2CH_2)_2C_2B_{10}H_{10}]^{4-}$ ligands in coordination chemistry. The reactivity of *closo*-metallacarboranes with an η^7-*arachno*-carboranyl ligand is also discussed in detail.

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Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents (except MeCN) were freshly distilled from sodium benzophenone ketyl immediately prior to use. MeCN was freshly distilled from $\mathrm{CaH_2}$ immediately prior to use. All chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise noted. Compounds $\mathrm{1\text{-}Me_2NCH_2CH_2\text{-}1,2\text{-}C_2B_{10}H_{11}}$ (**1**), $\mathrm{1,2\text{-}(Me_2NCH_2CH_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}}$ (**5**), and $\mathrm{1\text{-}Me_2NCH_2CH_2\text{-}2\text{-}MeOCH_2CH_2\text{-}1,2\text{-}C_2B_{10}H_{10}}$ (**7**) were prepared according to literature methods.[9] Infrared spectra were obtained from KBr pellets prepared in the glovebox on a Perkin-Elmer 1600 Fourier transform spectrometer. ^{1}H 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 are reported in δ units with references to the residual protons of the deuterated solvents for proton and carbon chemical shifts and to external $\mathrm{BF_3{\cdot}OEt_2}$ (0.00 ppm) for boron chemical shifts. Elemental analyses were performed by MEDAC Ltd., Middlesex, U.K.

Preparation of $[\{\eta^1{:}\eta^7\text{-}[(\mathrm{Me_2NCH_2CH_2})\mathrm{C_2B_{10}H_{11}}]\mathrm{Er}(\mathrm{THF})\}\{\mathrm{Na(THF)_3}\}]_2$ (2). To a THF (10 mL) solution of $\mathrm{1\text{-}Me_2NCH_2CH_2\text{-}1,2\text{-}C_2B_{10}H_{11}}$ (**1**; 215 mg, 1.0 mmol) was added finely cut Na metal (230 mg, 10.0 mmol), and the mixture was stirred at room temperature for 2 days. After addition of $\mathrm{ErCl_3}$ (274 mg, 1.0 mmol), the reaction mixture was stirred at room temperature for another 4 days. The precipitate and excess Na metal were filtered off and washed with THF (5 mL × 3). The THF solutions were then combined and concentrated to about 10 mL, to which was added toluene (7 mL). Complex **2** was isolated as pink crystals after this solution stood at room temperature for 3 days (243 mg, 35%). ^{1}H NMR (pyridine-d_5): δ 3.63 (br s), 1.58 (br s) (THF), and other broad, unresolved peaks. ^{11}B NMR (pyridine-d_5): many broad, unresolved resonances. IR (KBr, cm^{-1}): ν 2519 (vs) (BH), 2311 (w) (BH). Anal. Calcd for $\mathrm{C_{40}H_{98}B_{20}Er_2N_2Na_2O_7}$ (**2** − THF): C, 36.51; H, 7.51; N, 2.13. Found: C, 36.25; H, 7.34; N, 2.10.

Preparation of $[\{\eta^1{:}\eta^7\text{-}[(\mathrm{Me_2NCH_2CH_2})\mathrm{C_2B_{10}H_{11}}]\mathrm{Y}(\mathrm{MeCN})\}\{\mathrm{Na(MeCN)_3}\}]_2$ (3). This complex was prepared from $\mathrm{1\text{-}Me_2NCH_2CH_2\text{-}1,2\text{-}C_2B_{10}H_{11}}$ (**1**; 215 mg, 1.0 mmol), finely cut Na metal (230 mg, 10.0 mmol), and $\mathrm{YCl_3}$ (195 mg, 1.0 mmol), using the same procedure reported for **2**. Recrystallization from MeCN/toluene (3:1, 20 mL) at room temperature gave **3** as yellow crystals (167 mg, 34%). ^{1}H NMR (pyridine-d_5): δ 3.06 (m, 2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{N(CH_3)_2}$), 2.71 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2N(CH_3)_2}$), 2.27 (s, 6H, $\mathrm{CH_2CH_2N(C}\mathit{H}_3\mathrm{)_2}$), 1.84 (s, 12H, $\mathrm{C}\mathit{H}_3\mathrm{CN}$). ^{13}C NMR (pyridine-$d_5$): δ 119.0 ($\mathrm{CH_3}\mathit{C}\mathrm{N}$), 67.1 (cage *C*), 58.9 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2N(CH_3)_2}$), 44.9 ($\mathit{C}\mathrm{H_2CH_2N(CH_3)_2}$), 31.0 ($\mathrm{CH_2CH_2N(}\mathit{C}\mathrm{H_3)_2}$), 0.3 ($\mathit{C}\mathrm{H_3CN}$). ^{11}B NMR (pyridine-$d_5$): δ 10.0 (d, J = 125 Hz, 1B), −0.32 (d, J = 118 Hz, 1B), −8.1 (d, J = 145 Hz, 1B), −12.8 (d, J = 125 Hz, 1B), −19.8 (d, J = 156 Hz, 1B), −21.3 (d, J = 141 Hz, 2B), −28.9 (d, J = 152 Hz, 2B), −36.1 (d, J = 133 Hz, 1B). IR (KBr, cm^{-1}): ν 2511 (vs) (BH), 2444 (s) (BH), 2258 (m) (CN). Anal. Calcd for $\mathrm{C_{18}H_{51}B_{20}N_5Na_2Y_2}$ (**3** − 5MeCN): C, 27.80; H, 6.61; N, 9.01. Found: C, 27.58; H, 6.89; N, 9.33.

