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Synthesis and characterization of half- and full-sandwich lanthanacarboranes of the C_2B_9-carborane ligand. X-ray crystal structures of $[LnCl_2(THF)_5][nido\text{-}C_2B_9H_{12}]$ (Ln = Y, Yb)

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Dedicated to Professor Sheldon G. Shore on the occasion of his 70th birthday.

Abstract

Treatment of $LnCl_3(THF)_x$ with one equivalent of $Na_2[nido\text{-}7,8\text{-}C_2B_9H_{11}]$ in THF gave the half-sandwich lanthanacarborane chloride compound $(\eta^5\text{-}C_2B_9H_{11})Ln(THF)_2(\mu\text{-}Cl)_2Na(THF)_2$ (Ln = Y (**1**), Er (**2**), Yb (**3**), Lu (**4**)). Recrystallization of **1** or **3** from a wet THF–toluene solution afforded the ionic compound $[LnCl_2(THF)_5][nido\text{-}C_2B_9H_{12}]$ (Ln = Y (**5**), Yb (**6**)). Reaction of **1** or **3** with $Na_2[nido\text{-}7,8\text{-}C_2B_9H_{11}]$ in a molar ratio of 1:1 in THF generated the full-sandwich lanthanacarborane $\{(\eta^5\text{-}C_2B_9H_{11})_2Ln(THF)_2\}\{Na(THF)_2\}$ (Ln = Y (**7**), Yb (**8**)). All of these new compounds were characterized by ^{1}H-, ^{13}C-, and ^{11}B-NMR spectra and elemental analyses. The solid-state structures of **5** and **6** were further confirmed by single-crystal X-ray analyses. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Carboranes; Lanthanacarboranes; Metallacarboranes; Organolanthanides; Sandwich compounds

1. Introduction

Since the first lanthanacarborane was reported in 1988 [1], numerous lanthanacarboranes of C_2B_{10} [2,3], C_2B_9 [4–6], and C_2B_4 [7] ligand systems have been prepared; however, examples of the discrete half-sandwich lanthanacarboranes are very rare [4a,7i]. In comparison with the well known organolanthanide compounds of the types $(\eta^5\text{-}C_5R_5)LnCl_2$ and $(\eta^8\text{-}C_8H_8)LnCl$, the carboranyl analogs $(\eta^5\text{-}C_2B_9H_{11})LnCl$ have thus far remained elusive [8]. Since this type of compound furnishes important intermediates for the preparation of species containing Ln–C, Ln–N, and Ln–O bonds, we attempted without success to prepare the half-sandwich lanthanacarborane chloride $(\eta^5\text{-}C_2B_9H_{11})LaCl(THF)_x$; instead, a full-sandwich lanthanacarborane $\{(\eta^5\text{-}C_2B_9H_{11})_2La(THF)_2\}\{Na(THF)_2\}$ was isolated, probably owing to the larger La^{3+} ion that causes the ligand redistribution [6a]. We then focused our efforts on the smaller lanthanides and yttrium. By using the THF-solvated complexes $LnCl_3(THF)_x$ as the starting materials, the half-sandwich compounds could be stabilized. The synthesis, characterization, and reactivity of these half-sandwich lanthanacarboranes are reported in this paper.

2. Results and discussion

2.1. Synthesis and characterization

It was reported that early lanthanocene chloride compounds, $(\eta^5\text{-}C_5H_5)LnCl_2$ or $(\eta^5\text{-}C_5H_5)_2LnCl$, would undergo disproportionation to form thermodynamically stable compounds $(\eta^5\text{-}C_5H_5)_3Ln$ [9]. Many methods have been developed in order to prevent such ligand redistribution reactions [8]; among these, the simplest is to use the THF-solvated complexes $LnCl_3(THF)_x$ as the starting materials [10]. We have extended this method to lanthanacarborane chemistry. Treatment of $LnCl_3$-

