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Chemistry of *C*-Trimethylsilyl-Substituted Heterocarboranes. 22. Synthetic, Spectroscopic, Structural, and Bonding Studies on Half- and Full-Sandwich Gallacarboranes of 2,3- and 2,4-C$_2$B$_4$ Carborane Ligand Systems

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The reaction of the TMEDA-solvated group 1 salts of the carborane dianions [2,*n*-(SiMe$_3$)$_2$-2,*n*-C$_2$B$_4$H$_4$]$^{2-}$ (n = 3, 4) with GaCl$_3$ in a 2:1 carborane-to-GaCl$_3$ molar ratio gave the corresponding full-sandwich gallacarboranes [2,2′,*n*,*n*′-(SiMe$_3$)$_4$-1,1′-*commo*-Ga(1,2,*n*-GaC$_2$B$_4$H$_4$)$_2$]$^-$ (n = 3 (**I**), 4 (**II**)) in 36% and 38% yields, respectively. Lowering the carborane-to-GaCl$_3$ molar ratio to 1:1 produced the half-sandwich chlorogallacarboranes 1-(TMEDA)-1-Cl-2,*n*-(SiMe$_3$)$_2$-1,2,*n*-GaC$_2$B$_4$H$_4$ (n = 3 (**III**), 4 (**IV**)) in 51% and 41% yields, respectively. Compounds **I**−**IV** were characterized on the basis of ^{1}H, ^{11}B, and ^{13}C NMR spectra, IR spectra, and single-crystal X-ray analyses. The structures of the gallacarboranes show that the gallium atoms are not equally bonded to the atoms in the C$_2$B$_3$ faces of the carboranes but are slipped toward the more boron rich sides of the faces. Slippages in **I** and **II** are such that maximum differences in the Ga−C$_2$B$_3$ distances were 0.34 Å in **I** and 0.45 Å in **II**. The distortions were much larger in **III** and **IV** such that the carboranes are better described as being η^3- and η^2-bonded, respectively.

Introduction

Although the metallacarborane complexes of gallium in both the C$_2$B$_9$ and C$_2$B$_4$ cage systems have been the subject of a number of investigations,[1] thus far, the results have been quite uneven. The only report of an icosahedral gallacarborane is that from Hawthorne and co-workers on the synthesis and structure of the full-sandwich gallacarborane Tl[*commo*-3,3′-Ga(3,2,1-GaC$_2$B$_9$H$_{11}$)$_2$].[2] No half-sandwich complexes in this ligand system are known. Just the opposite is true in the smaller, C$_2$B$_4$ cage system, where only half-sandwich complexes have been reported.[3−7] The structures of the carbons-adjacent complexes 1-Me-1,2,3-GaC$_2$B$_4$H$_6$[3] and 1-(*t*-C$_4$H$_9$)-2,3-(SiMe$_3$)$_2$-1,2,3-GaC$_2$B$_4$H$_4$[4] show that the gallium atoms, in formal +3 states, occupy the apical positions above the C$_2$B$_3$ pentagonal faces of the carboranes but are slightly slipped toward the boron atoms of these faces. Each gallium is also bound to an alkyl group that is oriented over the adjacent cage carbons of the carborane. The metal atoms have been found to act as Lewis acid sites, and a number of complexes have been reported between the half-sandwich gallacarboranes and bidentate bases such as 2,2′-bipyridine and 2,2′-bipyrimidine, as well as the tridentate base 2,2′:6′,2″-terpyridine.[4−7] Similar adducts have been found between these same Lewis bases and the gallium atom in the isomeric carbons-apart gallacarborane 1-(*t*-C$_4$H$_9$)-2,4-(SiMe$_3$)$_2$-1,2,4-GaC$_2$B$_4$H$_4$.[7] In all cases, the gallium−alkyl bond seems quite stable and there was no hint of the formation of either the full-sandwich gallacarborane or half-sandwich complexes in which the alkyl group had been substituted. However, our report on the synthesis of the novel digallane complex *closo*-1-Ga[σ-*closo*-1-Ga-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$]-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$[8] raised the question as to whether it would be possible to develop synthetic methods to further react the half-sandwich gallacarboranes and prepare, in reasonable yields, either full-sandwich compounds or metal−metal-bonded half-sandwich gallacarboranes. One possible approach is to prepare compounds having better leaving groups, such as halogens, bound to the apical gallium atoms. It was this possibility that led us to investigate the reactions of the [2,*n*-(SiMe$_3$)$_2$-2,*n*-C$_2$B$_4$H$_4$]$^{2-}$ ligands with GaCl$_3$, under various conditions, to produce a series of hitherto unknown half-sandwich chlorogallacarborane complexes as well as the full-sandwich gallacarboranes. A later report will detail the reactivities of the chlorogallacarboranes.

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(1) (a) Hosmane, N. S. *Pure Appl. Chem.* **1991**, *63*, 375. (b) Saxena, A. K.; Maguire, J. A.; Banewicz, J. J.; Hosmane, N. S. *Main Group Chem. News* **1993**, *1*, 14. (c) Hosmane, N. S.; Maguire, J. A. *Adv. Organomet. Chem.* **1990**, *30*, 99. (d) Hosmane, N. S.; Maguire, J. A. *J. Cluster Sci.* **1993**, *4*, 297. (e) Hosmane, N. S. In *Main Group Elements and Their Compounds*; Kumar Das, V. G., Ed.; Narosa/Springer-Verlag: New Delhi, India, 1996, p 299. (f) Saxena, A. K.; Maguire, J. A.; Hosmane, N. S. *Chem. Rev.* **1997**, *97*, 2421.

(2) (a) Schubert, D. M.; Bandman, M. A.; Rees, W. S., Jr.; Knobler, C. B.; Lu, P.; Nam, W.; Hawthorne, M. F. *Organometallics* **1990**, *9*, 2046. (b) Bandman, M. A.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1989**, *28*, 1204.

(3) Grimes, R. N.; Rademaker, W. J.; Denniston, M. L.; Bryan, R. F.; Greene, P. T. *J. Am. Chem. Soc.* **1972**, *94*, 1865.

(4) Hosmane, N. S.; Lu, K.-J.; Zhang, H.; Jia, L.; Cowley, A. H.; Mardones, M. A. *Organometallics* **1991**, *10*, 963.

(5) Hosmane, N. S.; Zhang, H.; Lu, K.-J.; Maguire, J. A.; Cowley, A. H.; Mardones, M. A. *Struct. Chem.* **1992**, *3*, 183.

(6) Maguire, J. A.; Hosmane, N. S.; Saxena, A. K.; Zhang, H.; Gray, T. G. *Phosphorus, Sulfur and Silicon Relat. Elem.* **1994**, *87*, 129.

(7) Hosmane, N. S.; Saxena, A. K.; Lu, K. -J.; Maguire, J. A.; Zhang, H.; Wang, Y.; Thomas, C. J.; Zhu, D.; Grover, B. R.; Gray, T. G.; Eintracht, J. F.; Isom, H.; Cowley, A. H. *Organometallics* **1995**, *14*, 5104.

(8) Saxena, A. K.; Zhang, H.; Maguire, J. A.; Hosmane, N. S.; Cowley, A. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 332.