Preparation of $[\{\eta^1{:}\eta^7\text{-}[(\mathrm{Me_2NCH_2CH_2})\mathrm{C_2B_{10}H_{11}}]\mathrm{Y}(\mathrm{THF})\}\{\mathrm{Na(THF)_2}\}]_n$ (4). This complex was prepared from $\mathrm{1\text{-}Me_2NCH_2CH_2\text{-}1,2\text{-}C_2B_{10}H_{11}}$ (**1**; 215 mg, 1.0 mmol), finely cut Na metal (230 mg, 10.0 mmol), and $\mathrm{YCl_3}$ (195 mg, 1.0 mmol), using the same procedure reported for **2**. Recrystallization from the refluxed THF gave **4** as yellow crystals (228 mg, 42%). ^{1}H NMR (pyridine-d_5): δ 3.62 (m, 12H, THF), 2.62 (m, 2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{N(CH_3)_2}$), 2.21 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2N(CH_3)_2}$), 2.10 (s, 6H, $\mathrm{CH_2CH_2N(C}\mathit{H}_3\mathrm{)_2}$), 1.58 (m, 12H, THF). ^{13}C NMR (pyridine-d_5): δ 76.0 (cage *C*), 67.8 (THF), 57.8 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2N(CH_3)_2}$), 43.8 ($\mathit{C}\mathrm{H_2CH_2N(CH_3)_2}$), 31.6 ($\mathrm{CH_2CH_2N(}\mathit{C}\mathrm{H_3)_2}$), 25.7 (THF). ^{11}B NMR (pyridine-d_5): δ 10.0 (d, J = 125 Hz, 1B), −0.31 (d, J = 120 Hz, 1B), −7.4 (d, J = 142 Hz, 1B), −12.3 (d, J = 120 Hz, 1B), −19.1 (d, J = 155 Hz, 1B), −20.6 (d, J = 140 Hz, 2B), −28.8 (d, J = 150 Hz, 2B), −35.9 (d, J = 132 Hz, 1B). IR (KBr, cm^{-1}): ν 2423 (s) (BH), 2356 (s) (BH). Anal. Calcd for $\mathrm{C_{28}H_{74}B_{20}N_2Na_2O_4Y_2}$ (**4** − 2THF): C, 35.67; H, 7.91; N, 2.97. Found: C, 35.52; H, 8.22; N, 2.67.

Preparation of $[\{\eta^1{:}\eta^1{:}\eta^7\text{-}[(\mathrm{Me_2NCH_2CH_2})_2\mathrm{C_2B_{10}H_{10}}]\mathrm{Y}\}\{\mathrm{Na(MeCN)_2}\}]_n$ (6). This complex was prepared from $\mathrm{1,2\text{-}(Me_2NCH_2CH_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}}$ (**5**; 286 mg, 1.0 mmol), finely cut Na metal (230 mg, 10.0 mmol), and $\mathrm{YCl_3}$ (195 mg, 1.0 mmol) in THF using the same procedure reported for **2**. Recrystallization from MeCN/toluene (3:1, 20 mL) at room temperature gave **6** as yellow crystals (135 mg, 28%). ^{1}H NMR (pyridine-d_5): δ 3.08 (m, 4H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{N(CH_3)_2}$), 2.68 (m, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2N(CH_3)_2}$), 2.28 (s, 12H, $\mathrm{CH_2CH_2N(C}\mathit{H}_3\mathrm{)_2}$), 1.84 (s, 6H, $\mathrm{C}\mathit{H}_3\mathrm{CN}$). ^{13}C NMR (pyridine-$d_5$): δ 118.0 ($\mathrm{CH_3}\mathit{C}\mathrm{N}$), 60.6 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2N(CH_3)_2}$), 45.2 ($\mathit{C}\mathrm{H_2CH_2N(CH_3)_2}$), 31.0 ($\mathrm{CH_2CH_2N(}\mathit{C}\mathrm{H_3)_2}$), 0.3 ($\mathit{C}\mathrm{H_3CN}$), the cage carbon atoms were not observed. ^{11}B NMR (pyridine-d_5): δ −1.6 (d, J = 128 Hz, 1B), −8.9 (d, J = 150 Hz, 2B), −11.0 (d, J = 156 Hz, 2B), −17.2 (d, J = 145 Hz, 3B), −20.0 (d, J = 138 Hz, 2B). IR (KBr, cm^{-1}): ν 2444 (vs) (BH), 2353 (s) (BH), 2250 (m) (CN). Anal. Calcd for $\mathrm{C_{20}H_{60}B_{20}N_4Na_2Y_2}$ (**6** − 4MeCN): C, 30.15; H, 7.59; N, 7.03. Found: C, 30.04; H, 7.46; N, 6.61.

Preparation of $[\{\eta^1{:}\eta^1{:}\eta^7\text{-}[(\mathrm{Me_2NCH_2CH_2})(\mathrm{MeOCH_2CH_2})\mathrm{C_2B_{10}H_{10}}]\mathrm{Y}\}\{\mathrm{Na(MeCN)}\}]_n$ (8). This complex was prepared from $\mathrm{1\text{-}Me_2NCH_2CH_2\text{-}2\text{-}MeOCH_2CH_2\text{-}1,2\text{-}C_2B_{10}H_{10}}$ (**7**; 273 mg, 1.0 mmol), finely cut Na metal (230 mg, 10.0 mmol), and $\mathrm{YCl_3}$ (195 mg, 1.0 mmol) in THF using the same procedure reported for **2**. Recrystallization from MeCN/toluene (3:1, 20 mL) at room temperature gave **8** as yellow crystals (175 mg, 41%). ^{1}H NMR (pyridine-d_5): δ 3.87 (m, 2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{OCH_3}$), 3.50 (s, 3H, $\mathrm{CH_2CH_2OC}\mathit{H}_3$), 3.32 (m, 2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{N(CH_3)_2}$), 3.17 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2OCH_3}$), 2.72 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2N(CH_3)_2}$), 2.29 (s, 6H, $\mathrm{CH_2CH_2N(C}\mathit{H}_3\mathrm{)_2}$), 1.86 (s, 3H, $\mathrm{C}\mathit{H}_3\mathrm{CN}$). ^{13}C NMR (pyridine-$d_5$): δ 118.2 ($\mathrm{CH_3}\mathit{C}\mathrm{N}$), 78.3 (cage *C*), 67.2 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2OCH_3}$), 66.8 ($\mathrm{CH_2CH_2O}\mathit{C}\mathrm{H_3}$), 65.8 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2N(CH_3)_2}$) 43.6 ($\mathit{C}\mathrm{H_2CH_2OCH_3}$), 41.6 ($\mathit{C}\mathrm{H_2CH_2N(CH_3)_2}$), 25.1 ($\mathrm{CH_2CH_2N(}\mathit{C}\mathrm{H_3)_2}$), 0.4 ($\mathit{C}\mathrm{H_3CN}$). ^{11}B NMR (pyridine-$d_5$): δ −1.0 (d, J = 146 Hz, 2B), −16.5 (d, J = 156 Hz, 2B), −20.5 (d, J = 143 Hz, 1B), −23.1 (d, J = 139 Hz, 1B), −27.7 (d, J = 150 Hz, 2B), −35.4 (d, J = 139 Hz, 2B). IR (KBr, cm^{-1}): ν 2511 (vs) (BH), 2410 (vs) (BH), 2255 (m) (CN). Anal. Calcd for $\mathrm{C_{20}H_{57}B_{20}N_3Na_2O_2Y}$ (**8** − MeCN): C, 29.60; H, 7.08; N, 5.18. Found: C, 29.97; H; 6.60; N, 4.88.