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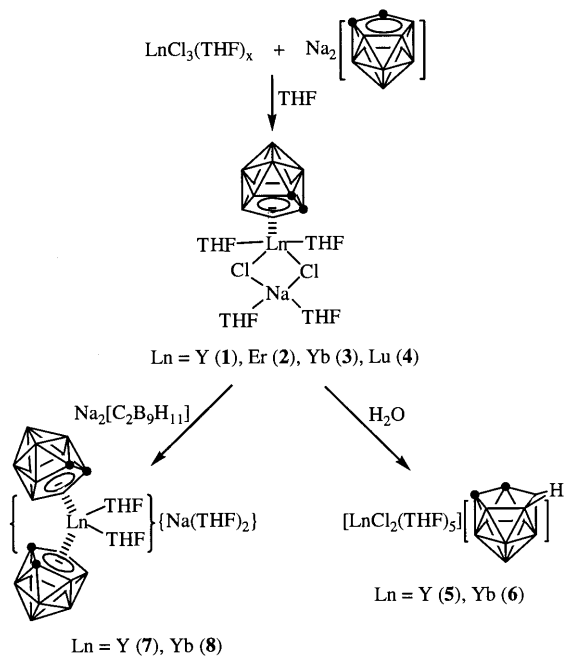
$(THF)_x$ with one equivalent of Na_2[*nido*-7,8-$C_2B_9H_{11}$] in THF gave, after work-up, half-sandwich lanthanacarborane chloride compounds of the general formula $(\eta^5$-$C_2B_9H_{11})Ln(THF)_2(\mu$-$Cl)_2Na(THF)_2$ (Ln = Y (**1**), Er (**2**), Yb (**3**), Lu (**4**)) in 40–52% yields. This formulation was made on the basis of elemental analyses, spectroscopic data, and reactivity patterns. The discrete half-sandwich samaracarborane of C_2B_4 ligand, {[η^5-$(Me_3Si)_2C_2B_4H_4$]Sm(OBu^t)($HOBu^t$)$_2$}{LiCl(THF)}, was recently reported [7i].

Compounds **1**–**4** are soluble in THF, sparely soluble in toluene, but insoluble in *n*-hexane. They are very air- and moisture-sensitive. Traces of air immediately converted **3** from orange–red microcrystals to a pale yellow powder.

Recrystallization of **3** from a wet THF–toluene solution gave a hydrolysis product [$YbCl_2(THF)_5$][*nido*-$C_2B_9H_{12}$] (**6**) as colorless crystals. Its Y analog, [$YCl_2(THF)_5$][*nido*-$C_2B_9H_{12}$] (**5**) could also be prepared in the same manner. It has been documented that inorganic ytterbium complexes are often colorless while organoytterbium compounds are intensely colored [8]. The orange–red colored **3** indicates the π interactions between Yb^{3+} and the $C_2B_9H_{11}^{2-}$ anion in compound **3**. Its hydrolysis product, **6**, is colorless, suggesting there is no obvious interaction between Yb^{3+} and $C_2B_9H_{12}^-$, which has been confirmed by X-ray analyses.

Since compounds **1**–**4** contain Ln–Cl bonds, they could react with another equivalent of carbollide ion to generate the full-sandwich lanthanacarboranes {(η^5-$C_2B_9H_{11})_2Ln(THF)_2$}{$Na(THF)_2$} (Ln = Y (**7**), Yb (**8**)) in about 64% yield. On the basis of elemental analyses and spectroscopic data, it could be suggested that these sandwich compounds have structures similar to that of {(η^5-$C_2B_9H_{11})_2La(THF)_2$}{$Na(THF)_2$} [6a]. All of the above-mentioned reactions are summarized in Scheme 1.



Scheme 1.