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Table 1. FT NMR Spectral Data for Gallacarboranes I−IV[a]

compd	δ, splitting, assignt ($^1J(^{11}B-^1H)$ or $^1J(^{13}C-^1H)$, Hz)	rel area
	200.13 MHz ^{1}H NMR Data[b]	
I	2.20, br overlapping, TMEDA; 2.05, br overlapping, TMEDA; 0.54, s, $SiMe_3$	2:6:9
II	2.37, s, TMEDA; 2.23, s, TMEDA; 0.09, s, $SiMe_3$	2:6:9
III	2.35, br, TMEDA; 2.02, br, TMEDA; 0.66, s, $SiMe_3$	2:6:9
IV	2.21, v br, TMEDA; 2.05, v br, TMEDA; 0.52, s, br, $SiMe_3$	2:6:9
	64.21 MHz ^{11}B NMR Data[c]	
I	14.25, v br, basal BH (unresolved); −1.90, v br, basal BH (unresolved); −46.24 , v br, apical BH (unresolved)	2:1:1
II	22.5, v br, basal BH (unresolved); 4.55, v br, basal BH (unresolved); −47.46, d, apical BH (188.7)	1:2:1
III	14.29, v br, basal BH (unresolved); −2.26, v br, basal BH (unresolved); −47.67, d, apical BH (145)	2:1:1
IV	24.02, v br, basal BH (unresolved); 6.01, v br, basal BH (unresolved); −46.27, d, br, apical BH (134.3)	1:2:1
	50.32 MHz ^{13}C NMR Data[b,d]	
I	117.77, s, cage C (SiCB); 56.85, t, CH_2 (133.2); 46.05, q, Me (134.6); 3.02, q, $SiMe_3$ (118.9)	1:1:2:3
II	99.92, s(br), cage C (SiCB); 56.72, t, CH_2 (130.45); 45.80, q, Me (133.8); 1.61, q, $SiMe_3$ (117.2)	1:1:2:3
III	118.32, s, cage C (SiCB); 57.07, t, br, CH_2 (123.3); 45.97, q, Me (130.2); 3.02, q, v br, $SiMe_3$ (118.2)	1:1:2:3
IV	101.8, s(br), cage C (SiCB); 56.17, t, br, CH_2 (132.3); 48.23, q, br, Me (130); 1.79, q, br, $SiMe_3$ (119)	1:1:2:3

[a] C_6D_6 was used as solvent and an internal standard at δ 7.15 ppm (in the ^{1}H NMR spectra) with a positive sign indicating a downfield shift. Legend: s = singlet, d = doublet, t = triplet, q = quartet, v = very, br = broad. [b] Shifts relative to external Me_4Si. [c] Shifts relative to external $BF_3{\cdot}OEt_2$. [d] Since relaxation of a quaternary carbon is much slower than that of a CH unit, the relative areas of the substituted carbons of the cage could not be measured accurately.

Experimental Section

Materials. 2,3-Bis(trimethylsilyl)-2,3-dicarba-*nido*-hexaborane(8) and 1,2-bis(trimethylsilyl)-1,2-dicarba-*closo*-hexaborane(6) were prepared using the literature methods.[9−11] The *closo*-carborane was subsequently converted to the corresponding *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA)-solvated carbons-apart dinatracarborane *closo*-*exo*-5,6-[(μ-H)$_2$Na(TMEDA)]-1-Na(TMEDA)-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$ by reduction with Na/$C_{10}H_8$ as outlined previously.[12] Prior to use, TMEDA (Aldrich) was distilled *in vacuo* and stored over sodium metal and its purity was checked by IR and NMR spectra and boiling point measurements. Before use, naphthalene (Aldrich) was sublimed *in vacuo*, Na metal (Aldrich) was freshly cut in a drybox, and anhydrous $GaCl_3$ (Strem Chemicals) was heated at 120 °C *in vacuo* overnight to remove any last traces of moisture in the sample. Benzene, THF, and *n*-hexane were dried over $LiAlH_4$ and doubly distilled; all other solvents were dried over 4−8 mesh molecular sieves (Aldrich) and either saturated with dry argon or degassed before use.

Spectroscopic and Analytical Procedures. Proton, boron-11, and carbon-13 pulse Fourier transform NMR spectra, at 200, 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(TMEDA)$_2$][2,2′,3,3′-(SiMe$_3$)$_4$-1,1′-*commo*-Ga(1,2,3-GaC$_2$B$_4$H$_4$)$_2$] (I). In a procedure identical with that described elsewhere,[11] a 2.624 g (11.94 mmol) sample of *nido*-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$ was first reacted *in vacuo* with an excess quantity (0.417 g, 17.38 mmol) of NaH in a 1:1 mixture (20 mL) of TMEDA and benzene at room temperature for 6 h, to produce the corresponding TMEDA-solvated dimeric monosodium compound [1-Na(TMEDA)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$]$_2$. After purification, the monosodium compound was dissolved in a 1:1 mixture (20 mL) of anhydrous TMEDA and benzene and was further reacted with a pentane solution of *t*-BuLi (7.03 mL of a 1.7 M solution, 11.95 mmol) *in vacuo* at 0 °C and then warmed to room temperature to obtain a pale orange solution of the mixed Na/Li compound *exo*-Li(TMEDA)-1-Na(TMEDA)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$. This solution was then poured, *in vacuo*, into a benzene (5 mL) solution of $GaCl_3$ (1.051 g, 5.97 mmol) at 0 °C. The resulting heterogeneous mixture was stirred constantly at room temperature overnight, during which time it turned gray to off-white. The mixture was filtered *in vacuo*, and the residue on the frit was washed several times with benzene to collect a clear filtrate. The solid residue, identified by qualitative analyses as a mixture of NaCl, LiCl, and elemental Ga (not measured), was discarded. After removal of all the solvents from the filtrate, a slightly colored semisolid residue remained in the flask. Anhydrous dry benzene (20 mL) was then condensed into this flask, and the resulting mixture was stirred constantly for 2 h. At this point, the stirring was stopped; the mixture was allowed to stand overnight and then filtered *in vacuo* to collect a clear filtrate. Upon slow removal of benzene from the filtrate, *in vacuo*, colorless crystals identified as [Li(TMEDA)$_2$][2,2′,3,3′-$(SiMe_3)_4$-1,1′-*commo*-Ga(1,2,3-Ga$C_2B_4H_4$)$_2$] (**I**) (1.591 g, 2.137 mmol, 36% yield) were obtained. The anionic full-sandwich carbons-adjacent gallacarborane **I** (mp 248 °C) is soluble in both polar and nonpolar organic solvents. Anal. Calcd for $C_{28}H_{76}B_8Si_4N_4GaLi$: C, 45.18; H, 10.28; N, 7.53. Found: C, 45.11; H, 10.26; N, 7.46. The NMR and IR spectral data for **I** are given in Tables 1 and 2, respectively.

Synthesis of [Na(TMEDA)$_2$][2,2′,4,4′-(SiMe$_3$)$_4$-1,1′-*commo*-Ga(1,2,4-GaC$_2$B$_4$H$_4$)$_2$] (II). A sample of the TMEDA-solvated dinatracarborane *closo*-*exo*-5,6-[(μ-H)$_2$Na(TMEDA)]-1-Na(TMEDA)-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$ was prepared from the reaction of 1.16 g (5.33 mmol) of *closo*-1,2-$(SiMe_3)_2$-1,2-$C_2B_4H_4$ with 0.25 g (10.87 mmol) of freshly cut Na metal and 0.683 g (5.33 mmol) of naphthalene in a 1:1 solvent mixture (20 mL) of TMEDA and benzene at 25 °C as described elsewhere.[12] After it was separated from naphthalene, the TMEDA-solvated dinatracarborane (2.64 g, 5.32 mmol), isolated as a brown solid, was transferred to a reaction flask containing a magnetic stirring bar. A benzene (20 mL) solution of $GaCl_3$ (0.469 g, 2.66 mmol) was slowly poured, *in vacuo*, onto the solid dinatracarborane at 0 °C, and the resulting heterogeneous

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(9) (a) Hosmane, N. S.; Sirmokadam, N. N.; Mollenhauer, M. N. *J. Organomet. Chem.* **1985**, *279*, 359. (b) Hosmane, N. S.; Mollenhauer, M. N.; Cowley, A. H.; Norman, N. C. *Organometallics* **1985**, *4*, 1194. (c) Barreto, R. D.; Hosmane, N. S. *Inorg. Synth.* **1992**, *29*, 89.

(10) Hosmane, N. S.; Barreto, R. D.; Tolle, M. A.; Alexander, J. J.; Quintana, W.; Siriwardane, U.; Shore, S. G.; Williams, R. E. *Inorg. Chem.* **1990**, *29*, 2698.

(11) Hosmane, N. S.; Saxena, A. K.; Barreto, R. D.; Zhang, H.; Maguire, J. A.; Jia, L.; Wang, Y.; Oki, A. R.; Grover, K. V.; Whitten, S. J.; Dawson, K.; Tolle, M. A.; Siriwardane, U.; Demissie, T.; Fagner, J. S. *Organometallics* **1993**, *12*, 3001.

(12) (a) Hosmane, N. S.; Jia, L.; Zhang, H.; Bausch, J. W.; Prakash, G. K. S.; Williams, R. E.; Onak, T. P. *Inorg. Chem.* **1991**, *30*, 3793. (b) Jia, L. M.S. Thesis, Southern Methodist University, Dallas, Texas, 1992. (c) Zhang, H.; Wang, Y.; Saxena, A. K.; Oki, A. R.; Maguire, J. A.; Hosmane, N. S. *Organometallics* **1993**, *12*, 3933.