Preparation of $[\{\eta^1{:}\eta^1{:}\eta^7\text{-}[(\mathrm{Me_2NCH_2CH_2})(\mathrm{MeOCH_2CH_2})\mathrm{C_2B_{10}H_{10}}]\mathrm{Er}\}\{\mathrm{Na(MeCN)(THF)}\}]_n$ (9). This complex was prepared from $\mathrm{1\text{-}Me_2NCH_2CH_2\text{-}2\text{-}MeOCH_2CH_2\text{-}1,2\text{-}C_2B_{10}H_{10}}$ (**7**; 273 mg, 1.0 mmol), finely cut Na metal (230 mg, 10.0 mmol), and $\mathrm{ErCl_3}$ (274 mg, 1.0 mmol) in THF using the same procedure reported for **2**. Recrystallization from MeCN/THF (1:1, 20 mL) at room temperature gave **9** as pink crystals (208 mg, 36%). ^{1}H NMR (pyridine-d_5): δ 3.62 (br s, THF), 1.84 (s, $\mathrm{C}\mathit{H}_3\mathrm{CN}$), 1.57 (br s, THF), and other broad, unresolved peaks. ^{11}B NMR (pyridine-d_5): many broad, unresolved resonances. IR (KBr, cm^{-1}): ν 2521 (vs) (BH), 2250 (w) (CN). Anal. Calcd for $\mathrm{C_{24}H_{65}B_{20}Er_2N_3Na_2O_3}$ (**9** − THF − MeCN): C, 27.70; H, 6.30; N, 4.04. Found: C, 27.58; H, 6.61; N, 4.38.

Preparation of $[\{\eta^1{:}\eta^7\text{-}[(\mathrm{Me_2NCH_2CH_2})\mathrm{C_2B_{10}H_{11}}]\mathrm{Er}(\mathrm{MeCN})\}\{\mathrm{K(18\text{-}crown\text{-}6)}\}]_2{\cdot}4\mathrm{toluene}$ (10·4toluene). To a THF (10 mL) solution of $[\{\eta^1{:}\eta^7\text{-}[(\mathrm{Me_2NCH_2CH_2})\mathrm{C_2B_{10}H_{11}}]\mathrm{Er}(\mathrm{THF})\}\{\mathrm{Na(THF)_3}\}]_2$ (**2**; 1.39 g, 1.0 mmol) were added KBr (0.24 g, 2.0 mmol) and 18-crown-6 ether (0.53 g, 2.0 mmol). The mixture was stirred at room temperature for 2 days. The pink precipitate was collected and redissolved in MeCN/toluene (3:1, 30 mL). The resulting solution was then concentrated under vacuum to about 10 mL, from which **10** was isolated as pink crystals after this solution stood at room temperature for one week (1.04 g, 57%). ^{1}H NMR (pyridine-d_5): δ 7.23 (m, toluene), 3.55 (s, $\mathrm{C_{12}}\mathit{H}_{24}\mathrm{O_6}$), and other broad, unresolved peaks. ^{11}B NMR (pyridine-d_5): many broad, unresolved resonances. IR (KBr, cm^{-1}): ν 2479 (s) (BH), 2380 (s)

Table 1. Selected Bond Lengths (Å)

	2	**3**	**4**	**6**	**8**	**9**	**11**	**12**
(Ln)	(Er)	(Y)	(Y)	(Y)	(Y)	(Er)	(Er)	(Er)
Ln−C(2)	2.370(10)	2.397(2)	2.386(6)	2.372(5)	2.379(1)	2.366(2)	2.359(3)	2.382(11)
Ln−C(5)	2.360(10)	2.360(2)	2.373(6)	2.401(5)	2.403(1)	2.358(2)	2.350(3)	2.346(10)
Ln−B(3)	2.637(13)	2.636(2)	2.642(6)	2.682(6)	2.679(1)	2.677(2)	2.637(4)	2.607(12)
Ln−B(4)	2.651(13)	2.652(2)	2.684(6)	2.677(6)	2.690(1)	2.682(2)	2.634(4)	2.667(13)
Ln−B(6)	2.711(13)	2.736(2)	2.726(7)	2.752(7)	2.756(1)	2.690(2)	2.708(4)	2.730(12)
Ln−B(7)	2.743(13)	2.817(2)	2.801(6)	2.777(7)	2.769(1)	2.735(2)	2.786(4)	2.820(12)
Ln−B(8)	2.737(14)	2.763(2)	2.758(7)	2.706(7)	2.714(1)	2.717(2)	2.750(4)	2.755(10)
Ln···B	2.726(13)	2.773(2)	2.777(6)	2.770(6)	2.760(1)	2.728(2)	2.776(3)	2.753(11)
	3.041(14)	2.882(2)	2.987(7)	3.053(6)	3.044(1)	3.040(2)	2.864(4)	2.897(12)
Ln−N(sidearm)	2.600(9)	2.635(2)	2.631(5)	2.591(4)	2.528(1)	2.539(1)	2.607(3)	2.608(9)
				2.730(4)				
Ln−O(sidearm)					2.568(1)	2.507(2)		
Ln−N(MeCN)		2.548(2)					2.588(3)	2.573(9)
Ln−O(THF)	2.564(7)		2.515(4)					

(BH), 2245 (w) (CN). Anal. Calcd for $C_{61}H_{120}B_{20}Er_2K_2N_4O_{12}$ (**10** + 3toluene): C, 42.29; H, 6.99; N, 3.24. Found: C, 42.36; H, 6.86; N, 3.38.

Preparation of $[\eta^1:\eta^7\text{-}\{(Me_2NCH_2CH_2)C_2B_{10}H_{11}\}Er(MeCN)]_2[Mg(MeCN)_6]\cdot MeCN$ (11·MeCN). This complex was prepared as pink crystals from $[\{\eta^1:\eta^7\text{-}[(Me_2NCH_2CH_2)C_2B_{10}H_{11}]Er(THF)\}\{Na(THF)_3\}]_2$ (**2**; 1.39 g, 1.0 mmol) and $MgCl_2$ (0.06 g, 1.0 mmol) in THF using the same procedure reported for **10**: yield 0.72 g (62%). ^1H NMR (pyridine-d_5): δ 1.60 (s, CH_3CN), and other broad, unresolved peaks. ^{11}B NMR (pyridine-d_5): many broad, unresolved resonances. IR (KBr, cm^{-1}): ν 2461 (s) (BH), 2286 (m) (BH), 2174 (m) (CN). Anal. Calcd for $C_{22}H_{57}B_{20}Er_2MgN_7$ (**11** − 3MeCN): C, 26.56; H, 5.78; N, 9.86. Found: C, 26.75; H, 5.81; N, 10.19.