Compounds **1**–**8** were all characterized by various spectroscopic data and elemental analyses; **5** and **6** were further confirmed by single-crystal X-ray analyses. The IR spectra of **1**–**4** and **7**–**8** exhibit a unique doublet centered at about 2530 cm^{-1}, typical of the interaction of a positive metal center and an anionic carboranyl ligand [2–7]. The IR spectra of **5** and **6** display a strong and broad characteristic B–H absorption at about 2524 cm^{-1}. The ^{1}H-NMR spectra support the ratios of four THF molecules per carbollide ligand for the half-sandwich lanthanacarboranes **1**–**4**, two THF molecules per ligand for the full-sandwich lanthanacarborane **7**, and five THF molecules per ligand for the hydrolysis compounds **5** and **6**. The ^{11}B-NMR spectra of compounds **1** and **4**–**7** display a 2:2:1:2:1:1 splitting pattern although the chemical shifts are different. The appearance of such a 'monoanion-like' spectrum in solution could be understood by placing the Ln ion closer to the unique boron than to one of the two symmetrical borons on the pentagonal bonding face, which could impose the correct symmetry for a spectrum similar to that displayed by a monoanion rather than a dianion [4,6a]. Other paramagnetic compounds show many very broad resonances in a very wide range from -45 to -295 ppm.

2.2. Crystal structures of compounds 5 and 6

Crystal data and details of data collection and structure refinement are given in Table 1. Selected bond distances and angles are listed in Table 2. The solid-state structures of compounds **5** and **6** as derived from single-crystal X-ray analyses reveal that they are isostructural and isomorphous. Fig. 1 shows the representative structure of **6**. It consists of well separated, alternating layers of discrete cations $[LnCl_2(THF)_5]^+$ and carboranyl monoanions [*nido*-$C_2B_9H_{12}]^-$. The cation adopts a pentagonal-bipyramidal geometry with two chloro ligands at the axial positions and the five THF molecules at the equatorial positions, similar to that of $[LnCl_2(THF)_5]^+$ [3e,11] and $[SmI_2(THF)_5]^+$ [12] reported in the literature. The anion is very similar in structure to that in $[H(dmso)_2][C_2B_9H_{12}]$ (dmso = dimethyl sulfoxide) [13]. However,it is not certain whether a B–H–B bridge exists in the present cases since the H positions cannot be located definitely from X-ray data. The average C–B and B–B distances of 2.700(10) and 2.767(10) Å in **5** and 2.708(4) and 2.736(4) Å in **6** are comparable to those of 2.681(3) and 2.783(3) Å in $[H(dmso)_2][C_2B_9H_{12}]$ [13], respectively.

Table 1
Crystal data and details of data collection and structure refinement for **5** and **6**

Compound	**5**	**6**
Empirical formula	$C_{22}H_{52}B_9Cl_2O_5Y$	$C_{22}H_{52}B_9Cl_2O_5Yb$
Crystal size (mm^3)	$0.28\times0.24\times0.22$	$0.80\times0.48\times0.38$
M	653.7	737.9
Crystal system	Monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions		
a (Å)	8.554(2)	8.547(2)
b (Å)	17.458(4)	17.386(3)
c (Å)	23.720(5)	23.674(5)
β (°)	99.18(3)	99.19(3)
U ($Å^3$)	3497(1)	3473(1)
Z	4	4
D_c (g cm^{-3})	1.242	1.411
2θ range (°)	3.0–51.0	3.4–55.0
μ (mm^{-1})	1.849	2.875
F(000)	1368	1492
Observed reflections	3537	7946
Parameters refined	404	353
Goodness-of-fit	1.089	0.993
R_1	0.075	0.053
wR_2	0.171	0.143

3. Experimental

3.1. General procedure

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 were freshly distilled from sodium benzophenone ketyl immediately prior to use. Anhydrous $LnCl_3$ [14] and $[Me_3NH][nido\text{-}C_2B_9H_{12}]$ [6a] 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. ^{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 reference to internal or external TMS (0.00 ppm) or with respect to the residual protons of the deuterated solvent 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 Analytical laboratory, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, China.

