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# Chemistry of *C*-Trimethylsilyl-Substituted Heterocarboranes. 24. Synthetic, Spectroscopic, Structural, and Reactivity Studies on Half- and Full-Sandwich Yttracarboranes of 2,3-C$_2$B$_4$- and 2,4-C$_2$B$_4$-Carborane Ligands

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The reaction of YCl$_3$ with *closo*-*exo*-5,6-[($\mu$-H)$_2$Li(THF)$_2$]-1-Li(THF)$_2$-2-(SiMe$_3$)-3-(R)-2,3-C$_2$B$_4$H$_4$ (R = SiMe$_3$ and Me) or *closo*-*exo*-5,6-[($\mu$-H)$_2$Na(THF)$_2$]-1-Na(THF)$_2$-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$ in 1:2 molar ratios in dry benzene produced the yttracarboranes [Li(THF)$_4$]{1-Cl-1-(THF)-2,2′-(SiMe$_3$)$_2$-3,3′-(R)$_2$-4,4′,5,5′-Li(THF)[1,1′-*commo*-Y(2,3-C$_2$B$_4$H$_4$)$_2$]} (R = SiMe$_3$ (**I**), Me (**II**)) or {Na(THF)$_3$}$_2${[1-(THF)-1-($\mu$-H)$_2$-2,2′,4,4′-(SiMe$_3$)$_4$-1,1′-*commo*-Y(2,4-C$_2$B$_4$H$_4$)$_2$]$_2$} (**III**) in yields of 83%, 80%, and 74%, respectively. Compound **I** was found to react with excess NaH in dry THF to give a hydridoyttracarborane sandwich 1-H-2,2′,3,3′-(SiMe$_3$)$_4$-[4,4′,5-Li(THF)]$_2$-[1,1′-*commo*-Y(2,3-C$_2$B$_4$H$_4$)$_2$] (**V**) in 80% yield. Attempts to prepare the half-sandwich yttracarboranes directly from the reaction of YCl$_3$, Me$_3$SiCH$_2$MgCl, and 2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_6$ proved unsuccessful, instead, the reaction produced the mixed magnesa-/yttracarborane *closo*-1-Y-{1,1′-($\mu$-Cl)$_2$-*exo*-[5,6-($\mu$-H)$_2$-Mg(THF)$_2$]-1,1′-($\mu$-Cl)$_2$-[*closo*-1-Mg(THF)-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$]}-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$(3.5C$_6$H$_6$) (**IV**). All compounds were characterized by their IR and $^1$H, $^{11}$B, and $^{13}$C NMR spectra; **V** was also characterized by its $^7$Li NMR spectrum. The structures of **I**, **III**, and **IV** were determined by single-crystal X-ray crystallography. Compound **I** is a bent-sandwich complex in which the Y atom is bonded to two carborane units, a Cl anion, and a THF molecule to give a very distorted tetrahedral arrangement around the metal. The structure of **III** is a dimer in which each Y atom is bonded to two carboranes and a THF, the fourth coordination site being occupied by a pair of Y−H−B bridges to two adjacent borons in a neighboring carborane.

## Introduction

Despite the difference in charges on the ligands, it has been established that the coordination chemistry of the dianionic carborane ligands, especially those in the [(CR)$_2$B$_9$H$_9$]$^{2-}$ and [(CR)$_2$B$_4$H$_4$]$^{2-}$ (R = H or a cage carbon substituent) cage systems, is very similar to that of the monoanionic cyclopentadienyl (Cp) ligands.[1] In particular, there have been a number of recent reports on the half- and full-sandwich metallacarboranes of the lanthanide metals, involving La,[2] Nd,[3] Sm,[4−7] Eu,[8,9] Gd,[6,7,10] Tb,[6,11] Dy,[6,7] Ho,[6,7,12,13] Er,[7,14] and Yb,[4,5] being incorporated into C$_2$B$_9$- and C$_2$B$_{10}$-carborane cages, as well as into both the 2,3-C$_2$B$_4$ (carbons-adjacent) and the 2,4-C$_2$B$_4$ (carbons-apart) cages. On the other hand, although the chemistry of the group 3 organometallic complexes involving Cp ligands has been extensively investigated,[15] the parallel studies in the carborane

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ligand systems are quite limited. The first description of a group 3 metallacarborane other than those of the lanthanides was in our preliminary report of the anionic yttracarborane sandwich [Y(Cl)(THF){$\eta^5$-$(Me_3Si)_2$-$C_2B_4H_4\}_2$·Li(THF)]$^-$.[16] Soon after, Bercaw and coworkers reported the synthesis and structure of the scandacarborane $[Li(THF)_3]Li[Sc(C_2B_9H_{11})(Cp^*)(CH\text{-}\{SiMe_3\}_2)]_2$ ($Cp^* = (C_5Me_5)^-$) as well as its hydrogenation product $[Cp^*(C_2B_9H_{11})ScH]_2[Li(THF)]_2$.[17] Both of these complexes were found to be inert to ligand substitution or addition, due to a possible combination of unfavorable charge, steric factors, or, in the case of the hydride, the formation of a very stable dimer. Since facile ligand addition would be the first step in the potential use of these Sc and Y d$^0$ complexes as Ziegler–Natta-type catalysts, it is of interest to further explore the syntheses and reactivities of the group 3 metallacarboranes. Since the larger Y complexes would be less likely to suffer steric complications, a study of the syntheses and reactivities of a number of half- and full-sandwich yttracarboranes of the $C_2B_4$-ligand systems was undertaken. Here, we report the details of this study.

## Experimental Section

**Materials.** 2,3-Bis(trimethylsilyl)-2,3-dicarba-*nido*-hexaborane(8), 2-(trimethylsilyl)-3-(methyl)-2,3-dicarba-*nido*-hexaborane(8) and 1,2-bis(trimethylsilyl)-1,2-dicarba-*closo*-hexaborane(6) were prepared using literature methods.[18–20] The *closo*-carborane was subsequently converted to the corresponding tetrahydrofuran (THF)-solvated carbons-apart disodium compound *closo-exo*-5,6-[($\mu$-H)$_2$Na(THF)$_2$]-1-Na(THF)$_2$-2,4-(SiMe$_3$)$_2$-2,4-$C_2B_4H_4$ by reduction with Na/$C_{10}H_8$ as outlined previously.[21] The *nido*-carborane precursors were converted to the corresponding THF-solvated dilithium compounds, *closo-exo*-5,6-[($\mu$-H)$_2$Li(THF)$_2$]-1-Li(THF)$_2$-2-(SiMe$_3$)-3-(R)-2,3-$C_2B_4H_4$ (R = SiMe$_3$, Me) as previously described.[20] Before use, naphthalene (Aldrich) was sublimed in vacuo, Na metal (Aldrich) was freshly cut in a drybox, anhydrous $YCl_3$ (Strem Chemicals) was heated at 110 °C in vacuo overnight to remove any last traces of moisture in the sample, and NaH (Aldrich) in a mineral oil dispersion was washed repeatedly with dry *n*-pentane. $Me_3SiCH_2MgCl$ (1.0 M solution in diethyl ether; Aldrich) and *tert*-butyllithium, *t*-BuLi (1.7 M solution in pentane, Aldrich), were used as received. Benzene, THF, and *n*-hexane were dried over $LiAlH_4$ and doubly distilled; all other solvents, including $C_6D_6$ and THF-$d_8$ (Aldrich), were dried over 4–8 mesh molecular sieves (Aldrich) and either saturated with dry argon or degassed before use.