Reaction of 4 with $AgBPh_4$. To a THF (10 mL) solution of **4** (0.55 g, 0.5 mmol) was added a THF solution of $AgBPh_4$ (0.86 g, 2.0 mmol) at room temperature, and the reaction mixture was stirred overnight. After removal of the black precipitate (Ag), the clear solution was concentrated to dryness, to which was added *n*-hexane (10 mL). The mixture was stirred for 0.5 h. The white solid was collected by filtration. Recrystallization from THF/*n*-hexane (2:1, 20 mL) gave a white solid (174 mg). $^{11}B\{^1H\}$ NMR (THF): δ −6.9. The *n*-hexane solution was concentrated to give a white solid (187 mg, 87%), which was identified as **1** by the ^1H and ^{11}B NMR spectra.

Reaction of 4 with Me_2SiCl_2. To a THF (10 mL) solution of **4** (0.55 g, 0.5 mmol) was slowly added Me_2SiCl_2 (258 mg, 2.0 mmol) at −78 °C, and the reaction mixture was stirred at room temperature overnight. After removal of the solvent, the solid was extracted with ether (10 mL × 2). The residue was dried under vacuum (134 mg). $^{11}B\{^1H\}$ NMR (THF): δ 14.9 (1B), 8.0 (1B), 3.4 (2B), −2.3 (3B), −9.8 (2B), −24.1 (1B). Slow evaporation of the ether solution afforded colorless crystals (300 mg, 67%), which were identified as $[YCl_2(THF)_5][YCl_4(THF)_2]$ by X-ray analyses.[10]

X-ray Structure Determination. All single crystals were immersed in Paratone-N oil and sealed under N_2 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.[11] 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 calculations on F^2 using the SHELXTL program package.[12] The carborane hydrogen atoms on the C_2B_5 bonding faces were located from difference Fourier syntheses. All other hydrogen atoms were geometrically fixed using the riding model. Selected bond distances are compiled in Table 1. Crystal data and details of data collection and structure refinements are included in the Supporting Information.

Results and Discussion

$[\{\eta^1:\eta^7\text{-}[(Me_2NCH_2CH_2)C_2B_{10}H_{11}]Ln(solvent)\}\{Na(solvent)_x\}]_n$. Treatment of 1-$Me_2NCH_2CH_2$-1,2-$C_2B_{10}H_{11}$ (**1**) with excess finely cut Na metal in THF, followed by reaction with 1 equiv of $LnCl_3$ gave, after recrystallization from a combination of different solvents, $[\{\eta^1:\eta^7\text{-}[(Me_2NCH_2CH_2)C_2B_{10}H_{11}]Er(THF)\}\{Na(THF)_3\}]_2$ (**2**), $[\{\eta^1:\eta^7\text{-}[(Me_2NCH_2CH_2)C_2B_{10}H_{11}]Y(MeCN)\}\{Na(MeCN)_3\}]_2$ (**3**), or $[\{\eta^1:\eta^7\text{-}[(Me_2NCH_2CH_2)C_2B_{10}H_{11}]Y(THF)\}\{Na(THF)_2\}]_n$ (**4**), shown in Scheme 1. The NMR spectra of **2** were not informative because of the strong paramagnetism of Er^{3+}. The diamagnetic yttrium complexes **3** and **4** were found to provide interpretable NMR data. The ^1H NMR spectra showed the presence of $Me_2NCH_2CH_2$ sidearm protons and supported the ratio of four MeCN molecules per carborane cage in **3**, and three THF molecules per carborane cage in **4**, respectively. Their ^{13}C NMR spectra were consistent with the results derived from the ^1H NMR data. A 1:1:1:1:1:2:2:1 splitting pattern was observed in the ^{11}B NMR spectra of both **3** and **4** with the chemical shifts spanning from 10 to −36 ppm. The solid-state IR spectra of **2**−**4** all displayed a very strong peak at about 2510 cm^{-1} and a medium strong peak at about 2355 cm^{-1}, implying B−H−Ln interactions.[13,14]

The molecular structures of **2**−**4** were confirmed by single-crystal X-ray diffraction studies. They contain a common structural motif of $[\eta^1:\eta^7\text{-}\{(Me_2NCH_2CH_2)C_2B_{10}H_{11}\}Ln(solvent)]_2^{2-}$, in which each rare earth metal ion is η^7-bound to the *arachno*-carboranyl ligand and σ-bound to two B−H bonds from the open seven-membered bonding face of the neighboring *arachno*-carboranyl cage and coordinated to one nitrogen atom

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[10] (a) Xie, Z.; Qian, C.; Sun, J. *Jiegou Huaxue (J. Struct. Chem.) (Engl. Ed.)* **1993**, *12*, 107. (b) Sobota, P.; Utko, J.; Szafert, S. *Inorg. Chem.* **1994**, *33*, 5203.

[11] Sheldrick, G. M. *SADABS*, Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen: Germany, 1996.

[12] Sheldrick, G. M. *SHELXTL*, 5.10 for Windows NT: Structure Determination Software Programs; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.

[13] (a) Xie, Z.; Wang, S.; Zhou, Z.-Y.; Xue, F,; Mak, T. C. W. *Organometallics* **1998**, *17*, 489. (b) Xie, Z.; Wang, S.; Zhou, Z.-Y.; Mak, T. C. W. *Organometallics* **1998**, *17*, 1907. (c) Xie, Z.; Wang, S.; Zhou, Z.-Y.; Mak, T. C. W. *Organometallics* **1999**, *18*, 1641. (d) Xie, Z.; Wang, S.; Yang, Q.; Mak, T. C. W. *Organometallics* **1999**, *18*, 2420. (e) Wang, S.; Yang, Q.; Mak, T. C. W.; Xie, Z. *Organometallics* **1999**, *18*, 4478. (f) Wang, S.; Yang, Q.; Mak, T. C. W.; Xie, Z. *Organometallics* **1999**, *18*, 1578.