Table 2
Selected bond distances (Å) and angles (°) for **5** and **6**

Compound **5**			
Y(1)–O(2)	2.378(8)	B(4)–B(6)	1.765(7)
Y(1)–O(1)	2.377(7)	B(4)–B(5)	1.744(10)
Y(1)–O(5)	2.396(8)	B(4)–B(10)	1.756(10)
Y(1)–O(4)	2.401(7)	B(5)–B(10)	1.778(10)
Y(1)–O(3)	2.390(7)	B(5)–B(9)	1.765(10)
Y(1)–Cl(2)	2.556(3)	B(6)–B(7)	1.765(10)
Y(1)–Cl(1)	2.562(3)	B(6)–B(11)	1.768(10)
C(1)–C(2)	1.658(10)	B(6)–B(10)	1.766(10)
C(1)–B(5)	1.687(10)	B(7)–B(8)	1.742(10)
C(1)–B(9)	1.708(10)	B(7)–B(11)	1.776(10)
C(1)–B(8)	1.702(10)	B(8)–B(9)	1.746(10)
C(2)–B(3)	1.679(10)	B(8)–B(11)	1.773(10)
C(2)–B(8)	1.704(10)	B(9)–B(11)	1.765(10)
C(2)–B(7)	1.720(10)	B(9)–B(10)	1.756(10)
B(3)–B(4)	1.729(10)	B(10)–B(11)	1.766(10)
		B(3)–B(7)	1.765(7)
Cl(2)–Y(1)–Cl(1)	179.20(12)		
Compound **6**			
Yb(1)–O(2)	2.352(2)	B(3)–B(8)	1.752(4)
Yb(1)–O(1)	2.357(2)	B(4)–B(5)	1.696(4)
Yb(1)–O(4)	2.360(2)	B(4)–B(8)	1.735(4)
Yb(1)–O(5)	2.362(2)	B(5)–B(10)	1.732(4)
Yb(1)–O(3)	2.366(2)	B(5)–B(9)	1.743(4)
Yb(1)–Cl(2)	2.516(1)	B(6)–B(10)	1.712(4)
Yb(1)–Cl(1)	2.529(1)	B(6)–B(7)	1.714(4)
C(1)–C(2)	1.521(4)	B(6)–B(11)	1.741(4)
C(1)–B(5)	1.680(4)	B(7)–B(8)	1.731(4)
C(1)–B(6)	1.709(4)	B(7)–B(11)	1.750(4)
C(1)–B(10)	1.735(4)	B(8)–B(11)	1.737(4)
C(2)–B(3)	1.680(4)	B(8)–B(9)	1.742(4)
C(2)–B(6)	1.713(5)	B(9)–B(10)	1.737(4)
C(2)–B(7)	1.732(4)	B(9)–B(11)	1.758(4)
B(3)–B(4)	1.721(4)	B(10)–B(11)	1.749(4)
		B(3)–B(7)	1.742(4)
Cl(2)–Yb(1)–Cl(1)	179.23(3)		

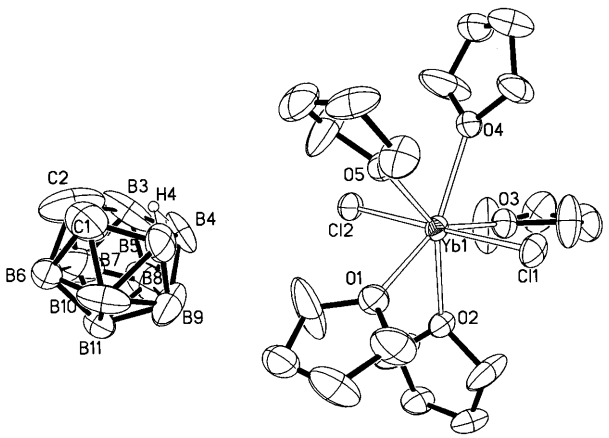


Fig. 1. Perspective view of the molecular structure of $[YbCl_2(THF)_5][nido\text{-}C_2B_9H_{12}]$ (**6**). The thermal ellipsoids are drawn at the 35% probability level.

