Chemistry of *C*-Trimethylsilyl-Substituted Heterocarboranes. 27. Synthetic, Spectroscopic, Structural, and Reactivity Studies on d^0 Hafnacarboranes of 2,3-C_2B_4-Carborane Ligands

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The sodium/lithium compounds *closo-exo*-Li(THF)-1-Na(THF)-2-($SiMe_3$)-3-(R)-2,3-$C_2B_4H_4$ (R = $SiMe_3$, Me, H), were found to react with several different hafnium reagents to produce half- and full-sandwich and mixed-ligand chlorohafnacarboranes in good yields. The reaction of the sodium/lithium compounds with $HfCl_4$ in 2:1 molar ratios produced the full-sandwich complexes 1-Cl-1-(THF)-2,2′-($SiMe_3$)$_2$-3,3′-(R)$_2$-4′,5,5′,6-Li(THF)$_n$-[1,1′-*commo*-Hf(2,3-$C_2B_4H_4$)$_2$] (R = $SiMe_3$, $n = 2$ (**I**); R = Me, $n = 1$ (**II**); R = H, $n = 1$ (**III**)) in yields of 77%, 65%, and 71%, respectively. When R = $SiMe_3$, a 1:1 molar ratio of carborane to $HfCl_4$ gave the half-sandwich species [Li(THF)$_2$][1,1,1-(Cl)$_3$-*closo*-1-Hf-2,3-($SiMe_3$)$_2$-2,3-$C_2B_4H_4$] (**V**) in 77% yield. On the other hand, both 2:1 and 1:1 reaction ratios of carborane (R = Me) to Cp*$HfCl_3$ gave only the mixed-ligand sandwich compound 1,1′-(Cl)$_2$-2-($SiMe_3$)-3-(Me)-4,5-Li(THF)-1,1′-*commo*-Hf[(η^5-C_5Me_5)(η^5-2,3-$C_2B_4H_4$)] (**IV**) in 82% yield. All compounds were characterized by infrared spectroscopy, ^1H, ^{13}C, and ^{11}B NMR spectroscopy, and chemical analysis. Compounds **I**−**III** were characterized further by single-crystal X-ray diffraction. The structures show the hafnacarboranes to have bent-sandwich structures in which a Hf atom, in a formal +4 state, was sandwiched between two carborane ligands and was also bonded to a Cl atom and a THF molecule to give a distorted-tetrahedral arrangement about the metal.

Introduction

The chemistry of the metal sandwich compounds of the early transition metals has been the subject of numerous studies, and a number of reviews and monographs on the subject are available.[1] The most studied are the metal d^0 complexes with cyclopentadienides (Cp) or substituted Cp ligands. The impetus for much of this research is the fact that such complexes are known to be active olefin polymerization catalysts.[2] Another class of compounds whose ligation chemistry has been found to parallel that of Cp are the carborane dianions *nido*-[7,8-$R_2C_2B_9H_9$]$^{2-}$ and *nido*-[2,3-$R_2C_2B_4H_4$]$^{2-}$ (R = cage carbon substituent, H).[3] Like Cp, they are donor ligands in which six electrons are delocalized in π-type orbitals around a five-membered ring. In the case of the carboranes the five metal-binding ring atoms are two carbons and three borons; the presence of these borons allows for stronger, more covalent metal−ligand binding.[3a] Another difference is that of charge; the carboranes are dianions, while the Cp ligands are monovalent. The higher negative ligand charges would be expected to favor higher metal oxidation states in metallacarboranes compared to the corresponding metallocenes; this has been found experimentally.[4,5] Both of these factors should make the early-transition-metal metallacarboranes attractive candidates for catalysts. However, the results to date have been mixed. Jordan reported that the mixed-sandwich complexes (Cp*)($C_2B_9H_{11}$)M(Me) (M = Zr, Hf, Cp* = C_5Me_5) underwent ligand addition−elimination reactions with some unsaturated compounds and were shown to be moderately active ethylene polymerization catalysts.[6] The corresponding titanium complexes (M = Ti) were found to catalyze the slow dimerization of ethylene to 1-butene but did not