Table 2. Infrared Absorptions for Gallacarboranes I−IV (cm^{-1}; C_6D_6 vs C_6D_6)[a]

compd	absorption
I	3101 (vs), 3077 (vs), 3041 (vs) [ν(C−H)], 2543 (br, m), 2494 (w) [ν(B−H)], 1821 (ms), 1648 (w), 1518 (w), 1481 (vs), 1335 (br, m), 1252 (w), 1135 (m), 1036 (vs), 1011 (m), 943 (m), 838 (m), 764 (w), 671 (vs), 486 (br, m)
II	2957 (vs), 2898 (vs), 2866 (ms), 2774 (ms) [ν(C−H)], 2531 (vs) [ν(B−H)], 2354 (ms), 2262 (ms), 2125 (m, br), 1886 (ms), 1561 (ms), 1508 (ms), 1462 (vs), 1364 (ms), 1252 (vs), 1200 (ms), 1108 (ms), 984 (w), 839 (vs), 754 (ms), 636 (w), 551 (w, br)
III	2957 (vs), 2898 (vs), 2859 (ms), 2762 (ms) [ν(C−H)], 2556 (vs), 2551 (vs) [ν(B−H)], 1639 (ms), 1548 (ms), 1515 (vs), 1456 (vs), 1284 (vs), 1253 (vs), 1102 (vs), 1046 (ms), 921 (ms), 839 (ms), 786 (ms), 620 (ms), 584 (br, m)
IV	2959 (vs), 2894 (ms) [ν(C−H)], 2534 (vs), 2501 (vs) [ν(B−H)], 2357 (w), 1912 (br, m), 1546 (ms), 1506 (vs), 1460 (vs), 1425 (vs), 1290 (ms), 1244 (vs), 1192 (ms), 1107 (ms), 1074 (ms), 993 (ms), 924 (w), 839 (vs), 747 (ms), 623 (w), 577 (br, m)

[a] Legend: v = very, s = strong or sharp, m = medium, w = weak, sh = shoulder, br = broad.

mixture was stirred at room temperature overnight, during which time it turned gray to off-white. At this point, the mixture was filtered *in vacuo* to collect a clear filtrate. The solid residue that remained on the frit after several washings with anhydrous benzene was later identified by qualitative analyses as a mixture of NaCl and elemental Ga (not measured) and was discarded. The clear filtrate was then concentrated *in vacuo* and allowed to stand for several days at room temperature; this resulted in the formation of colorless crystals (0.761 g, 1.00 mmol, 38% yield) that were identified as [Na(TMEDA)$_2$][2,2′,4,4′-(SiMe$_3$)$_4$-1,1′-*commo*-Ga(1,2,4-GaC$_2$B$_4$H$_4$)$_2$] (**II**). The anionic full-sandwich carbons-apart gallacarborane **II** (mp 197 °C) is soluble in both polar and nonpolar organic solvents. Anal. Calcd for $C_{28}H_{76}B_8Si_4N_4GaNa$: C, 44.22; H, 10.07; N, 7.37. Found: C, 43.97; H, 10.04; N, 7.23. The NMR and IR spectral data for **II** are given in Tables 1 and 2, respectively.

Synthesis of 1-Cl-1-(TMEDA)-2,3-(SiMe$_3$)$_2$-*closo*-1,2,3-GaC$_2$B$_4$H$_4$ (III). In a procedure identical with that described elsewhere,[11] a 1.464 g (6.66 mmol) sample of *nido*-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_6$ was reacted *in vacuo* with 7.84 mL of a 1.7 M pentane solution of *t*-BuLi (13.33 mmol) in a 1:1 mixture (20 mL) of TMEDA and benzene at 0 °C for 2 h, and then at room temperature for 4 h, to produce the corresponding TMEDA-solvated dilithium compound *closo-exo*-4,5-[(μ-H)$_2$Li(TMEDA)]-1-Li(TMEDA)-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$, in essentially quantitative yield (3.08 g, 6.64 mmol). All of the dilithium compound was redissolved in dry benzene (20 mL) and poured, *in vacuo*, onto anhydrous GaCl$_3$ (1.173 g, 6.66 mmol) in a reaction flask at 0 °C. The resulting heterogeneous mixture was stirred constantly at room temperature overnight, during which time the mixture turned gray to off-white. The mixture was filtered *in vacuo*, and the residue on the frit was washed with benzene several times to collect a clear filtrate. The solid residue on the frit, identified by qualitative analyses as a mixture of LiCl and elemental Ga (not measured), was discarded. The clear filtrate was concentrated *in vacuo* and then allowed to stand for several days at room temperature to produce transparent crystals, identified as 1-Cl-1-(TMEDA)-2,3-(SiMe$_3$)$_2$-*closo*-1,2,3-GaC$_2$B$_4$H$_4$ (**III**; 1.496 g, 3.41 mmol, 51% yield). The half-sandwich carbons-adjacent chlorogallacarborane **III** (mp 186 °C) is soluble in both polar and nonpolar organic solvents. Anal. Calcd. for $C_{14}H_{38}B_4Si_2N_2GaCl$: C, 38.29; H, 8.74; N, 6.38. Found: C, 38.13; H, 8.80; N, 6.12. The NMR and IR spectral data for **III** are given in Tables 1 and 2, respectively.

Synthesis of 1-Cl-1-(TMEDA)-2,4-(SiMe$_3$)$_2$-*closo*-1,2,4-GaC$_2$B$_4$H$_4$ (IV). In a procedure identical with that described elsewhere and above in the synthesis of **II**,[12] a 5.00 mmol (1.09 g) sample of *closo*-1,2-(SiMe$_3$)$_2$-1,2-C$_2$B$_4$H$_4$ was reacted overnight at 25 °C with 0.23 g (10.0 mmol) of freshly cut Na metal and 0.641 g (5.00 mmol) of freshly sublimed naphthalene in a 1:3 mixture of dry TMEDA and dry benzene, to produce the corresponding carbons-apart disodium compound *closo-exo*-5,6-[(μ-H)$_2$Na(TMEDA)]-1-Na(TMEDA)-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$. After removal of all the solvents and naphthalene, the TMEDA-solvated disodium compound was isolated as a brown crystalline solid in near-quantitative yield (2.45 g, 4.94 mmol). This solid was then transferred to a reaction flask containing a magnetic stirring bar. At this point, a benzene (25 mL) solution of GaCl$_3$ (0.881 g, 5.00 mmol) was slowly poured, *in vacuo*, onto the disodium compound in the flask at 0 °C and the resulting heterogeneous mixture was stirred at room temperature overnight, during which time the mixture turned from brown to a gray off-white. The mixture was filtered *in vacuo* to collect a clear filtrate. The solid residue that remained on the frit after several washings with anhydrous benzene, identified by qualitative analyses as a mixture of NaCl and elemental Ga (not measured), was discarded. The clear filtrate was concentrated *in vacuo* and then allowed to stand for several days at room temperature; this resulted in the formation of transparent crystals (0.898 g, 2.04 mmol, 41% yield), identified as 1-Cl-1-(TMEDA)-2,4-(SiMe$_3$)$_2$-*closo*-1,2,4-GaC$_2$B$_4$H$_4$ (**IV**). The half-sandwich carbons-apart chlorogallacarborane **IV** (mp 142 °C) is soluble in both polar and nonpolar organic solvents. Anal. Calcd for $C_{14}H_{38}B_4Si_2N_2GaCl$: C, 38.29; H, 8.74; N, 6.38. Found: C, 38.51; H, 8.58; N, 6.17. The NMR and IR spectral data for **IV** are given in Tables 1 and 2, respectively.