3.2. Preparation of $(\eta^5\text{-}C_2B_9H_{11})Y(THF)_2(\mu\text{-}Cl)_2Na(THF)_2$ (**1**)

A suspension of YCl_3 (0.21 g, 1.07 mmol) in THF (10 ml) was stirred at room temperature for 2 days, resulting in the formation of a THF-solvated compound $YCl_3(THF)_{3.5}$ [11a]. To a suspension of NaH (0.075 g, 3.12 mmol) in 15 ml of THF was added the THF solution (10 ml) of $[Me_3NH][nido\text{-}C_2B_9H_{12}]$ (0.20 g, 1.04 mmol) and the mixture was refluxed overnight. The generated Me_3N was then removed along with approximately half of the solvent under vacuum. The suspension was allowed to settle. The resulting solution ($Na_2[nido\text{-}7,8\text{-}C_2B_9H_{11}]$) was then added dropwise at room temperature through a cannula to the above THF solution of $YCl_3(THF)_{3.5}$, and the reaction mixture was stirred at room temperature for 2 days, then allowed to settle. The white precipitate was filtered off. Removal of three-quarters of the solvent and *n*-hexane vapor diffusion afforded colorless microcrystals (0.28 g, 45%). ^{1}H-NMR: δ_H (pyridine-d_5) 3.63 (m, 16H, THF), 2.42 (br s, 2H, cage C*H*), 1.59 (m, 16H, THF). ^{13}C-NMR: δ_C (pyridine-d_5) 67.8, 25.8 (THF), carboranyl *C*–H was not observed. ^{11}B-NMR: δ_B (pyridine-d_5) −17.3 (2), −23.0 (2), −24.0 (1), −28.5 (2), −39.4 (1), −43.9 (1). IR (KBr, cm^{-1}): μ_{BH} 2540s, 2526s. Anal. Found: C, 35.52; H, 7.01. Calc. for $C_{18}H_{43}B_9Cl_2NaO_4Y$: C, 35.81; H, 7.18%.

3.3. Preparation of $(\eta^5\text{-}C_2B_9H_{11})Er(THF)_2(\mu\text{-}Cl)_2Na(THF)_2$ (**2**)

This compound was prepared as pink microcrystals from $ErCl_3$ (0.29 g, 1.06 mmol), $[Me_3NH][nido\text{-}C_2B_9H_{12}]$ (0.20 g, 1.04 mmol) and NaH (0.075 g, 3.12 mmol) in THF using the procedures described above for **1**; yield 0.37 g (52%). ^{1}H-NMR: δ_H (pyridine-d_5) 3.64 (br s, 16H, THF), 2.58 (br s, 2H, cage C*H*), 1.58 (br s, 16H, THF). ^{13}C-NMR: δ_C (pyridine-d_5) 67.8, 25.8 (THF), carboranyl *C*–H was not observed. ^{11}B-NMR: δ_B (pyridine-d_5) many very broad resonances at −45.2, −100.0, −140.1, −180.6, −219.3, −246.5, −295.1. IR (KBr, cm^{-1}): μ_{BH} 2540s, 2520s. Anal. Found: C, 31.31; H, 6.01. Calc. for $C_{18}H_{43}B_9Cl_2ErNaO_4$: C, 31.70; H, 6.36%.

3.4. Preparation of $(\eta^5\text{-}C_2B_9H_{11})Yb(THF)_2(\mu\text{-}Cl)_2Na(THF)_2$ (**3**)

This compound was prepared as orange–red microcrystals from $YbCl_3$ (0.29 g, 1.04 mmol), $[Me_3NH][nido\text{-}C_2B_9H_{12}]$ (0.20 g, 1.04 mmol) and NaH (0.075 g, 3.12 mmol) in THF using the procedures described above for **1**; yield 0.33 g (46%). ^{1}H-NMR: δ_H (pyridine-d_5) 3.54 (br s, 16H, THF), 2.58 (br s, 2H, cage C*H*), 1.49 (br s, 16H, THF). ^{13}C-NMR: δ_C (pyridine-d_5) 67.8, 25.8 (THF), carboranyl *C*–H was not observed. ^{11}B-NMR: δ_B (pyridine-d_5) many very broad resonances at −67.9, −87.4, −101.1, −120.3, −138.6. IR (KBr, cm^{-1}): μ_{BH} 2560s, 2535s. Anal. Found: C, 31.00; H, 6.11. Calc. for $C_{18}H_{43}B_9Cl_2NaO_4Yb$: C, 31.44; H, 6.30%.