**Spectroscopic and Analytical Procedures.** Proton, lithium-7, boron-11, and carbon-13 pulse Fourier transform NMR spectra, at 200, 77.7, 64.2, and 50.3 MHz, respectively, were recorded on an IBM-WP200 SY multinuclear NMR spectrometer. Infrared spectra were recorded on a Nicolet Magna 550 FT-IR spectrophotometer. Elemental analyses were obtained from E+R Microanalytical Laboratory, Inc., Corona, NY.

**Synthetic Procedures.** All experiments were carried out in Pyrex glass round-bottom flasks of 100–250 mL capacities, containing magnetic stirring bars and fitted with high-vacuum Teflon valves. Nonvolatile substances were manipulated in either a drybox or an evacuable glovebag under an atmosphere of dry nitrogen. All known compounds among the products were identified by comparing their IR and NMR spectra with those of authentic samples.

**Synthesis of [Li(THF)$_4$]{1-Cl-1-(THF)-2,2′-(SiMe$_3$)$_2$-3,3′-(R)$_2$-4,4′,5,5′-Li(THF)[1,1′-*commo*-Y(2,3-$C_2B_4H_4$)$_2$]} (R = SiMe$_3$ (I); Me (II)).** In separate experiments, a 3.60 mmol (1.87 g) sample of *closo-exo*-5,6-[($\mu$-H)$_2$Li(THF)$_2$]-1-Li(THF)$_2$-2,3-(SiMe$_3$)$_2$-2,3-$C_2B_4H_4$ or a 3.0 mmol (1.39 g) sample of *closo-exo*-5,6-[($\mu$-H)$_2$Li(THF)$_2$]-1-Li(THF)$_2$-2-(SiMe$_3$)-3-(Me)-2,3-$C_2B_4H_4$ was reacted with 0.35 (1.79 mmol) or 0.29 g (1.5 mmol) of anhydrous $YCl_3$ in 25 mL of dry benzene at 0 °C for 24 h, during which time the solution turned turbid yellow. The mixture was filtered through a frit in vacuo, and the residue was washed repeatedly with a solvent mixture of hexane (90%) and THF (10%) to collect a clear pale yellow filtrate. An off-white solid that remained on the frit (not measured) was identified as LiCl and was discarded. The filtrate was then concentrated by slow removal of solvents in vacuo to obtain an off-white crystalline solid, which was later identified as [Li(THF)$_4$]{1-Cl-1-(THF)-2,2′-(SiMe$_3$)$_2$-3,3′-(R)$_2$-4,4′,5,5′-Li(THF)-[1,1′-*commo*-Y(2,3-$C_2B_4H_4$)$_2$]} (R = SiMe$_3$ (**I**, 1.45 g, 1.513 mmol, 83% yield; mp 110 °C (dec)) or Me (**II**, 1.0 g, 1.2 mmol, 80% yield, mp 98 °C (dec))). Anal. Calcd for $C_{40}H_{92}O_6B_8Si_4$-$ClLi_2Y$ (**I**) and $C_{36}H_{80}O_6B_8Si_2ClLi_2Y$ (**II**): C, 47.69 and 48.59; H, 9.21 and 9.06; Si, 11.15 and 6.31; Cl, 3.52 and 3.98. Found: C, 47.43 and 48.38; H, 9.16 and 9.08; Si, 11.54 and 6.63; Cl, 3.45 and 4.01.

**Spectroscopic Data for I.** $^1$H NMR ($C_6D_6$, external $Me_4Si$): $\delta$ 3.62 (s, 24H, $CH_2$, THF), 1.63 (s, 24H, $CH_2$, THF), 0.58 (s, 18H, SiMe$_3$), 0.48 (s, 18H, SiMe$_3$). $^{11}$B NMR (THF-$d_8$, external $BF_3$·$OEt_2$): $\delta$ 26.23 (br, 1B, basal BH, $^1J(^{11}B-^1H)$ = unresolved), 18.79 (br, 1B, basal BH, $^1J(^{11}B-^1H)$ = unresolved), 1.47 (br, 1B, basal BH, $^1J(^{11}B-^1H)$ = unresolved), −29.09 (br, 1B, apical BH, $^1J(^{11}B-^1H)$ = unresolved). $^{13}$C NMR ($C_6D_6$, external $Me_4Si$): $\delta$ 110.63 (s, v br, cage carbons), 68.63 (t, $CH_2$, THF, $^1J(^{13}C-^1H)$ = 147.0 Hz), 25.66 (t, $CH_2$, THF, $^1J(^{13}C-^1H)$ = 133.1 Hz), 3.82 (q (br), SiMe$_3$, $^1J(^{13}C-^1H)$ = 118.3 Hz). IR (cm$^{-1}$, $C_6D_6$ vs $C_6D_6$): 2530(s), 2480(s, sh), 2449(s) [$\nu$(BH)].

**Spectroscopic Data for II.** $^1$H NMR ($C_6D_6$, external $Me_4Si$): $\delta$ 3.63 (s, 24H, $CH_2$, THF), 2.88 (s, 6H, Me), 1.61 (s, 24H, $CH_2$, THF), 0.78 (s, 9H, SiMe$_3$), 0.57 (s, 9H, SiMe$_3$). $^{11}$B NMR (THF-$d_8$, external $BF_3$·$OEt_2$): $\delta$ 15.02 (br, 2B, basal BH, $^1J(^{11}B-^1H)$ = unresolved), 13.52 (br, 1B, basal BH, $^1J(^{11}B-^1H)$ = unresolved), −29.41 (br, 1B, apical BH, $^1J(^{11}B-^1H)$ = unresolved). $^{13}$C NMR ($C_6D_6$, external $Me_4Si$): $\delta$ 116.13 (s, v br, cage carbons (SiCB)), 108.13 (s, v br, cage carbons (MeCB)), 66.53 (t, $CH_2$, THF, $^1J(^{13}C-^1H)$ = 147.0 Hz), 25.66 (t, $CH_2$, THF, $^1J(^{13}C-^1H)$ = 133.1 Hz), 3.11 (q (br), SiMe$_3$, $^1J(^{13}C-^1H)$ = 116.8 Hz). IR (cm$^{-1}$, $C_6D_6$ vs $C_6D_6$): 2530(s), 2490(s,sh) [$\nu$(BH)].

**Synthesis of the Carbons-Apart Yttracarborane Sandwich Complex {Na(THF)$_3$}$_2${[1-(THF)-1-($\mu$-H)$_2$-2,2′,4,4′-(SiMe$_3$)$_4$-1,1′-*commo*-Y(2,4-$C_2B_4H_4$)$_2$]$_2$} (III).** To a suspension of 0.6 g (3.0 mmol) of $YCl_3$ in 15 mL of benzene, a solution of 2.22 g (6.0 mmol) of *closo-exo*-5,6-[($\mu$-H)$_2$Na(THF)$_2$]-1-Na(THF)$_2$-2,4-(SiMe$_3$)$_2$-2,4-$C_2B_4H_4$ in THF/benzene (2:3) was added in vacuo at 0 °C. The reaction mixture was stirred at room temperature overnight. The resulting white solid was separated from the solution by vacuum filtration. All solvents were removed from the filtrate slowly in vacuo to obtain a pale

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yellow solid, which was later washed with hexane and recrystallized in benzene to a give colorless crystalline solid, identified as $\{Na(THF)_3\}_2\{[1\text{-}(THF)\text{-}1\text{-}(\mu\text{-}H)_2\text{-}2,2',4,4'\text{-}(SiMe_3)_4\text{-}1,1'$-*commo*-$Y(2,4\text{-}C_2B_4H_4)_2]_2\}$ (**III**) (1.85 g, 2.21 mmol; mp > 250 °C (dec)) in 74% yield. Anal. Calcd for $C_{66}H_{156}B_{16}O_{8.5}Si_8Na_2Y_2$: C, 46.43; H, 9.14. Found: C, 46.49; H, 9.25.