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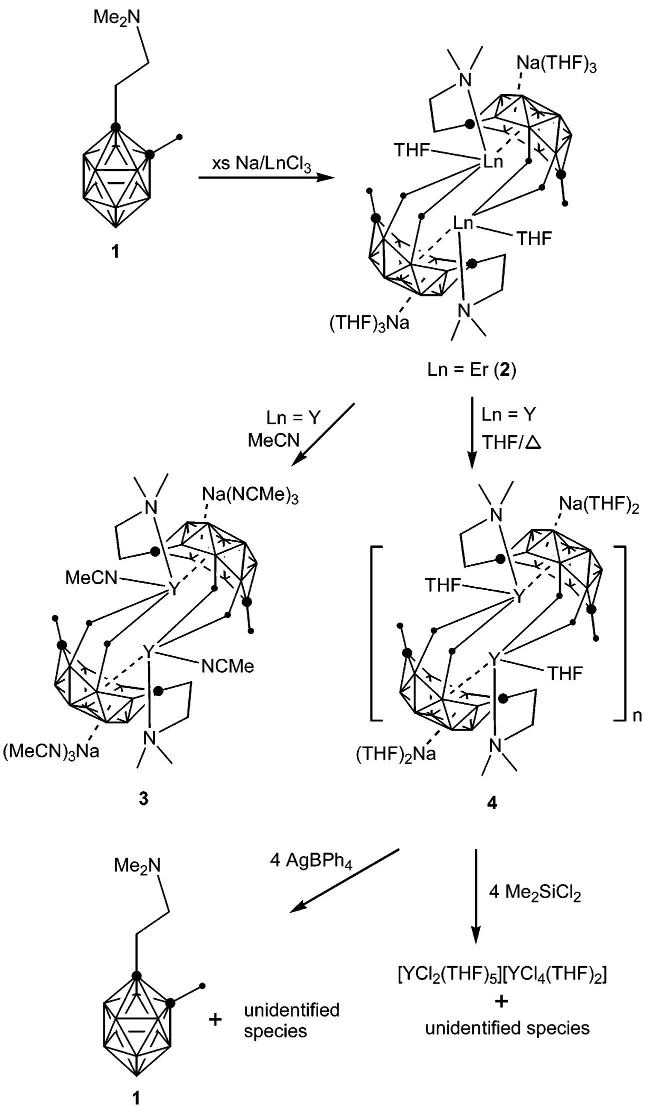
Scheme 1



of the pendant amido substituent and one solvent molecule (MeCN in **3** and THF in both **2** and **4**) in a four-legged piano stool arrangement. The representative structures of **2** and **4** are shown in Figures 1 and 2, respectively. The charge is then compensated by the associated complex cations $Na(solvent)_x^+$ through Na$\cdots$H$-$B interactions. If $x = 2$, the coordinatively unsaturated $Na(THF)_2^+$ will bind to B$-$H bonds of the neighboring cage to form an infinite polymeric chain as in **4**. These structures are very similar to that of $[\{\eta^1{:}\eta^7\text{-}[(CH_3OCH_2CH_2)C_2B_{10}H_{11}]Y(THF)\}\{Na(THF)_3\}]_2$[8] or $[\{\eta^1{:}\eta^7\text{-}[(CH_3OCH_2CH_2)C_2B_{10}H_{11}]Er(THF)\}\{Na(CH_3CN)(THF)\}]_n$.[8]

The Ln$-$C(cage) and Ln$-$B(cage) distances observed in **2**$-$**4**, as shown in Table 1, are close to the corresponding values found in $[\{\eta^1{:}\eta^7\text{-}[(MeOCH_2CH_2)C_2B_{10}H_{11}]Y(THF)\}\{Na(THF)_3\}]_2$[8] or $[\{\eta^1{:}\eta^7\text{-}[(MeOCH_2CH_2)C_2B_{10}H_{11}]Er(THF)\}\{Na(CH_3CN)(THF)\}]_n$,[8] respectively. These structural data indicate that the substituents ($Me_2NCH_2CH_2$ and $MeOCH_2CH_2$) on the bonding face of the carboranyl cage do not significantly change the coordination environments of the central metal ions, which is different from the results derived from $[Me_2Si\{(DCH_2CH_2)C_9H_5\}(C_2B_{10}H_{10})]^{2-}$ (D = MeO, Me_2N) ligands.[3]

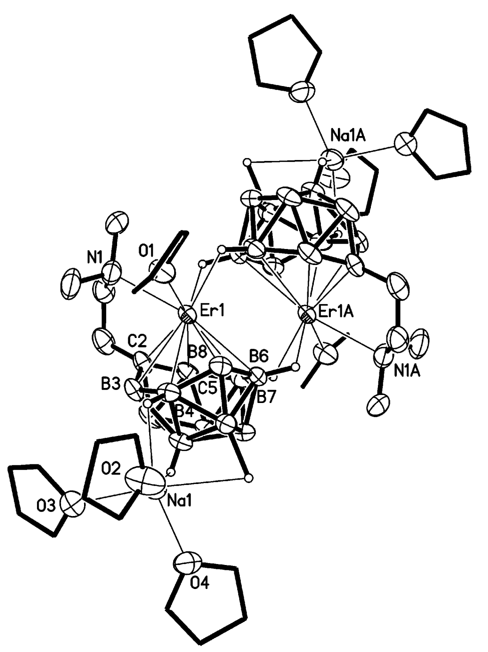


Figure 1. Molecular structure of $[\{\eta^1{:}\eta^7\text{-}[(Me_2NCH_2CH_2)C_2B_{10}H_{11}]Er(THF)\}\{Na(THF)_3\}]_2$ (**2**).

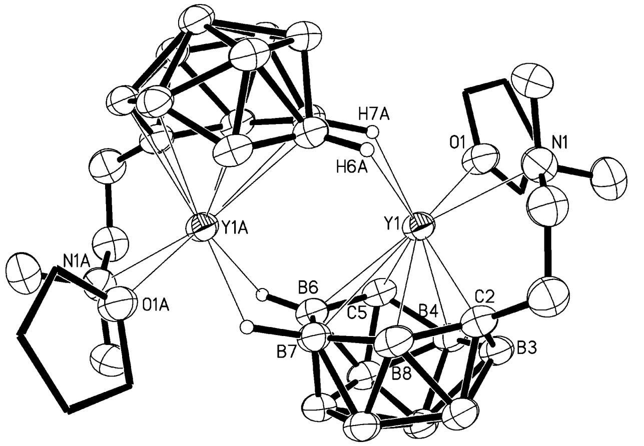
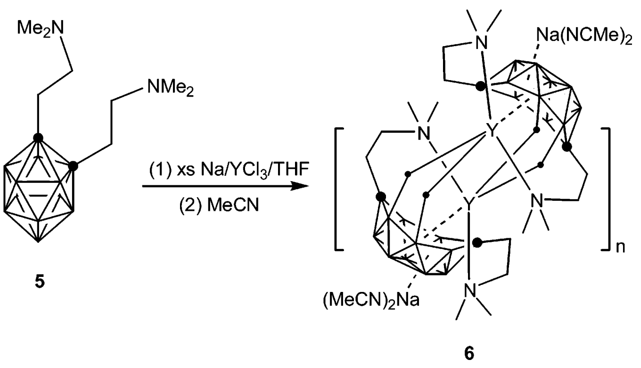


Figure 2. Molecular structure of the anion $[\eta^1{:}\eta^7\text{-}\{(Me_2NCH_2CH_2)C_2B_{10}H_{11}\}Y(THF)]_2^{2-}$ in **4**.