X-ray Analyses of Gallacarboranes I−IV. Colorless transparent X-ray-quality crystals of the gallacarboranes **I**−**IV** were grown very slowly from their respective benzene solutions. These crystals were transferred to a drybox and placed in a covered dish containing paraffin. After protection with paraffin, the crystals were removed from the drybox, coated with an epoxy resin in air, 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 3. Final unit cell parameters were obtained by a least-squares fit of the angles of 24−30 accurately centered reflections in the 2θ range from 16 to 32.0°. Intensity data were collected at 220 K 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 were corrected for Lorentz and polarization effects, and absorption corrections were also applied. The structures were solved by direct methods using the SHELXTL-Plus package[13] and subsequent Fourier syntheses. Full-matrix least-squares refinements were performed for all four structures. Scattering factors, as well as anomalous dispersion corrections for the heavy atoms, were taken from ref 14. While the anionic sandwich gallacarborane unit in **I** possesses a center of symmetry, the TMEDA-solvated Li cation has a 2-fold symmetric axis which is parallel to the crystallographic *b* axis. The structure of **II** is similar to that of **I**, with the exception that the Li(TMEDA)$_2$ cation is replaced by a Na(TMEDA)$_2$ cationic unit. In **I** the TMEDA nitrogens surround the Li in an approximately tetrahedral fashion, while in **II** the Na(TMEDA)$_2$ unit is sufficiently distorted such that the Na and the four nitrogens are almost coplanar. There are also 1.5 benzene molecules per gallacarborane sandwich molecule of **II** found in the crystal lattice. On the other hand, the crystal lattice of the half-sandwich chlorogallacarborane **III** contains two solvated benzene molecules and has a mirror plane of symmetry, with Ga, Cl, B(14), and B(16) residing on the mirror plane. The methyl groups of the SiMe$_3$ moieties in **III** were

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(13) Sheldrick, G. M. Structure Determination Software Programs; Siemens X-ray Analytical Instrument Corp., Madison, WI, 1991.

(14) *International Tables For X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974, Vol. IV.

Table 3. Crystallographic Data[a] for Gallacarboranes I−IV

	I	**II**	**III**	**IV**
formula	$C_{28}H_{76}N_4B_8Si_4LiGa$	$[C_{28}H_{76}N_4B_8Si_4NaGa]\cdot 1.5C_6H_6$	$[C_{14}H_{38}N_2B_4Si_2ClGa]\cdot 2C_6H_6$	$[C_{14}H_{38}N_2B_4Si_2ClGa]\cdot C_6H_6$
fw	744.4	877.6	595.3	517.2
space group	$C2/c$	$P2_1/c$	Cm	$P2_12_12_1$
a, Å	20.924(9)	13.512(4)	9.927(5)	12.085(1)
b, Å	11.927(5)	18.048(8)	18.621(9)	12.702(1)
c, Å	19.349(9)	22.433(9)	9.768(5)	19.280(2)
β, deg	90.87(3)	92.23(2)	103.99(3)	90
V, Å^3	4821(3)	5710(4)	1752(2)	2959.4(5)
Z	4	4	2	4
D_{calcd}, g cm^{-3}	1.026	1.021	1.128	1.161
abs coeff, mm^{-1}	0.692	0.600	0.947	1.111
crystal dmns, mm	0.15 × 0.35 × 0.30	0.20 × 0.30 × 0.10	0.30 × 0.35 × 0.10	0.35 × 0.25 × 0.10
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\theta/2\theta$
scan sp in ω: min, max	6.51, 29.30	5.0, 30.0	6.0, 30.0	3.5, 35.0
2θ range, deg	3.5−44.0	3.0−42.0	3.5−44.0	3.5−46.0
T, K	230	230	220	230
decay, %	0	0	0	0
no. of data collected	3063	5736	1160	2336
no. of obsd rflns, $F > 6.0\sigma(F)$	1289	1391	923	2060
no. of params refined	210	251	167	287
GOF	1.56	1.37	1.88	1.28
$\Delta\rho_{max,min}$, e/Å^3	0.40, −0.26	0.36, −0.32	0.68, −0.64	0.38, −0.50
R^b	0.061	0.067	0.065	0.036
$R_w{}^c$	0.073	0.075	0.081	0.052

[a] Graphite-monochromatized Mo Kα radiation, $\lambda = 0.710\,73$ Å. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = [\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{1/2}$. [c] $w = 1/[\sigma^2(F_o) + 0.001(F_o)^2]$.

disordered with occupancy factors of 55% for C(21), C(22), and C(23) and 45% for C(211), C(221), and C(231). There was one solvated benzene molecule per half-sandwich chlorogallacarborane in the unit cell of **IV**. The positions of the methyl, methylene, and benzene H atoms in all four structures were calculated using a riding model. All cage H atoms were located in difference Fourier maps and, with the exception of **IV**, were not refined. The hydrogen atoms of the carborane cage in **IV** were refined with their isotropical thermal parameters as a common variable. The final values of R and weighted R_w are listed in Table 3, while the selected interatomic distances and angles are given in Table 4. The atomic coordinates, a full list of bond distances and angles, anisotropic thermal parameters, and the positions of the H atoms are given in the Supporting Information.

Calculations. The ^{11}B NMR spectra of compounds **I**−**IV** were verified by GIAO (gauge independent atomic orbital)[15] *ab initio* molecular orbital calculations at the HF/6-311G** level on the model compounds 1-$(NH_3)_2$-1-Cl-1,2,*n*-$GaC_2B_4H_6$ (n = 3 (**V**), 4 (**VI**)) and [*commo*-1,1′-Ga(1,2,*n*-$GaC_2B_4H_4)_2]^-$ (n = 3 (**VII**), 4 (**VIII**)). The structures were optimized by approximate density function theory (DFT) hybrid methods using Becke's three-parameter method[16] and the correlation functional of Lee, Yang, and Parr[17] with the 3-21G* basis set (B3LYP/3-21G*).[18] All calculations were carried out on a Dec-αA or a Silicon Graphics Indigo2 RS10000 workstation using the Gausian 94[19] series of programs. The chemical shifts, listed in Table 5, are given relative to $BF_3\cdot OEt_2$ as a standard. The standard was subjected to the same optimization/GIAO cycle as were the compounds.

Results and Discussion

Synthesis. The half- and full-sandwich gallacarboranes were synthesized in basically the same manner, that is, from the reaction of the appropriate [2,*n*-$(SiMe_3)_2$-2,*n*-$C_2B_4H_4]^{2-}$ (n = 3, 4) dianionic ligand with $GaCl_3$ (see Scheme 1). The nature of the product was independent of the isomeric form of the carborane and the nature of the group 1 counterions but did depend on the beginning stoichiometry of the reaction. The yields for both carborane isomers were comparable, with the half-sandwich compounds being obtained in 51% and 41% yields for n = 3, 4, respectively, while those of the full−sandwich complexes were slightly less (36% and 38% for n = 3, 4, respectively). It is of interest that, even though only about half the maximum amounts of the half-sandwich gallacarboranes were obtained, there was no evidence of the "excess" carborane reagents reacting further with the chlorogallacarboranes. However, an initial 2:1 carborane-to-$GaCl_3$ molar ratio gave exclusively the full-sandwich compounds. This indicates that the initial reaction of $GaCl_3$ with carborane must be essentially quantitative; if an excess of carborane was not originally present, the reaction would cease at the half-sandwich compound. The less than quantitative yields in the syntheses of **III** and **IV** are more likely due to the high solubility of the chlorogallacarboranes in the benzene solvent, rather than to a lack of reactivity between the carboranes and $GaCl_3$. It should be noted that the yields reported in the Experimental Section were of the crystallized products and were not optimized; once the conditions are optimized, the controlled direct reaction of the carborane dianions with $GaCl_3$ should prove to be a very efficient synthetic route to both the full-sandwich gallacarboranes and the half-sandwich chlorogallacarboranes.

X-ray Crystal Structures. The solid-state structures of **I**−**IV** were determined by single-crystal X-ray diffraction. Figures 1 and 2 show the structures of the full-sandwich [2,2′,*n*,*n*′-$(SiMe_3)_4$-1,1′-*commo*-Ga(1,2,*n*-

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(15) Wolinski, K.; Hilton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.

(16) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(17) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev., B* **1988**, *37*, 785.

(18) For a discussion of DFT methods, see: Ziegler, T. *Chem. Rev.* **1991**, *91*, 651 and references therein.