3.5. Preparation of $(\eta^5\text{-}C_2B_9H_{11})Lu(THF)_2(\mu\text{-}Cl)_2Na(THF)_2$ (**4**)

This compound was prepared as colorless microcrystals from $LuCl_3$ (0.30 g, 1.07 mmol), $[Me_3NH][nido\text{-}C_2B_9H_{12}]$ (0.20 g, 1.04 mmol) and NaH (0.075 g, 3.12 mmol) in THF using the procedures described above for **1**; yield 0.29 g (40%). ^{1}H-NMR: δ_H (pyridine-d_5) 3.63 (m, 16H, THF), 2.40 (br s, 2H, cage C*H*), 1.59 (m, 16H, THF). ^{13}C-NMR: δ_C (pyridine-d_5) 67.8, 25.8 (THF), carboranyl *C*–H was not observed. ^{11}B-NMR: δ_B (pyridine-d_5) −12.2 (2), −17.8 (2), −18.8 (1), −23.3 (2), −34.2 (1), −38.7 (1). IR (KBr, cm^{-1}): μ_{BH} 2545s, 2522s. Anal. Found: C, 31.09; H, 6.12. Calc. for $C_{18}H_{43}B_9Cl_2LuNaO_4$: C, 31.34; H, 6.28%.

3.6. Preparation of $[YCl_2(THF)_5][nido\text{-}C_2B_9H_{12}]$ (**5**)

This compound was initially isolated as colorless crystals from many recrystallizations of **1** from a THF–toluene solution. It was then prepared by a controlled hydrolysis reaction. A stock solution of toluene containing 0.1% water was prepared by adding 0.5 ml of water to 500 ml of dry toluene. Compound (η^5-$C_2B_9H_{11}$)Y(THF)$_2$(μ-Cl)$_2$Na(THF)$_2$ (**1**; 0.15 g, 0.25 mmol) was dissolved in a mixed solvent of THF (10 ml) and toluene (4 ml) from the stock solution under stirring to give a clear colorless solution. Slow evaporation of the solvents over days afforded **5** as colorless crystals which were suitable for X-ray analyses (0.067 g, 41%). ^{1}H-NMR: δ_H (pyridine-d_5) 3.63 (m, 20H, THF), 2.10 (br s, 2H, cage C*H*), 1.59 (m, 20H, THF). ^{13}C-NMR: δ_C (pyridine-d_5) 67.8, 25.8 (THF), carboranyl *C*–H was not observed. ^{11}B-NMR: δ_B (pyridine-d_5) −17.3 (2), −23.0 (2), −24.0 (1), −28.5 (2), −39.4 (1), −43.9 (1). IR (KBr, cm^{-1}): μ_{BH} 2524s. Anal. Found: C, 40.00; H, 8.12. Calc. for $C_{22}H_{52}B_9Cl_2O_5Y$: C, 40.42; H, 8.02%.

3.7. Preparation of $[YbCl_2(THF)_5][nido\text{-}C_2B_9H_{12}]$ (**6**)

This compound was prepared as colorless crystals from an orange–red compound (η^5-$C_2B_9H_{11}$)Yb(THF)$_2$(μ-Cl)$_2$Na(THF)$_2$ (**3**; 0.17 g, 0.25 mmol) in a THF–toluene solution using the procedures described above for **5**; yield 0.065 g (35%). It is noted that the color of **3** immediately changed from orange–red to colorless upon dissolution. ^{1}H-NMR: δ_H (pyridine-d_5) 3.63 (br s, 20H, THF), 2.00 (br s, 2H, cage C*H*), 1.59 (br s, 20H, THF). ^{13}C-NMR: δ_C (pyridine-

d_5) 67.9, 25.9 (THF), carboranyl *C*–H was not observed. ^{11}B-NMR: δ_B (pyridine-d_5) −17.2 (2), −23.0 (2), −23.8 (1), −28.4 (2), −39.3 (1), −43.9 (1). IR (KBr, cm^{-1}): μ_{BH} 2524vs. Anal. Found: C, 36.27; H, 7.49. Calc. for $C_{22}H_{52}B_9Cl_2O_5Yb$: C, 35.81; H, 7.10%.