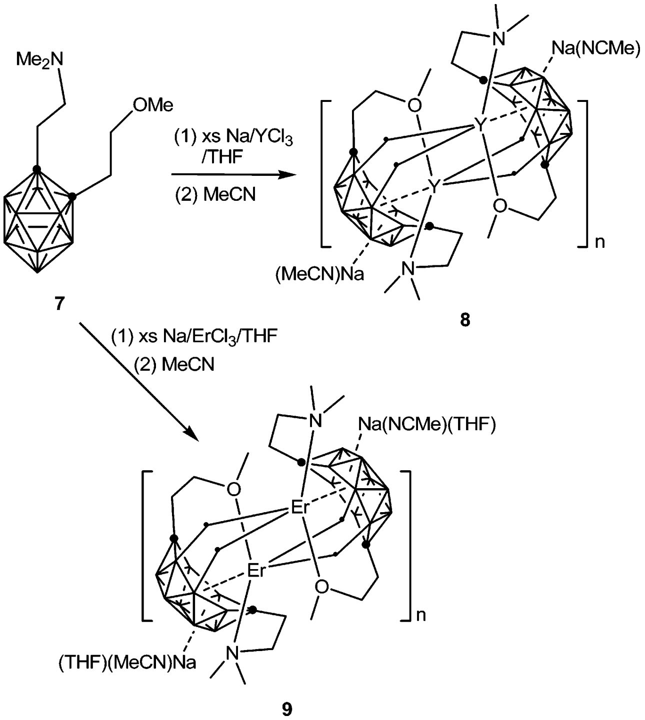
$\boldsymbol{[\{\eta^1{:}\eta^1{:}\eta^7\text{-}[(Me_2NCH_2CH_2)RC_2B_{10}H_{10}]Ln\}\{Na(solvent)_x\}]_n}$**.** Previous work showed that Me_2N and MeO groups in monofunctional carboranyl ligand systems did not cause any significant differences in the coordination environments of the central metal ion, probably due to the very large bonding face of η^7-carboranyl ligands, which diminishes steric effects imposed by the functional sidearms. We then examined the bisfunctional carborane systems. Treatment of $1,2\text{-}(Me_2NCH_2CH_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ (**5**) or $1\text{-}Me_2NCH_2CH_2\text{-}2\text{-}MeOCH_2CH_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ (**7**) with excess finely cut Na metal in THF, followed by reaction with 1 equiv of $LnCl_3$, gave, after recrystallization from MeCN/toluene/THF, $[\{\eta^1{:}\eta^1{:}\eta^7\text{-}[(Me_2NCH_2CH_2)_2C_2B_{10}H_{10}]Y\}\{Na(MeCN)_2\}]_n$ (**6**), $[\{\eta^1{:}\eta^1{:}\eta^7\text{-}[(Me_2NCH_2CH_2)(MeOCH_2CH_2)C_2B_{10}H_{10}]Y\}\{Na(MeCN)\}]_n$ (**8**), or $[\{\eta^1{:}\eta^1{:}\eta^7\text{-}[(Me_2NCH_2CH_2)(MeOCH_2CH_2)C_2B_{10}H_{10}]Er\}\{Na(MeCN)(THF)\}]_n$ (**9**) in 28$-$41% yields. These transformations are summarized in Schemes 2 and 3, respectively.

The ^1H NMR spectrum of **6** showed that two sidearms have the same chemical environment in solution and supported the ratio of two MeCN molecules per carbo-

Scheme 2



Scheme 3



rane cage. Its ^{11}B NMR spectrum exhibited a 1:2:2:3:2 splitting pattern with the chemical shifts ranging from −1.6 to −20.0 ppm. The ^{1}H NMR spectrum of **8** displayed the resonances of $MeOCH_2CH_2$ and $Me_2NCH_2CH_2$ protons and supported the ratio of one MeCN molecule per carborane cage. A 2:2:1:1:2:2 splitting pattern was observed in the ^{11}B NMR spectrum of **8** with the chemical shifts spanning from −1.0 to −35.4 ppm. The solid-state IR spectra of **6**, **8**, and **9** displayed a very strong peak at about 2500 cm^{-1} and a medium strong peak at about 2355 cm^{-1}, implying B−H−Ln interactions.[13,14]

Single-crystal X-ray analyses revealed that the molecular structures of **6**, **8**, and **9** bear the common structural motif of $[\eta^1:\eta^1:\eta^7\text{-}\{(Me_2NCH_2CH_2)(DCH_2CH_2)C_2B_{10}H_{10}\}Ln]_2^{2-}$ (D = Me$_2$N, MeO), and the coordination environments around the central metal ion are very similar to those observed in complexes **2**−**4** except for one DCH_2CH_2 moiety replacing one solvent molecule, as shown in Figures 3 and 4. These results show that the coordination of the second sidearm, regardless of Me$_2$N or MeO, does not largely alter the basic structural unit. Because of the differences in recrystallization conditions, the number of coordinated solvent molecules around the Na$^+$ ion is less than three, leading to the formation of polymeric chains. The bond distances are comparable with those observed in **2**−**4**, shown in Table 1.