(19) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.;. Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94, Revision B.3; Gaussian, Inc., Pittsburgh, PA, 1995.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for Gallacarboranes I−IV

Bond Lengths (Å)

		Compound **I**			
Ga−Cnt(1)	1.878	Li−N(31)	2.095 (17)	C(12)−B(16)	1.724 (17)
Ga−C(11)	2.489 (11)	Li−N(32)	2.086 (17)	B(13)−B(14)	1.670 (20)
Ga−C(12)	2.468 (11)	C(11)−C(12)	1.527 (16)	B(13)−B(16)	1.761 (19)
Ga−B(13)	2.243 (14)	C(11)−B(15)	1.584 (19)	B(14)−B(15)	1.674 (20)
Ga−B(14)	2.141 (13)	C(11)−B(16)	1.728 (18)	B(14)−B(16)	1.797 (19)
Ga−B(15)	2.249 (13)	C(12)−B(13)	1.573 (16)	B(15)−B(16)	1.776 (19)
		Compound **II**			
Ga−Cnt(21)	1.920	Na−N(51)	2.488 (25)	B(14)−B(16)	1.713 (39)
Ga−Cnt(22)	1.929	Na−N(52)	2.522 (25)	B(15)−B(16)	1.767 (40)
Ga−C(11)	2.431 (21)	Na−N(61)	2.432 (29)	C(21)−B(22)	1.587 (38)
Ga−B(12)	2.605 (25)	Na−N(62)	2.491 (25)	C(21)−B(25)	1.604 (34)
Ga−C(13)	2.390 (21)	C(11)−B(12)	1.521 (32)	C(21)−B(26)	1.698 (36)
Ga−B(14)	2.119 (30)	C(11)−B(15)	1.638 (36)	B(22)−C(23)	1.500 (37)
Ga−B(15)	2.190 (30)	C(11)−B(16)	1.663 (34)	B(22)−B(26)	1.774 (39)
Ga−C(21)	2.483 (23)	B(12)−C(13)	1.563 (32)	C(23)−B(24)	1.545 (32)
Ga−B(22)	2.544 (31)	B(12)−B(16)	1.785 (36)	C(23)−B(26)	1.712 (34)
Ga−C(23)	2.418 (20)	C(13)−B(14)	1.578 (35)	B(24)−B(25)	1.705 (37)
Ga−B(24)	2.159 (27)	C(13)−B(16)	1.693 (34)	B(24)−B(26)	1.755 (38)
Ga−B(25)	2.141 (26)	B(14)−B(15)	1.707 (42)	B(25)−B(26)	1.777 (38)
		Compound **III**			
Ga−Cnt(3)	2.126	Ga−B(14)	2.073 (18)	C(11)−C(11A)	1.425 (33)
Ga−Cl	2.237 (5)	Ga−N(31)	2.121 (15)	B(13)−B(14)	1.635 (25)
Ga−C(11)	2.833 (17)	C(11)−B(13)	1.522 (26)	B(13)−B(16)	1.708 (26)
Ga−B(13)	2.334 (20)	C(11)−B(16)	1.674 (25)	B(14)−B(16)	1.655 (35)
		Compound **IV**			
Ga−Cnt(4)	2.273	Ga−N(31)	2.166 (5)	B(12)−B(16)	1.793 (11)
Ga−Cl	2.193 (2)	Ga−N(32)	2.099 (5)	C(13)−B(14)	1.560 (10)
Ga−C(11)	2.747 (6)	C(11)−B(12)	1.528 (10)	C(13)−B(16)	1.702 (10)
Ga−B(12)	3.078 (7)	C(11)−B(15)	1.594 (10)	B(14)−B(15)	1.758 (11)
Ga−C(13)	2.877 (6)	C(11)−B(16)	1.688 (10)	B(14)−B(16)	1.761 (11)
Ga−B(14)	2.248 (7)	B(12)−C(13)	1.520 (10)	B(15)−B(16)	1.721 (11)
Ga−B(15)	2.157 (8)				

Bond Angles (deg)

			Compound **I**				
Cnt(1)−Ga−Cnt(1A)	180	Si(2)−C(12)−B(13)	119.2(9)	B(13)−B(14)−B(15)	103.0(10)	C(12)−B(16)−B(13)	53.6(7)
N(31)−Li−N(32)	88.5(5)	C(11)−C(12)−B(13)	110.7(10)	B(13)−B(14)−B(16)	60.9(7)	C(11)−B(16)−B(14)	97.0(8)
N(31)−Li−N(31A)	118.7(13)	Si(2)−C(12)−B(16)	136.5(8)	B(15)−B(14)−B(16)	61.4(8)	C(12)−B(16)−B(14)	96.6(9)
N(31)−Li−N(32A)	121.6(5)	C(11)−C(12)−B(16)	63.9(7)	C(11)−B(15)−B(14)	108.2(10)	B(13)−B(16)−B(14)	56.0(8)
N(32)−Li−N(32A)	121.5(13)	B(13)−C(12)−B(16)	64.4(8)	C(11)−B(15)−B(16)	61.6(8)	C(11)−B(16)−B(15)	53.7(7)
C(12)−C(11)−B(15)	109.8(10)	C(12)−B(13)−B(14)	108.2(11)	B(14)−B(15)−B(16)	62.7(8)	C(12)−B(16)−B(15)	93.3(9)
C(12)−C(11)−B(16)	63.6(7)	C(12)−B(13)−B(16)	62.0(8)	C(11)−B(16)−C(12)	52.5(7)	B(13)−B(16)−B(15)	95.5(9)
B(15)−C(11)−B(16)	64.7(8)	B(14)−B(13)−B(16)	63.1(8)	C(11)−B(16)−B(13)	93.9(9)	B(14)−B(16)−B(15)	55.9(8)
Si(2)−C(12)−C(11)	129.9(8)						
			Compound **II**				
Cnt(21)−Ga−Cnt(22)	178.2	B(14)−C(13)−B(16)	63.0(15)	B(12)−B(16)−B(15)	98.1(18)	B(25)−B(24)−B(26)	61.8(15)
N(51)−Na−N(52)	78.8(8)	C(13)−B(14)−B(15)	106.9(20)	C(13)−B(16)−B(15)	99.4(18)	C(21)−B(25)−B(24)	104.3(19)
N(51)−Na−N(61)	171.4(11)	C(13)−B(14)−B(16)	61.8(15)	B(14)−B(16)−B(15)	58.7(16)	C(21)−B(25)−B(26)	60.1(15)
N(52)−Na−N(61)	100.2(9)	B(15)−B(14)−B(16)	62.2(16)	B(22)−C(21)−B(25)	108.4(20)	B(24)−B(25)−B(26)	60.5(15)
N(52)−Na−N(62)	171.5(10)	C(11)−B(15)−B(14)	99.6(19)	B(22)−C(21)−B(26)	65.3(17)	C(21)−B(26)−B(22)	54.3(15)
N(51)−Na−N(62)	100.8(8)	C(11)−B(15)−B(16)	58.4(15)	B(25)−C(21)−B(26)	65.0(16)	C(21)−B(26)−C(23)	94.6(17)
N(61)−Na−N(62)	81.5(9)	B(14)−B(15)−B(16)	59.0(16)	C(21)−B(22)−C(23)	108.5(21)	B(22)−B(26)−C(23)	50.9(14)
B(12)−C(11)−B(15)	116.2(19)	C(11)−B(16)−B(12)	52.2(13)	C(21)−B(22)−B(26)	60.4(16)	C(21)−B(26)−B(24)	98.3(18)
B(12)−C(11)−B(16)	68.0(15)	C(11)−B(16)−C(13)	93.3(17)	C(23)−B(22)−B(26)	62.4(16)	B(22)−B(26)−B(24)	92.0(18)
B(15)−C(11)−B(16)	64.7(16)	B(12)−B(16)−C(13)	53.3(13)	B(22)−C(23)−B(24)	112.9(19)	C(23)−B(26)−B(24)	52.9(13)
C(11)−B(12)−C(13)	104.6(18)	C(11)−B(16)−B(14)	98.3(18)	B(22)−C(23)−B(26)	66.7(17)	C(21)−B(26)−B(25)	54.9(14)
C(11)−B(12)−B(16)	59.8(15)	B(12)−B(16)−B(14)	96.7(18)	B(24)−C(23)−B(26)	65.0(15)	B(22)−B(26)−B(25)	93.6(18)
C(13)−B(12)−B(16)	60.3(14)	C(13)−B(16)−B(14)	55.2(15)	C(23)−B(24)−B(25)	105.1(19)	C(23)−B(26)−B(25)	95.5(17)
B(12)−C(13)−B(14)	112.7(19)	C(11)−B(16)−B(15)	56.9(15)	C(23)−B(24)−B(26)	62.1(15)	B(24)−B(26)−B(25)	57.7(15)
B(12)−C(13)−B(16)	66.4(15)						
			Compound **III**				
Cnt(3)−Ga−Cl	102.7	B(13)−C(11)−C(11A)	111.5(10)	B(13)−B(14)−B(16)	62.5(11)	B(13)−B(16)−B(14)	58.1(11)
Cnt(3)−Ga−N(31)	134.6	B(16)−C(11)−C(11A)	64.8(6)	B(13)−B(14)−B(13A)	102.0(18)	C(11)−B(16)−C(11A)	50.4(13)
Cl−Ga−N(31)	96.7(4)	C(11)−B(13)−B(14)	107.1(15)	B(16)−B(14)−B(13A)	62.5(11)	B(13)−B(16)−C(11A)	92.2(13)
N(31)−Ga−N(31A)	82.1(8)	C(11)−B(13)−B(16)	62.1(13)	C(11)−B(16)−B(13)	53.5(10)	B(13)−B(16)−B(13A)	96.1(18)
B(13)−C(11)−B(16)	64.4(12)	B(14)−B(13)−B(16)	59.3(13)	C(11)−B(16)−B(14)	99.5(14)		
			Compound **IV**				
Cnt(4)−Ga−Cl	98.9	B(12)−C(11)−B(16)	67.5(5)	C(13)−B(14)−B(15)	103.3(5)	B(12)−B(16)−C(13)	51.5(4)
Cnt(4)−Ga−N(31)	130.7	B(15)−C(11)−B(16)	63.2(4)	C(13)−B(14)−B(16)	61.3(4)	C(11)−B(16)−B(14)	98.8(5)
Cnt(4)−Ga−N(32)	136.7	C(11)−B(12)−C(13)	108.1(6)	B(15)−B(14)−B(16)	58.5(4)	B(12)−B(16)−B(14)	92.8(5)
Cl−Ga−N(31)	99.1(2)	C(11)−B(12)−B(16)	60.5(5)	C(11)−B(15)−B(14)	102.7(5)	C(13)−B(16)−B(14)	53.5(4)
Cl−Ga−N(32)	99.9(2)	C(13)−B(12)−B(16)	61.2(4)	C(11)−B(15)−B(16)	61.1(4)	C(11)−B(16)−B(15)	55.7(4)
N(31)−Ga−N(32)	83.9(2)	B(12)−C(13)−B(14)	113.3(6)	B(14)−B(15)−B(16)	60.8(4)	B(12)−B(16)−B(15)	95.0(5)
B(12)−C(11)−B(15)	112.1(5)	B(12)−C(13)−B(16)	67.3(5)	C(11)−B(16)−C(13)	93.4(5)	C(13)−B(16)−B(15)	99.1(5)
Si(1)−C(11)−B(16)	125.5(4)	B(14)−C(13)−B(16)	65.2(4)	C(11)−B(16)−B(12)	52.0(4)	B(14)−B(16)−B(15)	60.6(4)