**Spectroscopic Data for III.** $^1H$ NMR (THF-$d_8$, relative to external $Me_4Si$): $\delta$ 3.59 (m, 16H, $CH_2$, THF), 1.74 (m, 16H, $CH_2$, THF), 0.11 (s, 9H, $SiMe_3$), 0.04 (s, 9H, $SiMe_3$), −0.06 (s, 18H, $SiMe_3$). $^{11}B$ NMR (THF-$d_8$, relative to external $BF_3.OEt_2$): $\delta$ 19.18 (vbr, 6B, basal BH, $^1J(^{11}B-^1H)$ = unresolved), −31.80 (d, br, 1B, apical BH, $^1J(^{11}B-^1H)$ = unresolved), −37.06 (d, br, 1B, apical BH, $^1J(^{11}B-^1H)$ = unresolved). $^{13}C$ NMR (THF-$d_8$, relative to external $Me_4Si$): $\delta$ 105.56, 104.84, 100.23 (s, br, cage carbons), 68.21 (t, $CH_2$, THF, $^1J(^{13}C-^1H)$ = 145 Hz), 26.33 (t, $CH_2$, THF, $^1J(^{13}C-^1H)$ = 131 Hz), 2.43 (q, $SiMe_3$, $^1J(^{13}C-^1H)$ = 116 Hz), 2.13 (q, $SiMe_3$, $^1J(^{13}C-^1H)$ = 118 Hz). IR ($cm^{-1}$, $C_6D_6$ vs $C_6D_6$): 2532.4(s), 2470.4(s) [ν(B−H)].

**Attempted Synthesis of the Half-Sandwich Alkylyttracarborane *closo*-1-Y($CH_2SiMe_3$)-2,3-($SiMe_3$)$_2$-2,3-$C_2B_4H_4$: Synthesis of *closo*-1-Y-{1,1′-(μ-Cl)$_2$-*exo*-[5,6-(μ-H)$_2$-Mg(THF)$_2$]-1,1′-(μ-Cl)$_2$-[*closo*-1-Mg(THF)-2,3-($SiMe_3$)$_2$-2,3-$C_2B_4H_4$]}-2,3-($SiMe_3$)$_2$-2,3-$C_2B_4H_4$ (IV).** A 9.0 mL sample of a solution of $Me_3SiCH_2MgCl$ (9.0 mmol) in diethyl ether was added to a suspension of 0.55 g (2.81 mmol) of $YCl_3$ in 15 mL of THF and 10 mL of *n*-hexane at 0 °C. The mixture was stirred overnight and then filtered through a frit in vacuo to collect a clear filtrate. This filtrate was then poured onto a frozen sample of the neutral *nido*-carborane precursor 2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$ (0.5 g, 2.3 mmol), and the resulting mixture was slowly warmed to room temperature and then stirred constantly at this temperature for 2 days to generate a turbid off-white mixture. This mixture was filtered in vacuo to obtain a pale yellow filtrate. All solvents were removed from the filtrate in vacuo to yield an off-white solid, which was later recrystallized from its benzene solution to collect colorless crystals, identified as the magnesium salt of the novel mixed chloroyttra/chloromagnesa-carborane half-sandwich compound *closo*-1-Y-{1,1′-(μ-Cl)$_2$-*exo*-[5,6-(μ-H)$_2$-Mg(THF)$_2$]-1,1′-(μ-Cl)$_2$-[*closo*-1-Mg(THF)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$]}-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$(3.5 $C_6H_6$) (**IV**) (1.52 g, 1.1 mmol; mp 150 °C (dec)) in 39% yield, based on the $YCl_3$. Anal. Calcd for $C_{28}H_{68}O_3B_8Si_4Cl_3Mg_2Y{\cdot}3.5\ C_6H_6$: C, 50.35; H, 7.67; Cl, 9.10. Found (duplicate analysis): C, 50.96 (50.41); H, 7.97 (7.47); Cl, 9.67 (9.89).

**Spectroscopic Data for IV.** $^1H$ NMR (THF-$d_8$, external $Me_4Si$): $\delta$ 7.15 (s, $C_6H_6$), 3.50 (m, 12H, $CH_2$, THF), 1.62 (m, 12H, $CH_2$, THF), 0.12 (s, 36 H, $SiMe_3$). $^{11}B$ NMR (THF-$d_8$, external $BF_3.OEt_2$): $\delta$ 23.26 (br, 2B, basal BH, $^1J(^{11}B-^1H)$ = unresolved), 13.44 (br, 3B, basal BH, $^1J(^{11}B-^1H)$ = unresolved), 1.27 (br, 1B, basal BH, $^1J(^{11}B-^1H)$ = unresolved), −28.54 (br, 1B, apical BH, $^1J(^{11}B-^1H)$ = unresolved), −46.46 (d, 1B, apical BH, $^1J(^{11}B-^1H)$ = 148 Hz). $^{13}C$ NMR (THF-$d_8$, external $Me_4Si$): $\delta$ 128.78 (d, $C_6H_6$, $^1J(^{13}C-^1H)$ = 159 Hz), 111.71 (s, br, cage carbons (SiCB)), 110.09 (s, br, cage carbons(SiCB)), 68.21 (t, $CH_2$, THF, $^1J(^{13}C-^1H)$ = 145 Hz), 26.16 (t, $CH_2$, THF, $^1J(^{13}C-^1H$ = 132.1 Hz), 3.75 (q, $SiMe_3$, $^1J(^{13}C-^1H)$ = 118.2 Hz). IR ($cm^{-1}$, $C_6D_6$ vs $C_6D_6$): 2550.9(s), 2487.9(s), 2431.2(s) [ν(B−H)].

**Reaction of Yttracarborane Sandwich I with NaH: Synthesis of the Hydridoyttracarborane Sandwich 1-H-2,2′,3,3′-($SiMe_3$)$_4$-[4,4′,5-Li(THF)]$_2$-[1,1′-*commo*-Y(2,3-$C_2B_4H_4$)$_2$] (V).** A 1.00 g (1.00 mmol) sample of [Li(THF)$_4$]{1-Cl-1-(THF)-2,2′,3,3′-($SiMe_3$)$_4$-4,4′,5,5′-Li(THF)[1,1′-*commo*-Y(2,3-$C_2B_4H_4$)$_2$]} (**I**) was reacted with 0.10 g (4.00 mmol) of NaH in 20 mL of dry THF at 25 °C for 3 days, during which time the heterogeneous mixture turned turbid yellow. The mixture was filtered through a frit in vacuo, and the residue was washed repeatedly with a 1:1 solvent mixture of hexane and THF to collect a clear pale yellow filtrate. An off-white solid that remained on the frit (not measured), identified as a mixture of unreacted NaH and NaCl, was later discarded. The filtrate was then concentrated by slow removal of solvents in vacuo to obtain an off-white solid, identified by spectroscopy and elemental analysis as the hydridoyttracarborane sandwich 1-*H*-2,2′,3,3′-($SiMe_3$)$_4$-[4,4′,5-Li(THF)]$_2$-[1,1′-*commo*-Y(2,3-$C_2B_4H_4$)$_2$] (**V**), which was later recrystallized from its benzene solution to give colorless crystals in 80% yield (0.55 g, 0.805 mmol; mp 118 °C (dec)). Anal. Calcd for $C_{24}H_{61}O_2B_8Si_4Li_2Y$ (**V**): C, 42.18; H, 9.00; Li, 2.03. Found: C, 42.19; H, 8.86; Li, 2.13.