3.8. Preparation of $\{(\eta^5\text{-}C_2B_9H_{11})_2Y(THF)_2\}\{Na(THF)_2\}$ (7)

To a suspension of NaH (0.075 g, 3.12 mmol) in 15 ml of THF was added the THF solution (10 ml) of [Me_3NH][*nido*-$C_2B_9H_{12}$] (0.20 g, 1.04 mmol) and the mixture was refluxed overnight. The generated Me_3N was then removed along with approximately half of the solvent under vacuum. The suspension was allowed to settle. The resulting solution (Na_2[*nido*-7,8-$C_2B_9H_{11}$]) was then slowly added to a THF solution (15 ml) of (η^5-$C_2B_9H_{11}$)Y(THF)$_2$(μ-Cl)$_2$Na(THF)$_2$ (**1**; 0.62 g, 1.03 mmol) at room temperature through a cannula, and the reaction mixture was stirred at room temperature for 2 days, then allowed to settle. The white precipitate was filtered off. Concentration of the solution and *n*-hexane vapor diffusion afforded colorless microcrystals over days (0.44 g, 64%). ^{1}H-NMR: δ_H (pyridine-d_5) 3.63 (m, 16H, THF), 2.42 (br s, 4H, cage C*H*), 1.59 (m, 16H, THF). ^{13}C-NMR: δ_C (pyridine-d_5) 67.8, 25.8 (THF), carboranyl *C*–H was not observed. ^{11}B-NMR: δ_B (pyridine-d_5) −17.2 (2), −23.0 (2), −24.0 (1), −28.5 (2), −39.4 (1), −44.0 (1). IR (KBr, cm^{-1}): μ_{BH} 2543s, 2521s. Anal. Found: C, 36.20; H, 7.85. Calc. for $C_{20}H_{54}B_{18}NaO_4Y$: C, 36.11; H, 8.18%.

3.9. Preparation of $\{(\eta^5\text{-}C_2B_9H_{11})_2Yb(THF)_2\}\{Na(THF)_2\}$ (8)

This compound was prepared as an orange–red crystalline solid from (η^5-$C_2B_9H_{11}$)Yb(THF)$_2$(μ-Cl)$_2$Na(THF)$_2$ (**3**; 0.71 g, 1.03 mmol) and Na_2[*nido*-7,8-$C_2B_9H_{11}$] (1.04 mmol) in THF using the procedures described above for **7**; yield 0.50 g (65%). ^{1}H- and ^{13}C-NMR spectra could not be recorded owing to the loss of lock signals. The ^{11}B-NMR spectrum consisted of many very broad, unresolved resonances. IR (KBr, cm^{-1}): μ_{BH} 2546s, 2520s. Anal. Found: C, 32.21; H, 7.45. Calc. for $C_{20}H_{54}B_{18}NaO_4Yb$: C, 32.06; H, 7.27%.

3.10. X-ray structure determination

Single crystals were immersed in Paraton-N oil and sealed under N_2 in thin-walled glass capillaries. Data were collected at 293 K on a Rigaku AFC7R diffractometer using Mo–K_α radiation from a Rigaku rotating-anode X-ray generator operating at 50 kV and 90 mA. An absorption correction was applied by correlation of symmetry-equivalent reflections using the ABSCOR program [15]. 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 Siemens SHELXTL program package (PC version) [16]. Most of the carborane hydrogen atoms were located from different Fourier syntheses. All other hydrogen atoms were geometrically fixed using the riding model. Three out of the five THF molecules (C7–C18) in **5** are disordered over two sets of positions with 0.5:0.5 occupancies.

4. Supplementary material

Crystallographic data for the structural analysis (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC no. 141754 for **5** and no. 141755 for **6**. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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