[a] Cnt = centroid of the C_2B_3 bonding face.

Table 5. Calculated ^{11}B NMR Chemical Shifts of Model Full- and Half-Sandwich Gallacarboranes[a]

	δ^b		
compd	basal[c]	unique[d]	apical[e]
[*commo*-1,1′-Ga(1,2,3-$GaC_2B_4H_6$]$^-$ (**V**)	13.37(2)	−4.56(1)	−46.47(1)
[*commo*-1,1′-Ga(1,2,4-$GaC_2B_4H_6$]$^-$ (**VI**)	5.01(2)	19.36(1)	−47.14(1)
1,1-$(NH_3)_2$-1-Cl-1,2,3-$GaC_2B_4H_6$ (**VII**)	9.67(2)	−2.37(1)	−46.73(1)
1,1-$(NH_3)_2$-1-Cl-1,2,4-$GaC_2B_4H_6$ (**VIII**)	7.71(2)	20.12(1)	−44.17(1)

[a] Geometries optimized at the B3LYP/3-21G* level. [b] GIAO calculated chemical shifts at the HF/6-311G** level, relative to $BF_3 \cdot OEt_2$ calculated at the same level. Relative areas are given in parentheses. [c] Equivalent to B(13,15) in Figure 1, B(14,15,24,25) in Figure 2, B(13) in Figure 3, or B(14,15) in Figure 4. [d] Equivalent to B(14) in Figure 1, B(12,22) in Figure 2, B(14) in Figure 3, or B(12) in Figure 4. [e] Equivalent to B(16) in Figures 1, 3, and 4 or B(16,26) in Figure 2.

$GaC_2B_4H_4$]$^-$ complexes for $n = 3$ (**I**), 4 (**II**), respectively. The structures of the half-sandwich 1-Cl-1-(TMEDA)-2,n-$(SiMe_3)_2$-2,n-$C_2B_4H_4$ ($n = 3$ (**III**), 4 (**IV**)) are given in Figures 3 and 4, respectively. Table 4 lists some important bond distances and bond angles. In both of the full-sandwich complexes the galliums are located between the two C_2B_3 pentagonal faces of the carborane ligands. Gallacarborane **I** is the more symmetric of the two complexes, with the gallium atom being a center of symmetry for the complex, while in the less symmetric **II** the dihedral angle between the two C_2B_3 faces is 4.68°. In addition, the C_2B_4 cages in **II** are slightly twisted with respect to one another such that the B(12)−B(16)−B(26)−B(22) dihedral angle is 171.97° (see Figure 2). While the two carborane cages in **II** are crystallographically unique, an inspection of the interatomic distances given in Table 4 reveals that the differences in equivalent bond distances in the two cages are almost within their combined experimental indeterminations.

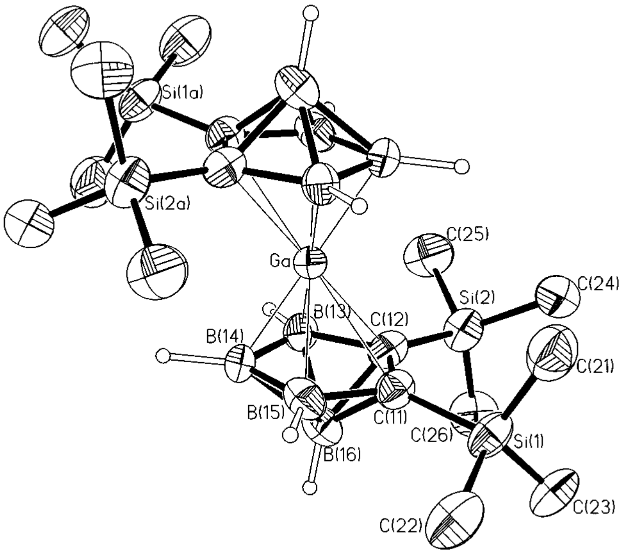
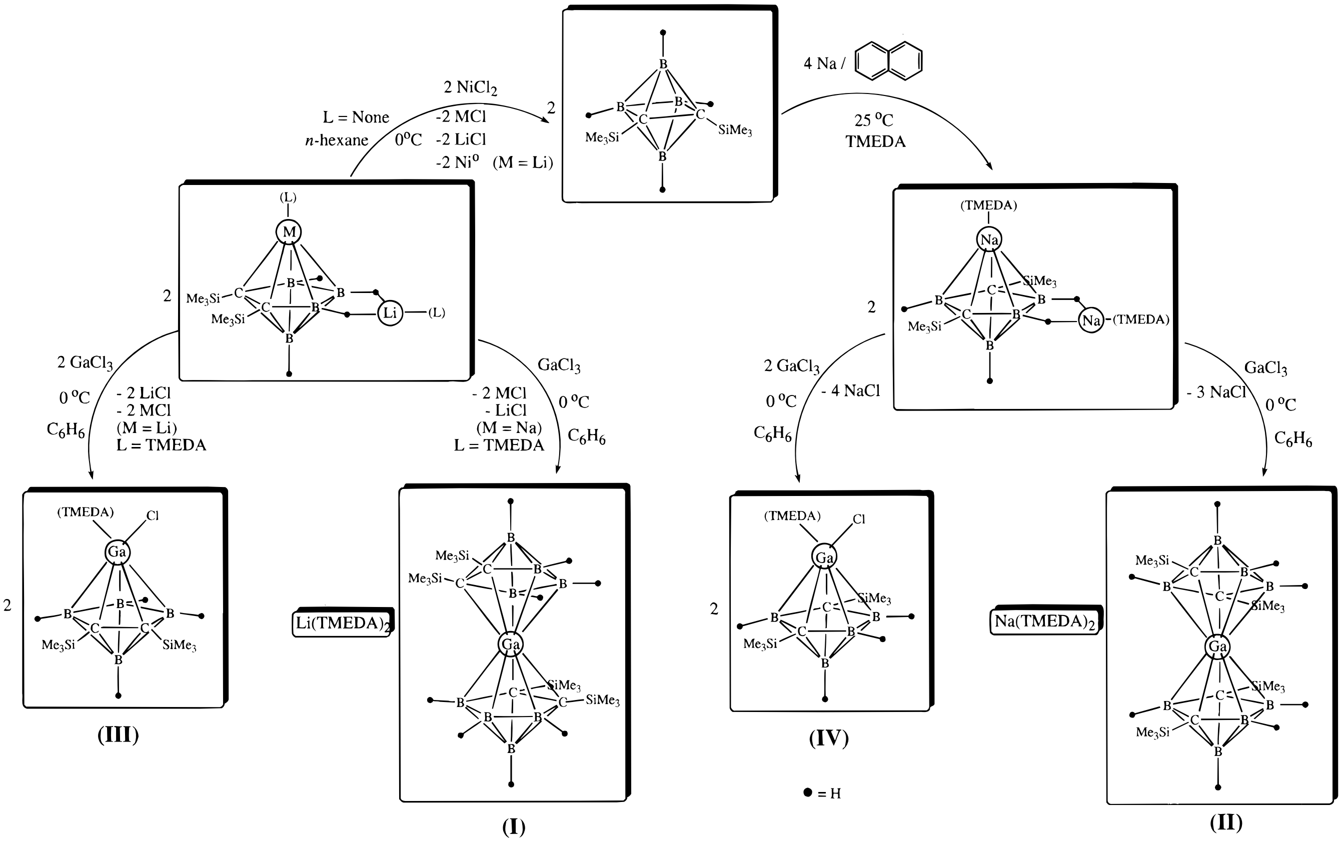