**Spectroscopic Data for V.** $^1H$ NMR ($C_6D_6$, external $Me_4Si$): $\delta$ 3.64 (s, 8H, $CH_2$, THF), 1.62 (s, 8H, $CH_2$, THF), 0.61 (s, 18H, $SiMe_3$), 0.49 (s, 18H, $SiMe_3$). $^{11}B$ NMR (THF-$d_8$, external $BF_3{\cdot}OEt_2$): $\delta$ 23.29−18.48 (vbr, 2B, basal BH, $^1J(^{11}B-^1H)$ = unresolved), −4.47 (vbr, 1B, basal BH, $^1J(^{11}B-^1H)$ = unresolved), −39.29 (br, 1B, apical BH, $^1J(^{11}B-^1H)$ = unresolved). $^{13}C$ NMR ($C_6D_6$, external $Me_4Si$): $\delta$ 111.18 (s, v br, cage carbons), 68.43 (t, $CH_2$, THF, $^1J(^{13}C-^1H)$ = 146.0 Hz), 25.36 (t, $CH_2$, THF, $^1J(^{13}C-^1H)$ = 133.6 Hz), 3.33 (q (br), $SiMe_3$, $^1J(^{13}C-^1H)$ = 119.1 Hz). $^7Li$ NMR ($C_6D_6$, external aqueous $LiNO_3$): $\delta$ −3.59 (s(br), *exo*-cage Li). IR ($cm^{-1}$, $C_6D_6$ vs $C_6D_6$): 2560(s), 2495(sh), 2453(s) [ν(BH)].

**X-ray Analyses of Yttracarboranes I, III, and IV.** Colorless transparent X-ray quality crystals of the yttracarboranes **I**, **III**, and **IV** were grown very slowly from their respective benzene solutions. These crystals were coated with paraffin and then sequentially mounted on a Siemens R3m/V diffractometer under a low-temperature nitrogen stream. The pertinent crystallographic data and conditions for data collection are summarized in Table 1. Final unit cell parameters were obtained by a least-squares fit of the angles of 24−30 accurately centered reflections in the 2$\theta$ range from 16° to 32.0°. Intensity data were collected at 230 K for **I** and **III** and at 220 K for **IV** using graphite-monochromated Mo Kα radiation. Three standard reflections were monitored during the data collection and did not show any significant changes in intensities. The data for all three structures were corrected for Lorentz and polarization effects and for absorption. The structures were solved by direct methods using the SHELXTL-Plus package[22] and subsequent Fourier syntheses. Full-matrix least-squares refinements were performed for all three structures. Scattering factors, as well as anomalous-dispersion corrections for the heavy atoms, were taken from ref 23. Two of the four cationic $Li^+$-bound THF's (O(60), C(61)−C(64) and O(65), C(66)−C(69)) in **I** were disordered. In **III**, all six solvated THF's and the one-half THF solvent of crystallization in the lattice were disordered. Due to severe disorder, no attempts were made to locate the H atoms in the structure of **III**. In **IV**, the two benzene molecules of crystallization were disordered. All of the relevant bonds of the disordered THF and benzene molecules were elastically constrained during the final stages of refinement. Cage H atoms in both **I** and **IV** were located in difference Fourier maps and placed in calculated positions without refinements. The final values of *R* and weighted $R_w$ are listed in Table 1, while selected interatomic distances are given in Table 2. The atomic coordinates, a full list of bond distances, bond angles, anisotropic thermal parameters, and the positions of the H atoms are given in the Supporting Information.

## Results and Discussion

**Synthesis.** The yttracarboranes [Li(THF)$_4$]{1-Cl-1-(THF)-2,2′-($SiMe_3$)$_2$-3,3′-(R)$_2$-4,4′,5,5′-Li(THF)[1,1′-*commo*-Y(2,3-$C_2B_4H_4$)$_2$]} (R = $SiMe_3$ (**I**) and Me (**II**)) and {Na(THF)$_3$}$_2${[1-(THF)-1-(μ-H)$_2$-2,2′,4,4′-($SiMe_3$)$_4$-1,1′-*commo*-Y(2,4-$C_2B_4H_4$)$_2$]$_2$} (**III**) were synthesized from

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[22] Sheldrick, G. M. *Structure Determination Software Programs;* Siemens X-ray Analytical Instrument Corp.: Madison, WI, 1991.

[23] *International Tables For X-ray Crystallography;* Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

**Table 1. Crystallographic Data[a] for Yttracarboranes I, III, and IV**

| | **I** | **III** | **IV** |
|---|---|---|---|
| formula | $C_{40}H_{92}O_6B_8Si_4Li_2ClY$ | $[C_{64}H_{152}Na_2B_{16}O_8Si_8Y_2]\cdot{}^1/_2[C_4H_8O]$ | $C_{56}H_{136}Mg_4B_{16}Si_8O_6Cl_6Y_2\cdot 4[C_6H_6]$ |
| fw | 1006.2 | 1707.4 | 2103.6 |
| space group | $P2_1/c$ | $C2/c$ | $P\bar{1}$ |
| $a$, Å | 12.123(5) | 52.79(2) | 14.116(3) |
| $b$, Å | 26.480(9) | 14.260(4) | 14.864(3) |
| $c$, Å | 18.795(6) | 27.153(7) | 15.372(4) |
| α, deg | 90.00 | 90.00 | 77.77(2) |
| $\beta$, deg | 95.00(3) | 90.36(2) | 71.65(2) |
| $\gamma$, deg | 90.00 | 90.00 | 77.440(10) |
| $V$, Å$^3$ | 6011(4) | 20441(11) | 2952.1(10) |
| $Z$ | 4 | 8 | 1 |
| $D_{\mathrm{calcd}}$, g cm$^{-3}$ | 1.112 | 1.110 | 1.183 |
| abs coeff, mm$^{-1}$ | 1.148 | 1.274 | 1.258 |
| crystal dimens, mm | 0.30 × 0.35 × 0.25 | 0.10 × 0.30 × 0.20 | 0.20 × 0.15 × 0.05 |
| scan type | $\omega/2\theta$ | $\omega/2\theta$ | $\omega/2\theta$ |
| scan speed in $\omega$; min, max | 5.00, 25.00 | 5.33, 29.30 | 5.33, 19.53 |
| $2\theta$ range, deg | 3.5−40.0 | 3.5−38.0 | 3.0−38.0 |
| $T$, $K$ | 230 | 220 | 220 |
| decay, % | 0 | 0 | 0 |
| no. of data collected | 5874 | 10083 | 4902 |
| no. of obsd reflns | 2675 [$F > 4.0\sigma(F)$] | 5807 [$F > 6.0\sigma(F)$] | 1833 [$F > 6.0\sigma(F)$] |
| no. of params refined | 484 (BLOCed) | 672 | 311 |
| GOF | 1.65 | 2.52 | 1.25 |
| $\Delta\rho_{(\mathrm{max,\ min})}$, e/Å$^3$ | 0.66, −0.60 | 0.76, −0.62 | 0.37, −0.43 |
| $R^b$ | 0.0882 | 0.0885 | 0.0604 |
| w$R^{c,d}$ | 0.0905 | 0.1148 | 0.0664 |

[a] Graphite-monochromatized Mo Kα radiation, $\lambda = 0.710\ 73$ Å. [b] $R = \sum//F_o/ - /F_c///\sum/F_o/$, w$R = [\sum w(F_o - F_c)^2/\sum w(F_o)^2]^{1/2}$. [c] $w = 1/[\sigma^2(F_o) + 0.001(F_o)^2]$. [d] $w = 1/[\sigma^2(F_o{}^2) + (0.0410P)^2 + 14.4051P]$, where $P = (F_o{}^2 + 2F_c{}^2)/3$.