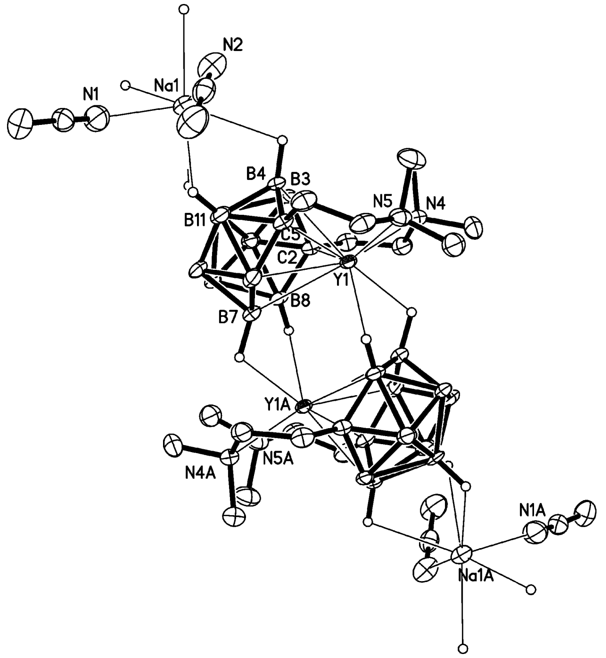


Figure 3. Molecular structure of $[\{\eta^1:\eta^1:\eta^7\text{-}[(Me_2NCH_2CH_2)_2C_2B_{10}H_{10}]Y\}\{Na(MeCN)_2\}]_n$ (**6**), showing a portion of the infinite polymeric chain.

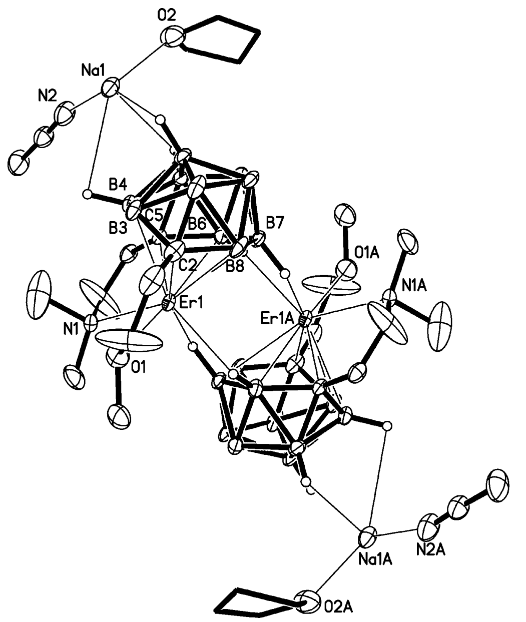


Figure 4. Molecular structure of $[\{\eta^1:\eta^1:\eta^7\text{-}[(MeOCH_2CH_2)(Me_2NCH_2CH_2)C_2B_{10}H_{10}]Er\}\{Na(MeCN)(THF)\}]_n$ (**9**), showing a portion of the infinite polymeric chain.

Reactivity. The chemical properties of 13-vertex *closo*-lanthanacarboranes bearing the η^7-carboranyl ligand are essentially unexplored.[15] It is generally believed that the bonding interactions between lan-

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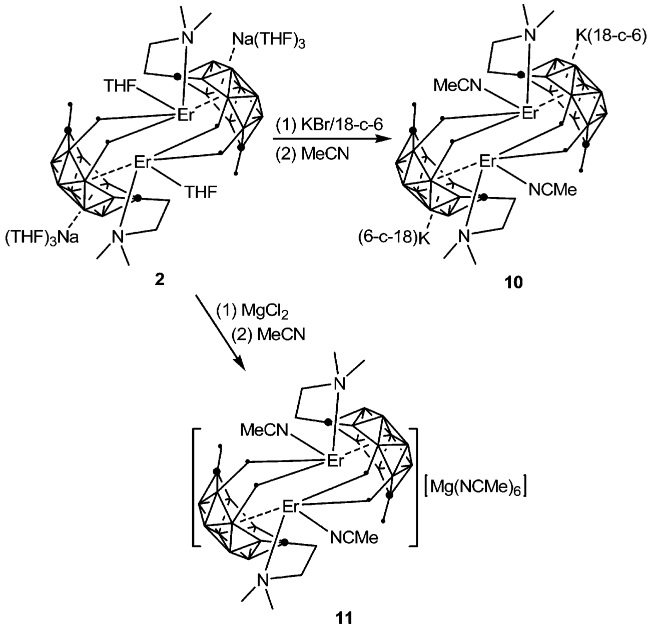
(15) (a) Xie, Z. *Coord. Chem. Rev.* **2002**, *23*, 231. (b) Xie, Z. *Acc. Chem. Res.* **2003**, *36*, 1. (c) Xie, Z. *Pure Appl. Chem.* **2001**, *73*, 361. (d) Xie, Z. *Pure Appl. Chem.* **2003**, *75*, 1335. (e) Saxena, A. K.; Hosmane, N. S. *Chem. Rev.* **1993**, *93*, 1081. (f) Grimes, R. N. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 1, p 373.

Scheme 4



thanide ions and ligands are ionic in nature.[2a] Could the η^7-carboranyl ligand be transferred from lanthanides to other transition metal ions? We examined the reactions of **2** with YCl_3 and $ZrCl_4$. No transmetalation between Er^{3+} and Y^{3+} or Zr^{4+} was observed, although both Y^{3+} and Zr^{4+} ions were known to be able to form stable bonds with η^7-*arachno*-carboranyl ligands.[8,16] Other reactions were also attempted. Treatment of **4** with 4 equiv of $AgBPh_4$ in THF led to the isolation of the neutral ligand **1** in 87% isolated yield, and other unidentified species (Scheme 1). Obviously, Ag^+ oxidized *arachno*-$[(Me_2NCH_2CH_2)C_2B_{10}H_{11}]^{4-}$ tetraanion to *closo*-$(Me_2NCH_2CH_2)C_2B_{10}H_{11}$ (**1**) during the reaction. Interaction between **4** and 4 equiv of Me_2SiCl_2 in THF resulted in the isolation of $[YCl_2(THF)_4][YCl_4(THF)_2]$ in 67% yield and other unidentified species (Scheme 1). The ^{11}B NMR spectrum indicated that the resulting boron-containing species was neither **1** nor **4**. Many attempts to isolate pure boron-containing complexes failed. In addition, **4** showed no reactivities toward unsaturated molecules such as PhNCO, ^nBuNC, and $2,6\text{-}Me_2C_6H_3NC$. Although displacement of the central metal ions in the 13-vertex *closo*-lanthanacarboranes was not successful, substitution of the associated complex cation $Na(THF)_3^+$ was facile. Treatment of **2** with 2 equiv of KBr and 18-crown-6 ether in THF afforded, after recrystallization from MeCN/toluene, $[\{\eta^1{:}\eta^7\text{-}[(Me_2NCH_2CH_2)C_2B_{10}H_{11}]Er(MeCN)\}\{K(18\text{-crown-}6)\}]_2\cdot 4$toluene (**10**·4toluene) in 57% yield. Under the same reaction conditions, reaction of **2** with 1 equiv of $MgCl_2$ in THF gave, after recrystallization from MeCN/toluene, $[\eta^1{:}\eta^7\text{-}\{(Me_2NCH_2CH_2)C_2B_{10}H_{11}\}Er(MeCN)]_2[Mg(MeCN)_6]\cdot MeCN$ (**11**·MeCN) in 62% yield. These transformations are summarized in Scheme 4. It was noted that both **10** and **11** were soluble in MeCN and pyridine, but insoluble in THF, toluene, and *n*-hexane, which facilitated the purification of the products.