Figure 1. Perspective view of the carbons adjacent gallacarborane sandwich [Li$(TMEDA)_2$][2,2′,3,3′-$(SiMe_3)_4$-1,1′-*commo*-Ga(1,2,3-$GaC_2B_4H_4)_2$] (**I**), showing the atom-numbering scheme. The thermal ellipsoids are drawn at the 40% probability level. For clarity, the cationic Li$(TMEDA)_2$ unit and all H's except those of the carborane cage in the anionic unit are removed.

In both compounds the galliums are not symmetrically bound to the C_2B_3 facial atoms but are dislocated or slipped away from the centroidal positions above the faces. The bond distances listed in Table 4 show that in the carbons-adjacent complex **I** the slippage is toward the unique boron (B(14) in Figure 1), while in the carbons-apart complex **II**, the slippage is in the opposite direction, that is, away from the unique borons (B(12)

Scheme 1. Syntheses of Half- and Full-Sandwich Gallacarboranes of the C_2B_4 Cage Systems



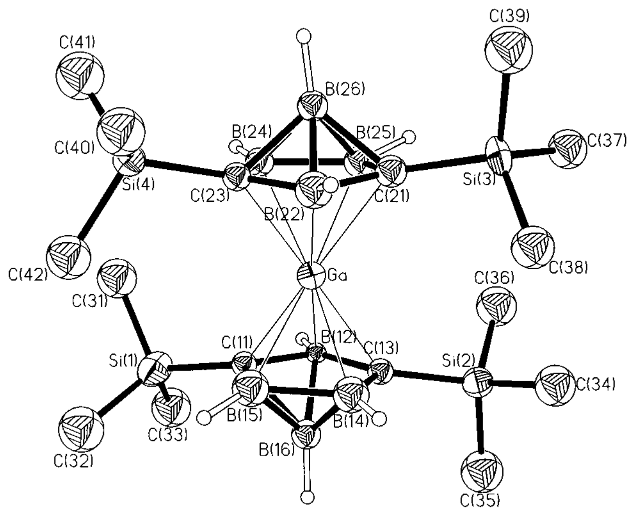


Figure 2. Perspective view of the carbons apart gallacarborane sandwich $[Na(TMEDA)_2][2,2',4,4'-(SiMe_3)_4-1,1'-$*commo*-$Ga(1,2,4-GaC_2B_4H_4)_2]$ (**II**), showing the atom-numbering scheme. The thermal ellipsoids are drawn at the 40% probability level. For clarity, the cationic Na(TMEDA)$_2$ unit and all H's except those of the carborane cage in the anionic unit are removed.

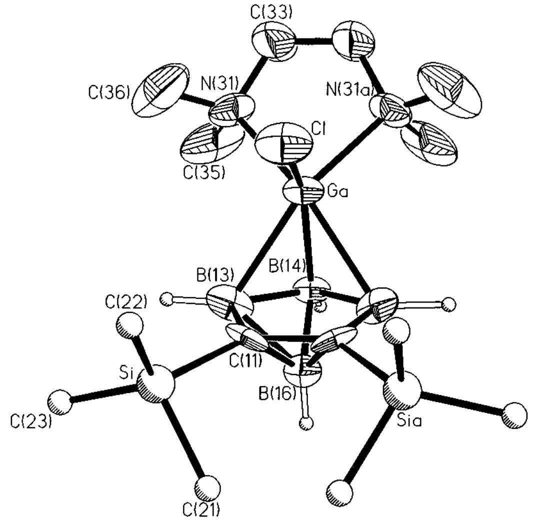


Figure 3. Perspective view of the carbons adjacent half-sandwich gallacarborane $1-Cl-1-(TMEDA)-2,3-(SiMe_3)_2-$*closo*-$1,2,3-GaC_2B_4H_4$ (**III**), showing the atom-numbering scheme. The thermal ellipsoids are drawn at the 40% probability level. For clarity, all H's except those of the carborane cage are removed.

and B(22) in Figure 2). In both compounds the extent of slippage is sufficient so as to produce a disparity between the Ga–C(11,12) and the Ga–B(14) distances of 0.34 Å in **I** and a 0.45 Å difference between the Ga–B(13,14) and the Ga–B(12) distances in **II** (see Table 4). A similar slip distortion was observed by Hawthorne and co-workers in the carbons-adjacent [*commo*-3,3′-$Ga(3,2,1-GaC_2B_9H_{11})_2]^-$,[2] where a disparity of 0.44 Å was found between the gallium and the C_2B_3 facial atoms, which are equivalent to C(11,12) and B(14) in Figure 1.[2]

The structures of the half-sandwich chlorogallacarboranes, given in Figures 3 and 4, show each complex to be a very distorted pentagonal bipyramid in which a (TMEDA)ClGa moiety occupies the apical position above the C_2B_3 pentagonal face of the carborane. However, in both compounds the galliums are severely slip-distorted. As was the case in the *commo* complexes, the gallium is slipped toward the unique boron (B(14) in Figure 3) in the carbons-adjacent complex **III** and in the opposite direction in **IV**. The extent of the slip distortion in **III** is such that the carborane is η^3-bonded to the metal (the relevant distances are Ga–B(14) = 2.073 Å, Ga–B(13) = 2.334 Å, and Ga–C(11) = 2.833 Å). Similar slippages were found in the compounds 1-L-1-*t*-$C_4H_9-2,3-(SiMe_3)_2-1,2,3-GaC_2B_4H_4$ (L = $2,2'-C_{10}H_8N_2$, $2,2'-C_8H_6N_4$),[5,7] which show the same general geometry as given in Figure 3 on the replacement of the Cl by a *tert*-butyl group and the TMEDA by the heterocyclic base. It turns out that the Ga–C_2B_4 distances in the complex where L = $2,2'-C_8H_6N_4$ are almost identical with those found for **III** listed in Table 4 (the equivalent distances in the bipyrimidine complex are Ga–B(14) = 2.077 Å, Ga–B(13) = 2.379 Å, and Ga–C(11) = 2.883 Å).[5] Such a similarity is found when the structure of **IV** is compared to that of the carbons-apart *tert*-butyl-substituted species $1-(2,2'-C_8H_6N_4)-1-$*t*-$C_4H_9-2,4-(SiMe_3)_2-1,2,4-GaC_2B_4H_4$;[7] the distances equivalent to those in **IV** for the bipyrimidine complex are Ga–B(12) = 3.018 Å, Ga–B(14,15) = 2.193 Å, and Ga–C(11,13) = 2.826 Å. In both **IV** and its *tert*-butyl analogue metal slippage is severe enough so that the carboranes are best described as being η^2-bonded to the galliums. However, the metal causes distortions in the carborane cage such that the unique boron, B(12) in Figure 4, is lifted above the C(11)–C(13)–B(14)–B(15) plane, indicating that there is some interaction between the gallium and the more remote facial atoms.[7,20] The structures of the bipyridine complexes $1-(2,2'-C_{10}H_8N_2)-1-$*t*-$C_4H_9-2,$*n*-$(SiMe_3)_2-1,2,$*n*-$C_2B_4H_4$ (*n* = 3, 4) show geometries similar to those of **III** and **IV** and the bipyrimidine complexes, with the exception that the former seem to be a bit more slip-distorted.[7]