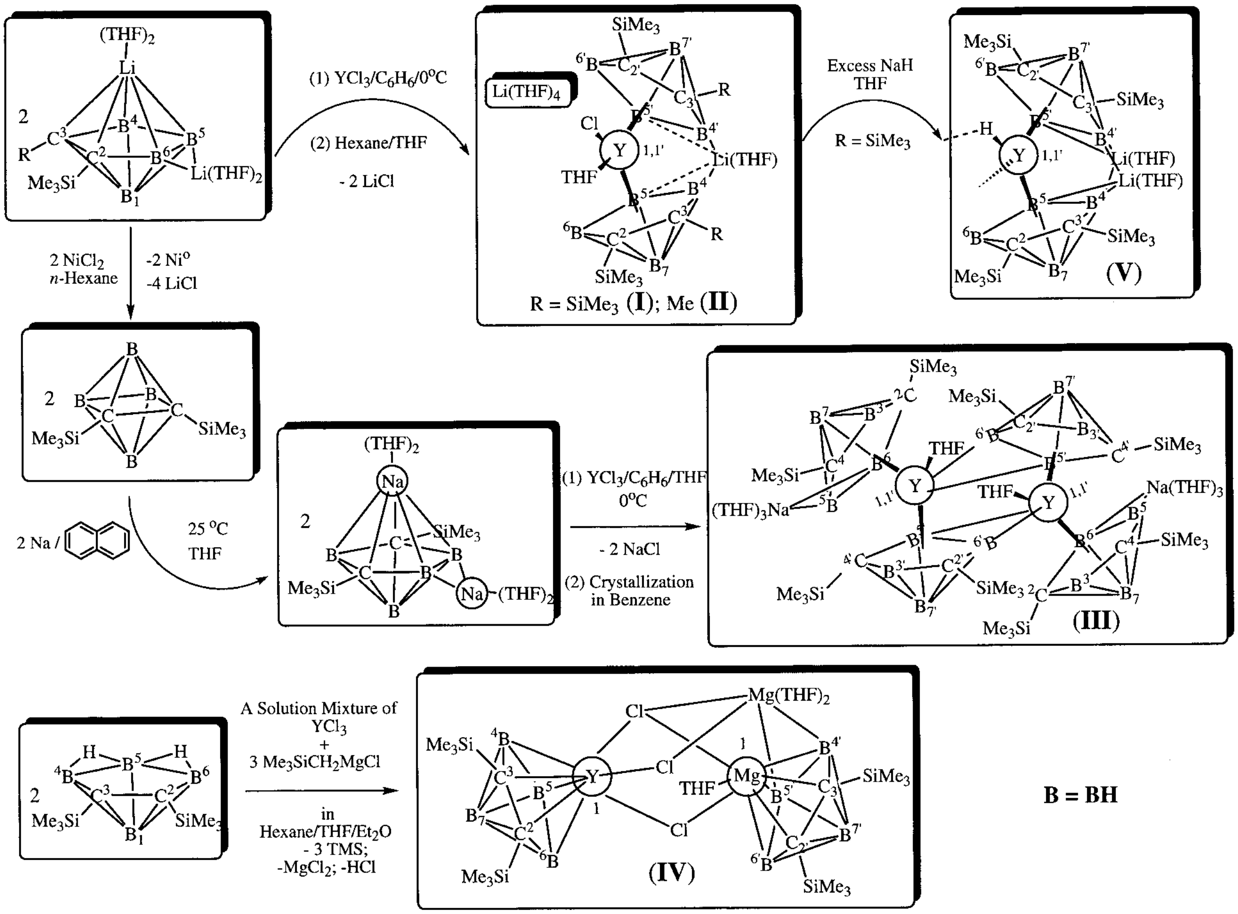
**Table 2. Selected Bond Lengths (Å) for Yttracarboranes I, III, and IV[a]**

| | | | | | |
|---|---|---|---|---|---|
| Compound **I** | | | | | |
| Y−Cnt(l) | 2.362 | Y−B(23) | 2.750(22) | B(4)−B(5) | 1.601(31) |
| Y−Cnt(2) | 2.389 | Y−B(24) | 2.779(22) | B(4)−B(6) | 1.736(32) |
| Y−Cl | 2.582(4) | Y−B(25) | 2.698(23) | B(4)−Li(1) | 2.406(42) |
| Y−O(40) | 2.353(10) | C(1)−C(2) | 1.488(23) | B(5)−B(6) | 1.749(31) |
| Y−C(1) | 2.699(16) | C(1)−B(5) | 1.581(25) | B(23)−Li(l) | 2.307(42) |
| Y−C(2) | 2.730(16) | C(1)−B(6) | 1.719(29) | B(24)−Li(1) | 2.269(42) |
| Y−B(3) | 2.708(21) | C(2)−B(3) | 1.543(26) | Li(1)−O(45) | 1.904(42) |
| Y−B(4) | 2.725(22) | C(2)−B(6) | 1.692(28) | Li(2)−O(50) | 1.908(44) |
| Y−B(5) | 2.714(22) | B(3)−B(4) | 1.663(28) | Li(2)−O(55) | 1.886(44) |
| Y−C(21) | 2.742(16) | B(3)−B(6) | 1.713(33) | Li(2)−O(60) | 1.927(41) |
| Y−C(22) | 2.740(17) | B(3)−Li(1) | 2.385(41) | Li(2)−O(65) | 1.860(41) |
| Compound **III** | | | | | |
| Y(1)−Cnt(1) | 2.538 | Y(1)−C(22) | 2.866 (19) | Y(1)−O(81) | 2.673 (16) |
| Y(1)−C(12) | 2.916 (19) | Y(1)−B(23) | 2.920 (23) | Y(2)−Cnt(3) | 2.602 |
| Y(1)−B(13) | 2.916 (24) | Y(1)−C(24) | 3.027 (20) | Y(2)−B(25) | 2.911 (22) |
| Y(1)−C(14) | 2.905 (17) | Y(1)−B(25) | 3.028 (22) | Y(2)−B(26) | 2.906 (20) |
| Y(1)−B(15) | 2.851 (22) | Y(1)−B(26) | 2.920 (20) | Y(2)−C(32) | 2.879 (18) |
| Y(1)−B(16) | 2.854 (22) | Y(1)−B(35) | 2.917 (23) | Y(2)−B(33) | 2.816 (21) |
| Y(1)−Cnt(2) | 2.618 | Y(1)−B(36) | 2.869 (22) | Y(2)−C(34) | 2.983 (20) |
| Y(2)−B(35) | 3.058 (23) | Y(2)−C(44) | 2.878 (16) | Na(1)−O(111) | 2.246 (17) |
| Y(2)−B(36) | 2.950 (21) | Y(2)−B(45) | 2.879 (22) | Na(1)−O(121) | 2.250 (18) |
| Y(2)−Cnt(4) | 2.561 | Y(2)−B(46) | 2.871 (23) | Na(2)−O(131) | 2.284 (21) |
| Y(2)−C(42) | 2.987 (18) | Y(2)−O(91) | 2.609 (13) | Na(2)−O(141) | 2.243 (19) |
| Y(2)−B(43) | 2.946 (24) | Na(1)−O(101) | 2.271 (23) | Na(2)−O(151) | 2.286(17) |
| Compound **IV** | | | | | |
| Y−Cnt(1) | 2.308 | Y−C(12) | 2.662 (16) | Mg(2)−Cl(1) | 2.667 (9) |
| Y−C(13) | 2.636 (16) | Mg(1)−Cnt(2) | 2.032 | Mg(1)−Cl(2) | 2.466 (8) |
| Y−B(14) | 2.678 (20) | Mg(1)−C(22) | 2.449 (18) | Mg(2)−Cl(3) | 2.399 (8) |
| Y−B(15) | 2.721 (24) | Mg(1)−C(23) | 2.421 (21) | C(12)−C(13) | 1.461 (30) |
| Y−B(16) | 2.658 (26) | Mg(1)−B(24) | 2.396 (23) | C(22)−C(23) | 1.484 (28) |
| Y−B(14A) | 2.695 (21) | Mg(1)−B(25) | 2.472 (23) | Mg(1)−O(51) | 2.017 (16) |
| Y−B(15A) | 2.675 (22) | Mg(1)−B(26) | 2.454 (24) | Mg(2)−O(61) | 2.029 (15) |
| Y−Cl(1) | 2.812 (5) | Mg(2)−B(25) | 2.413 (29) | Mg(2)−O(66) | 2.035(15) |
| Y−Cl(2) | 2.671 (7) | Mg(2)−B(26) | 2.536 (28) | | |
| Y−Cl(3) | 2.734 (6) | Mg(1)−Cl(1) | 2.491 (9) | | |