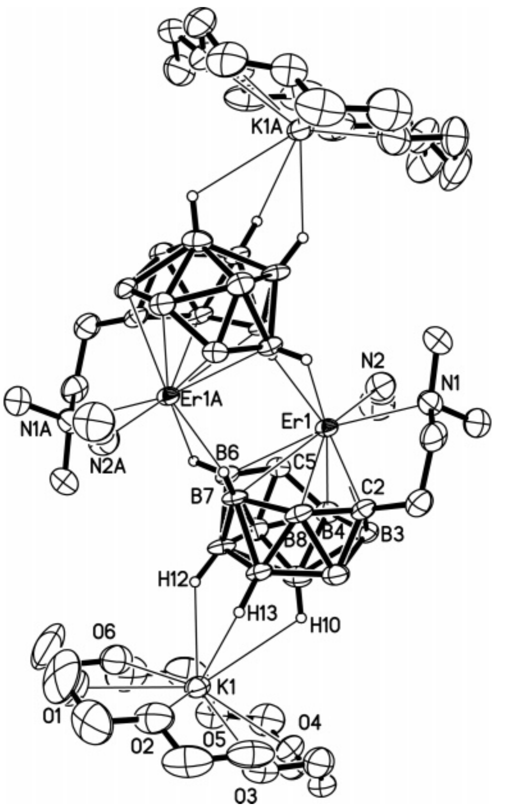


Figure 5. Molecular structure of $[\{\eta^1{:}\eta^7\text{-}[(Me_2NCH_2CH_2)C_2B_{10}H_{11}]Er(MeCN)\}\{K(18\text{-crown-}6)\}]_2$ (**10**).

The NMR spectra of both **10** and **11** were not informative because of the strong paramagnetism of Er^{3+}. They were characterized by single-crystal X-ray analyses. Both of them contain the common structural motif $[\eta^1{:}\eta^7\text{-}\{(Me_2NCH_2CH_2)C_2B_{10}H_{11}\}Er(MeCN)]_2^{2-}$, which differs from their parent core structural unit $[\eta^1{:}\eta^7\text{-}\{(Me_2NCH_2CH_2)C_2B_{10}H_{11}\}Er(THF)]_2^{2-}$ in **2** by only one solvent molecule, as shown in Figure 5. The associated complex cations are $K(18\text{-crown-}6)^+$ in **10** and $[Mg(MeCN)_6]^{2+}$ in **11**, respectively.

The key structural data around the Er atom in **2**, **10**, and **11** are very similar (Table 1). However, the Er(1)–N(2)–C(15) (coordinated MeCN) bond angle of 135.9(3)° in **10** is significantly different from that of 170.2(10)° in **11**. This phenomenon was also observed in a number of complexes in which M–NCMe coordination is involved.[17] It has been proposed that the angular position of the metal cation may allow interaction with electron density in both lone pairs and π orbitals on MeCN.[18] On the other hand, the energy gain or loss involved in the bonding of MeCN may be so small that the crystal packing forces would suffice to cause the deviation of the Er–N–C bond from linearity.

Conclusion

Several 13-vertex *closo*-lanthanacarboranes incorporating functionalized η^7-*arachno*-carboranyl ligands were prepared and structurally characterized. The results show that the effects of different Lewis base-appended functional sidearms on the resultant lanthanacarbo-

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[16] (a) Wang, Y.; Wang, H.; Li, H.-W.; Xie, Z. *Organometallics* **2002**, *21*, 3311. (b) Chui, K.; Yang, Q.; Mak, T. C. W.; Lam, W. H.; Lin, Z.; Xie, Z. *J. Am. Chem. Soc.* **2000**, *122*, 5758. (c) Wang, S.; Wang, Y.; Cheung, M.-S.; Xie, Z. *Tetrahedron* **2003**, *59*, 10373. (d) Chui, K.; Yang, Q.; Mak, T. C. W.; Xie, Z. *Organometallics* **2000**, *19*, 1391.

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[18] Darensbourg, M. Y. *Prog. Inorg. Chem.* **1985**, *33*, 221.

ranes are relatively small, which do not significantly alter the overall coordination environments around the lanthanide ions. Unlike Lewis base-appended indenyl–carboranyl ligands,[3] the differences among $[(Me_2NCH_2CH_2)C_2B_{10}H_{11}]^{4-}$, $[(Me_2NCH_2CH_2)_2C_2B_{10}H_{10}]^{4-}$, $[(Me_2NCH_2CH_2)(MeOCH_2CH_2)C_2B_{10}H_{10}]^{4-}$, and $[(MeOCH_2CH_2)_2C_2B_{10}H_{10}]^{4-}$ ligands in coordination chemistry are not significant.

The structural motif of $[\eta^1:\eta^7\text{-}\{(Me_2NCH_2CH_2)C_2B_{10}H_{11}\}Ln(solvent)]_2^{2-}$ or $[\eta^1:\eta^1:\eta^7\text{-}\{(Me_2NCH_2CH_2)(DCH_2CH_2)C_2B_{10}H_{10}\}Ln]_2^{2-}$ is observed in all cases. The coordinated solvent molecule around Ln can be replaced by other Lewis bases. The associate complex cations can also be displaced by other group 1 or 2 metal complexes. However, the lanthanide ion in the lanthanacarboranes cannot be substituted by other transition metal ions, although the bonding interactions between the lanthanide and the η^7-*arachno*-carboranyl ligand are ionic in nature. On the other hand, the lanthanides can be easily removed from lanthanacarboranes by reacting with silver(I) salt since Ag^+ can oxidize *arachno*-carborane to *closo*-carborane.

Acknowledgment. The work described in this article was supported by grants from the Research Grants Council of the Hong Kong Special Administration Region (Project No. CUHK4254/01P) and Direct Grant (Project No. 2060274).

Supporting Information Available: Tables of crystallographic data collection details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for complexes **2**–**4**, **6**, and **8**–**11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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