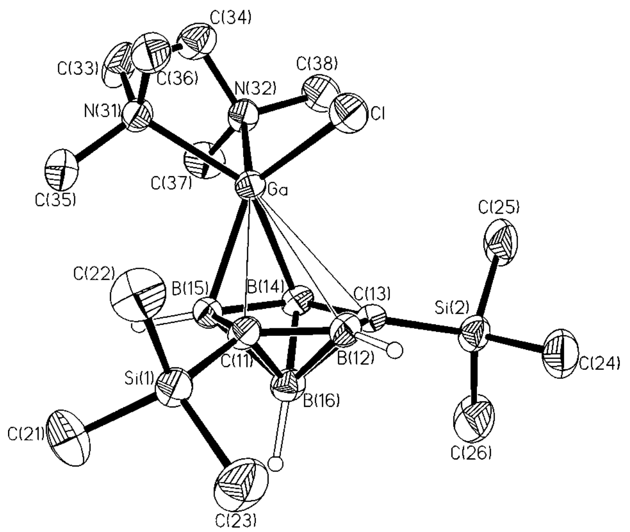


Figure 4. Perspective view of the carbons apart half-sandwich gallacarborane $1-Cl-1-(TMEDA)-2,4-(SiMe_3)_2-$*closo*-$1,2,4-GaC_2B_4H_4$ (**IV**), showing the atom-numbering scheme. The thermal ellipsoids are drawn at the 40% probability level. For clarity, all H's except those of the carborane cage are removed.

NMR and IR Spectra. The ^1H, ^{11}B and ^{13}C NMR spectra of the compounds **I**–**IV** are listed in Table 1.

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[20] For details, see ref 6.

All spectra show the expected resonances for the carborane cages and TMEDA molecules and are consistent with the formulations and structures of the compounds shown in Figures 1−4. The ^{11}B NMR spectra of all the gallacarboranes show the same general pattern exhibited by the C_2B_4 metallacarboranes, that is, an upfield resonance (δ −46 to −47 ppm) due to the apical boron, with the peaks for the less shielded C_2B_3 facial boron atoms being shifted downfield by some 40−70 ppm. In the carbons-adjacent complexes **I** and **III** the basal borons are the least shielded and a 2:1:1 peak area ratio pattern is found, while in the carbons-apart isomers (**II** and **IV**) the relative shielding of the basal and unique borons is reversed and a 1:2:1 peak area ratio pattern results. These same patterns are found in the other group 13−C_2B_4 metallacarboranes, as well as in the precursor group 1 compounds.[5,7,11,12] The changes in the chemical shifts of the cage borons on complexation of the ligand with different metal groups have been interpreted in terms of changing metal−carborane bonding interactions,[5,7] with the apical boron resonance being especially affected.[21] Thus, the most striking aspect of the data in Table 1 is the apparent insensitivity of the ^{11}B NMR spectra to the nature of the capping groups. In both the carbons-adjacent and carbons-apart isomers, the NMR spectra of the full- and half-sandwich gallacarboranes are almost identical. This could indicate that a dianionic carborane ligand would, fortuitously, perturb the electron density in another metal-bound C_2B_4 cage to about the same extent as does a TMEDA molecule and a chloride ion, so that any differences in the ^{11}B NMR spectra of the half- and full-sandwich species would be masked by experimental indetermination. Because of interactions with the $^3/_2$ spin of gallium,[22] the ^{11}B NMR spectra of the gallacarboranes are quite broad, and small chemical shift changes may not be detected. On the other hand, the spectral similarity could indicate that equilibria are set up such that the dominant forms in solution are not those shown in Figures 1−4. In an effort to gain some insight into the effects of ligand substitution on the ^{11}B NMR spectra of the gallacarboranes, ^{11}B NMR chemical shifts for the model compounds [*commo*-1,1′-Ga(1,2,*n*-$C_2B_4H_6)_2]^-$ ($n = 3$ (**V**), 4 (**VI**)) and 1,1′-$(NH_3)_2$-1-Cl-1,2,*n*-$GaC_2B_4H_6$ ($n = 3$ (**VII**), 4 (**VIII**)) were carried out using GIAO methods at the HF/6-311G** level. This level of theory was found to give good results for a number of neutral and anionic *closo*- and *nido*-carboranes.[23] The model compounds differ from **I**−**IV** in that hydrogen atoms replace $SiMe_3$ groups on the cage carbons and two NH_3 molecules are substituted for the TMEDA molecules. It has been shown that the former simplification does not materially effect the GIAO calculated ^{11}B chemical shifts;[23] the replacement of TMEDA by two NH_3's, while a more severe simplification, does at least provide for coordination of the gallium with two sp^3-hybridized nitrogens. The calculated ^{11}B NMR chemical shifts of these model compounds are listed in Table 5. A comparison of these results with those found for compounds **I**−**IV**, given in Table 1, shows that the chemical shifts calculated for the model compounds agree well with the experimental values of the analogous trimethylsilyl-substituted gallacarboranes. The calculated chemical shifts of the model compounds show very little change in chemical shifts on replacing the ammonia/Cl groups with a carborane ligand. Therefore, the nearly equivalent ^{11}B NMR spectra found experimentally for the half- and full-sandwich gallacarboranes should not raise concerns about possible decomposition in solution.

The IR absorptions of compounds **I**−**IV** are given in Table 2. Other than providing confirmation for the absences of bridging hydrogens in the compounds, the spectra contain no unusual features and are listed for the purposes of qualitative analysis.

Conclusions. The direct reaction of the dianions of the carbons-adjacent and carbons-apart carboranes in the C_2B_4 cage system with $GaCl_3$ in a 1:1 molar ratio was found to produce the half-sandwich chlorogallacarboranes 1-Cl-2,*n*-$(SiMe_3)_2$-1,2,*n*-$GaC_2B_4H_4$ ($n = 3, 4$), which could be isolated as their TMEDA adducts. The gallium-bound chloride was found to be reactive and could be replaced by other groups, as demonstrated by the formation of the corresponding full-sandwich gallacarboranes [2,2′,*n*,*n*′-$(SiMe_3)_4$-1,1′-*commo*-Ga(1,2,*n*-$GaC_2B_4H_4)_2]^-$. The reactivity of the chlorogallacarboranes toward other functional groups is currently under investigation and will be the subject of a future report.

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Supporting Information Available: Atomic coordinates (Table S-1), all bond lengths and bond angles (Table S-2), anisotropic displacement parameters (Table S-3), and H-atom coordinates and isotropic displacement coefficients (Table S-4) for **I**−**IV** (24 pages). Ordering information is given on any current masthead page.

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[21] (a) Hermánek, S.; Hnyk, D.; Havlas, Z. *J. Chem. Soc., Chem. Commun.* **1989**, 1859. (b) Bühl, M.; Schleyer, P. v. R.; Havlas, Z.; Hnyk, D.; Hermánek, S. *Inorg. Chem.* **1991**, *30*, 3107. (c) Fehlner, T. P.; Czech, P. T.; Fenske, R. F. *Inorg. Chem.* **1990**, *29*, 3103.

[22] Brevard, C.; Granger, P. *Handbook of High Resolution Multinuclear NMR*; Wiley: New York, 1981.

[23] Ezhova, M. B.; Zhang, H.; Maguire, J. A.; Hosmane, N. S. *J. Organomet. Chem.*, in press.