[a] The bond values of two disordered THF [O(60)···C(64), O(65)···C(69)] in **I** are not included. Cnt(l): the centroid of C(l), C(2), ..., and B(5). Cnt(2): the centroid of C(21), C(22), ..., and B(25).

the reactions of $YCl_3$ with either the corresponding THF-solvated, carbons-adjacent dilithium carborane (for **I** and **II**) or the THF-solvated, carbons-apart disodium carborane (for **III**), in 1:2 stoichiometries, as shown in Scheme 1. The yields in these reactions are quite good, being 83%, 80%, and 74% for **I**, **II**, and **III**, respectively.

**Scheme 1**



The conditions for the formation of **I** and **II** are very similar to those used in the preparation of the THF-solvated trinuclear lanthanacarborane clusters {[$\eta^5$-1-Ln-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4]_3[(\mu_2$-1-Li-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4)_3(\mu_3$-OMe)][$\mu_2$-Li(THF)]$_3$ ($\mu_3$-O)} (Ln = Sm, Gd, Tb, Dy, and Ho).[6,10,11] These clusters were produced in moderate yields (49−59%) from the benzene reaction of $LnCl_3$ with the same THF-solvated dilithiacarborane precursor at the same temperature as that shown in Scheme 1.[6] The full-sandwich lanthanacarboranes could be obtained only when the THF molecules were replaced by tetramethylethylenediamine (TMEDA).[7] Since the chemistry of yttrium has been found to be similar to that of the lanthanides and is often included with them, the different products obtained from these similar reactions is surprising. It is of interest to note that the full-sandwich chlorozirconacarborane 1-Cl-1-(THF)-2,2′-$(SiMe_3)_2$-3,3′-$(R)_2$-4,4′,5,5′-Li(THF)-1,1′-*commo*-Zr(2,3-$C_2B_4H_4)_2$, whose structure is very similar to that of **I** and **II**, was obtained from the reaction of the mixed THF-solvated Na/Li compound of [2-$(SiMe_3)$-3-(R)-2,3-$C_2B_4H_4]^{2-}$ with $ZrCl_4$ in a solvent mixture of THF and benzene. In this regard, Y resembles its second-row neighbor (Zr) more than the lanthanides. The yttracarboranes differ from their zirconium analogue in that while the Cl and THF ligands in the latter complex have proved to be substitutionally inert, both could be removed from **I** by reaction with NaH to give the hydrido complex 1-H-2,2′,3,3′-$(SiMe_3)_4$-[4,4′,5-Li(THF)]$_2$-[1,1′-*commo*-Y(2,3-$C_2B_4H_4)_2$] (**V**) (see Scheme 1). Although the structure of **V** was not determined, it most likely exists as a dimer with two Y−H−Y bridge bonds and should better be formulated as {1-H-2,2′,3,3′-$(SiMe_3)_4$-[4,4′,5-Li(THF)]$_2$-[1,1′-*commo*-Y(2,3-$C_2B_4H_4)_2$]}$_2$. Dimer formation was also found in the carbons-apart yttracarborane {Na$(THF)_3$}$_2${[1-(THF)-1-($\mu$-H)$_2$-2,2′,4,4′-$(SiMe_3)_4$-1,1′-*commo*-Y(2,4-$C_2B_4H_4)_2$]$_2$} (**III**), which was produced from the reaction of $YCl_3$ with the THF-solvated disodium compound *closo*-*exo*-5,6-[($\mu$-H)$_2$Na$(THF)_2$]-1-Na$(THF)_2$-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$ in a 1:2 molar ratio (see Scheme 1). Scheme 1 shows that for every mole of **III** produced, 4 mol of the carborane and 2 mol of $YCl_3$ are consumed; 6 mol of NaCl also accompany the formation of **III**. The reaction most likely involves an initial formation of a full-sandwich chloroyttracarborane similar to **I**, which then dimerizes with the elimination of two additional equivalents of NaCl to give the dimer. It may well be that the introduction of a BH unit between the trimethylsilyl-bound cage carbons in going from the carbons-adjacent to the carbons-apart carborane cages sufficiently reduces the steric crowding in the vicinity of the metal to permit dimerization. Relief of steric strain has been used to rationalize the pattern of dimer formation in the titanacarboranes.[24]

The direct synthesis of an alkyl-substituted yttracarborane was unsuccessful. Scheme 1 shows the result of an attempted synthesis of such a complex by an initial reaction of $YCl_3$ with the Grignard reagent, $Me_3SiCH_2$-

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[24] Hosmane, N. S.; Wang, Y.; Zhang, H.; Lu, K.-J.; Maguire, J. A.; Gray, T. G.; Brooks, K. A.; Waldhör, E.; Kaim, W.; Kremer, R. K. *Organometallics* **1997**, *16*, 1365.

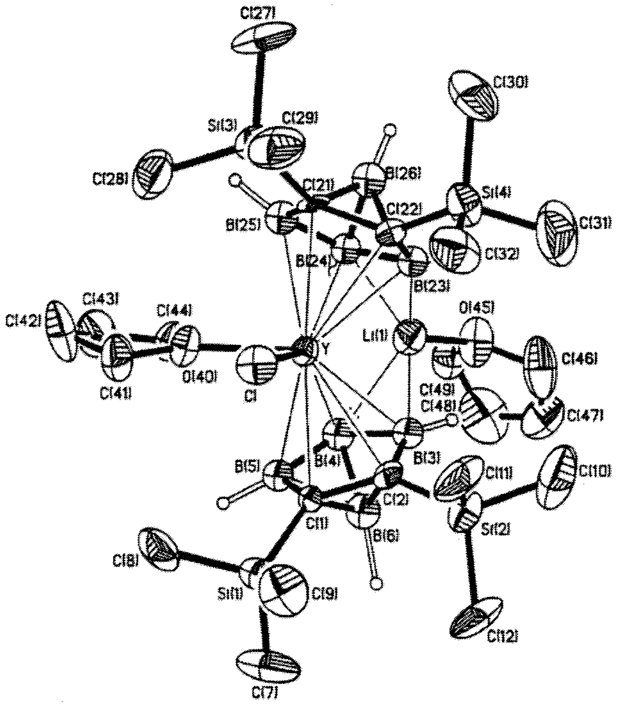

**Figure 1.** Perspective view of [Li(THF)$_4$]{1-Cl-1-(THF)-2,2′,3,3′-(SiMe$_3$)$_4$-4,4′,5,5′-Li(THF)[1,1′-*commo*-Y(2,3-C$_2$B$_4$H$_4$)$_2$]} (**I**), showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 40% probability level. For clarity, the cationic Li(THF)$_4$ unit and all H's except the carborane cage in the anionic unit are removed.

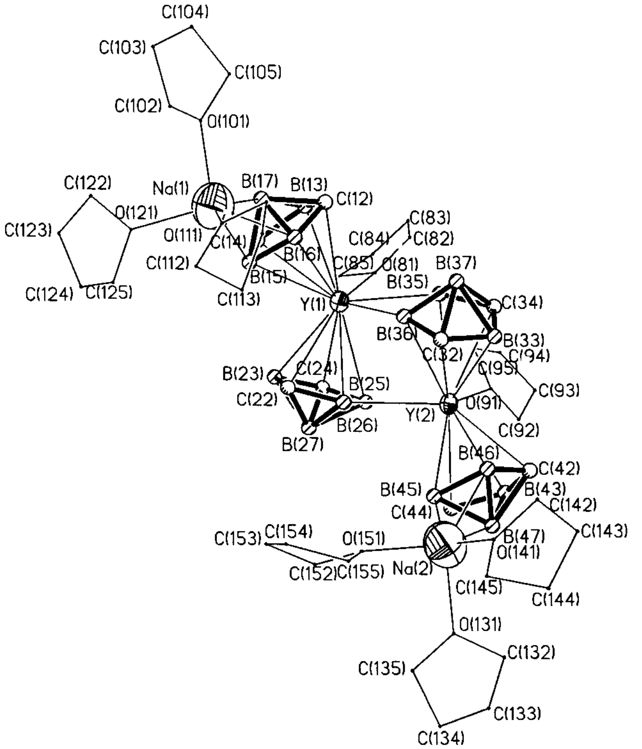

**Figure 2.** Perspective view of {Na(THF)$_3$}$_2${[1-(THF)-1-($\mu$-H)$_2$-2,2′,4,4′-(SiMe$_3$)$_4$-1,1′-*commo*-Y(2,4-C$_2$B$_4$H$_4$)$_2$]$_2$} (**III**), showing the atom-numbering scheme. For clarity, the C$_{(cage)}$-bound SiMe$_3$ groups and all H's were omitted. Except for Y's and Na's, the cage atoms were drawn with circles of arbitrary radii.

MgCl, followed by reaction with the neutral carborane, *nido*-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_6$, in a 1:2 molar ratio. The synthetic strategy was first to form the trialkyl compound Y(CH$_2$SiMe$_3$)$_3$, which would then form *closo*-1-Y(CH$_2$SiMe$_3$)-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$ with the elimination of 2 equiv of Me$_3$SiCH$_3$ (TMS). Instead of the anticipated *closo*-yttracarborane, the novel mixed magnesa-/yttracarborane *closo*-1-Y-{1,1′-($\mu$-Cl)$_2$-*exo*-[5,6-($\mu$-H)$_2$-Mg(THF)$_2$]-1,1′-($\mu$-Cl)$_2$-[*closo*-1-Mg(THF)-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$]}-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$ (**IV**) was obtained in 39% yield, based on the original amount of YCl$_3$ used. Although this yield seems modest, it constitutes the consumption of 96% of the original carborane used. The formulation of the compound is based primarily on its single-crystal X-ray analysis, which also shows two benzenes of solvation. Duplicate analyses of **IV** gave acceptable agreement between the calculated and found C and H percentages but a high Cl analysis. However, considering the complexity of the compound and the fact that small amounts of unreacted YCl$_3$ or Grignard products could materially increase the chlorine content, the analyses are consistent with the formula of **IV**. While the mechanism of this reaction is not known, it is quite clear that the reaction of the Grignard with YCl$_3$ did not produce the trialkylyttrium compound. At this point, it is not known whether the Cl ions in **IV** came from the yttrium chloride, the Grignard reagent, or any magnesium chloride that may have been formed. However, it is known that the reactions of Grignard reagents with carboranes are complex and may go through Schlenk-type equilibria.[28b]

**Crystal Structures of [Li(THF)$_4$]{1-Cl-1-(THF)-2,2′3,3′-(SiMe$_3$)$_4$-4,4′,5,5′-Li(THF)[1,1′-*commo*-Y(2,3-C$_2$B$_4$H$_4$)$_2$]} (I), {Na(THF)$_3$}$_2$ {[1-(THF)-1-($\mu$-H)$_2$-2,2′,4,4′-(SiMe$_3$)$_4$-1,1′-*commo*-Y(2,4-C$_2$B$_4$H$_4$)$_2$]$_2$} (III), and *closo*-1-Y-{1,1′-($\mu$-Cl)$_2$-*exo*-[5,6-($\mu$-H)$_2$-Mg(THF)$_2$]-1,1′-($\mu$-Cl)$_2$-[*closo*-1-Mg(THF)-2,3-(SiMe$_3$)$_2$-2,3C$_2$B$_4$H$_4$]}-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$ (IV).** The solid-state structures of compounds **I, III**, and **IV** were determined by single-crystal X-ray crystallography and are shown in Figures 1−3, respectively. Some important bond distances are given in Table 2; a complete list of bond angles and distances is given in the Supporting Information. Inspection of Figures 1 and 2 show that the yttracarboranes, **I** and **III** (and presumably **II**), are bent-sandwich complexes in which a Y, in a formal +3 state, is sandwiched between two carborane ligands, in structures similar to those of the yttrocenes[25] and other full-sandwich cyclopentadienide complexes of the lanthanide metals;[15] bent-sandwich complexes were also found in the larger C$_2$B$_9$ cage lanthacarboranes.[4] In both **I** and **III**, the carboranes are $\eta^5$-bonded to the Y, with average Y−C$_2$B$_3$ atom distances of 2.728 ± 0.014 and 2.922 ± 0.051 Å, respectively.[26] The Y in **I** is also

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(25) (a) Evans, W. J.; Peterson, T. T.; Rausch, M. D.; Hunter, W. E.; Zhang, H.; Atwood, J. L. *Organometallics* **1985**, *4*, 554. (b) Evans, W. J.; Grate, J. W.; Levan, K. R.; Bloom, I.; Peterson, T. T.; Doedens, R. J.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1986**, *25*, 3614.

(26) Whenever the average value of a parameter is given, the uncertainty listed is the average deviation.

(27) Raymond, K. N.; Eigenbrot, C. W., Jr. *Acc. Chem. Res.* **1980**, *13*, 276.

(28) (a) Hosmane, N. S.; Zhu, D.; McDonald, J. E.; Zhang, H.; Maguire, J. A.; Gray, T. G.; Helfert, S. C. *J. Am. Chem. Soc.* **1995**, *117*, 12362. (b) Hosmane, N. S.; Zhu, D.; McDonald, J. E.; Zhang, H.; Maguire, J. A.; Gray, T. G.; Helfert, S. C. *Organometallics* **1998**, *17*, 1426.

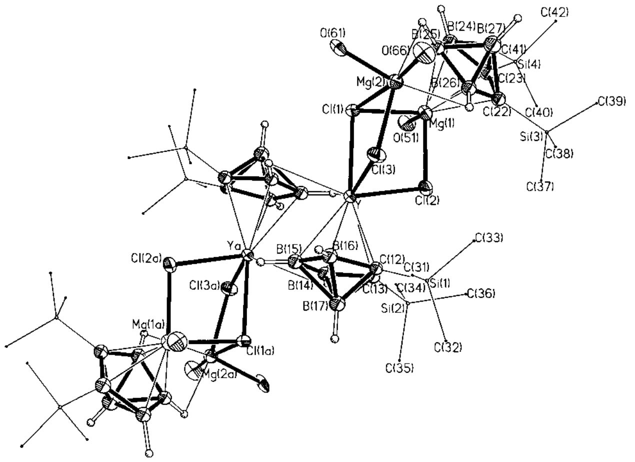

**Figure 3.** Perspective view of the THF-solvated magnesium salt of mixed half-sandwich chloroyttra-/chloromagnesacarborane (**IV**), showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 40% probability level. For clarity, all H's except the carborane cage and all $CH_2$units of THF molecules are removed. The $C_{(cage)}$-bound $SiMe_3$ groups are drawn with circles of arbitrary radii.

bonded to a Cl ligand and a THF molecule to give a very distorted tetrahedral arrangement about the metal; the relevant angles are Cl−Y−THF = 89.5°, Cnt(1,2)−Y−Cl = 111°, and Cnt(1)−Y−Cnt(2) = 129.7°. The average $Y-C_2B_3$ atom distance in **I** is similar to the value of 2.718 ± 0.023 Å found for the equivalent distances in the TMEDA-solvated holmium carborane [Li(TMEDA)$_2$][1-Cl-1-($\mu$-Cl)-2,2′,3,3′-$(SiMe_3)_4$-5,6-[($\mu$-H)$_2$Li(TMEDA)]-4,4′,5′-[($\mu$-H)$_3$Li(TMEDA)]-1,1′-*commo*-Ho(2,3-$C_2B_4H_4$)$_2$]. Since the ionic radii of the two metals are essentially the same,[27] the similarities in the two metal−carborane bond distances are consistent with a predominantly electrostatic metal−carborane interaction.[7] The structure of the pentamethylcyclopentadienide analogue of **I**, $(Cp^*)_2YCl(THF)$, also shows a distorted tetrahedral arrangement around the Y, with Cl−Y−THF, Cnt−Y−Cl, and Cnt(1)−Y−Cnt(2) bond angles of 90°, 106°, and 136°,[25b] which are very similar to the values found in **I**. In the carbons-apart yttracarborane **III**, the *commo*-yttrium is bonded to a THF and a neighboring carborane via a set of two Y−H−B bridges. These bridge bonds seem to be quite strong in that the Y−B bond distances involved in the bridges are 2.911 and 2.906 Å, which are well within the range of the $Y-C_2B_3$ atom distances (2.922 ± 0.051 Å). The Cnt−Y−Cnt and Cnt−Y−THF bond angles in **III** are 131 ± 1° and 103 ± 3°, respectively, which are similar to the analogous distances in **I**. If one assumes that the two Y−H−B bridges occupy a single coordination site on the metal, the distorted tetrahedral arrangement around the Y is preserved. However, a comparison of bond distances in the two yttracarboranes shows systematic increases in equivalent distances in going from **I** to **III**, for example, the Y−O(THF) distance in **I** is 2.353(10) Å compared to an average of 2.641 ± 0.032 Å in **III**, with the Y−Cnt distances increasing from 2.376 ± 0.013 Å in **I** to 2.580 ± 0.036 Å in **III**. These increases are probably a result of the increase in steric strain about the metal on replacing the chloride in **I** with a bridging carborane in **III**. Steric effects may also play a role in the lower Y−Cnt distance in **IV** (2.308 Å) compared to **I** and **III**. The Mg−Cnt distance of 2.032 Å found in **IV** is similar to the analogous Mg−Cnt distances in the *closo*-1-(TMEDA)-1-Mg-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ half-sandwich complex (2.132 Å) and the full-sandwich $\{commo\text{-}1,1'\text{-}Mg[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_2\}^{2-}$ (2.018 Å).[28]

**Spectroscopy.** Compounds **I**−**V** were characterized by their infrared spectra as well as by their $^1H$, $^{13}C$, and $^{11}B$ NMR spectra; compound **V** was additionally characterized by its $^7Li$ NMR spectrum. The major features of these spectra are summarized in the Experimental Section under each compound. The most significant features of the IR spectra are the multiple peaks found in the B−H stretching region (2300−2500 $cm^{-1}$). Such multiplicity has been observed in the spectra of compounds possessing B−H−M bridges (M = exopolyhedrally bound metal).[6,7,20] Figures 1−3 all show such metal bridges in the solid state, and it is reasonable that such clustering would persist in a low-dielectric-constant solvent such as $C_6D_6$, which was the solvent used in the IR studies.

The proton, carbon-13, and boron-11 NMR spectra of all the compounds show signals due to the carborane cage and THF molecules. Of these, $^{11}B$ NMR spectra have been found to be the most sensitive to the nature of the capping metal. Unfortunately, all spectra are quite broad and no coupling could be measured, so that little can be deduced. However, the general features of these spectra are similar to those found for other metallacarboranes in this ligand system[20,28,29] in that all show resonances for the apical boron in the $\delta$ −30 to −50 ppm region, with the resonances of the less-shielded facial borons on the $C_2B_3$ faces being shifted downfield by 40−70 ppm. In general, the order of the facial boron resonances is dictated by the nature of the adjacent ring atoms; in the 2,4-$C_2B_4$ system, the unique boron is the least shielded and 1:2:1 peak area ratios are found, while in the 2,3-$C_2B_4$ system, the relative shieldings are reversed, giving rise to 2:1:1 peak area patterns. Compound **II** shows the expected 2:1:1 ratio; however, in **I** there are four resonances, indicating nonequivalent basal borons. Inspection of Figure 1 shows that one of the two basal borons is involved in a Li−H−B bridge, and such bridging has been shown to lead to an upfield shift of the $^{11}B$ NMR resonance.[29] In the carbons-apart yttracarborane **III**, the broadness of the spectrum prevents the differentiation of the different facial boron resonances and only a single downfield resonance at $\delta$ 19.18 ppm is found. It is of interest that this yttracarborane has two apical boron resonances at $\delta$ −28.54 and −37.06 ppm. Reference to Figure 2 shows that a sodium ion interacts strongly with only one of the two apical borons in the sandwich, therefore nonequivalence would be expected. The $^{11}B$ NMR spectrum of the mixed yttra-/magnesacarborane compound, **IV**, also shows two apical boron resonances at $\delta$ −28.54 and −46.46 ppm. Since *closo*-1-Mg(TMEDA)-2,3-$(SiMe_3)$2-2,3−$C_2B_4H_4$ and $\{commo\text{-}1,1'\text{-}Mg[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_2\}^{2-}$ show apical boron resonances at $\delta$ −49.77 and −48.34 ppm, respectively,[28] the $\delta$ −46.46 ppm resonance can be ascribed to the magnesacarborane fragment (B(27)) with that of the yttracarborane frag-

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(29) Ezhova, M. B.; Zhang, H.; Maguire, J. A.; Hosmane, N. S. *J. Organomet. Chem.* **1998**, *550*, 409.

ment (B(17)) accounting for the peak at $\delta$ −28.54 ppm. Thus, while the $^{11}$B NMR spectra of the yttracarboranes can be rationalized in terms of the structures given in Figures 1−3, it would be extremely difficult to use NMR as the primary structural tool.

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**Supporting Information Available:** Tables of atomic coordinates (Table S-1), full listing of bond lengths and angles (Table S-2), anisotropic displacement parameters (Table S-3), H-atom coordinates, and isotropic displacement coefficients (Table S-4) for **I**, **III**, and **IV** (29 pages). Ordering information is given on any current masthead page.

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