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support further polymerization.[7] Grimes and co-workers reported the syntheses and properties of several group 5 metallacarboranes and found that the d^0 tantalum(V) carborane $(Et_2C_2B_4H_4)(Cp)TaMe_2$ underwent photochemical insertion with alkynes and other unsaturated compounds.[8,9] On the other hand, Bercaw found that the group 3 mixed-ligand complex $[(Cp^*)(C_2B_9H_{11})ScCH(SiMe_3)_2Li]Li(THF)_3$ reacted only slowly with H_2 to give $[(Cp^*)(C_2B_9H_{11})ScH]_2[Li(THF)_n]_2$, which proved to be very unreactive.[10] Chemical inertness to metal substitution was also found in the smaller cage zirconacarborane $[Mg(TMEDA)]_2[1\text{-}Cl\text{-}(THF)\text{-}1,1'\text{-}Zr\{2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4\}_2]$.[11] It was argued that steric crowding around the zirconium by the nearby $SiMe_3$ groups, coupled with the propensity of the compounds to dimerize, could prevent reaction at the metal center. Similar steric effects were also thought to be important in determining the metal coordination in a number of $SiMe_3$-substituted titanacarboranes.[12] Other than our preliminary report on the synthesis and structure of the full-sandwich complex 1-Cl-1(THF)-2,2′-$(SiMe_3)_2$-3,3′-$(Me)_2$-4,4′,5,5′-Li(THF)-1,1′-*commo*-Hf$(2,3\text{-}C_2B_4H_4)_2$,[13] very little has been reported on the small-cage hafnacarboranes. Preparatory to a systematic study of the reactivity of the structures and chemistry of these potentially useful d^0 systems, several full-sandwich, half-sandwich, and mixed-ligand sandwich hafnacarboranes were prepared and characterized. We report herein the results of that investigation.

Experimental Section

Materials. 2,3-Bis(trimethylsilyl)-2,3-dicarba-*nido*-hexaborane(8), 2-(trimethylsilyl)-3-methyl-2,3-dicarba-*nido*-hexaborane(8), and 2-(trimethylsilyl)-2,3-dicarba-*nido*-hexaborane(8) were prepared by the methods of Hosmane *et al.*[14,15] Samples of anhydrous $HfCl_4$ and Cp^*HfCl_3 were purchased from Strem Chemicals, Inc., and used as received. Benzene, tetrahydrofuran (THF), and *n*-hexane were dried over $LiAlH_4$ and doubly distilled before use. All other solvents were dried over 4−8 mesh molecular sieves (Aldrich) and either saturated with dry argon or degassed. *tert*-Butyllithium, *t*-BuLi (1.7 M solution in pentane), oil-free NaH, and anhydrous NaOMe were purchased from Aldrich Chemical Co. and used without further purification. Solutions of the Na/Li compounds of the *nido*-carborane dianions *closo-exo*-Li(THF)-1-Na(THF)-2-$(SiMe_3)$-3-(R)-2,3-$C_2B_4H_4$ (R = $SiMe_3$, Me, or H) in THF were prepared by the method described elsewhere.[14,15]

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 Perkin-Elmer Model 283 infrared spectrophotometer and a Fourier transform Nicolet Magna-550 IR spectrometer equipped with OMNIC software. Elemental analyses were obtained from Oneida Research Services, Inc., Whitesboro, NY, and E + R Microanalytical Laboratory, Inc., Corona, NY.

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

Synthesis of 1-Cl-1-(THF)-2,2′-$(SiMe_3)_2$-3,3′-$(R)_2$-4′,5,5′,6-Li$(THF)_n$-[1,1′-*commo*-Hf$(2,3\text{-}C_2B_4H_4)_2$] (R = $SiMe_3$, $n = 2$ (I); R = Me, $n = 1$ (II); R = H, $n = 1$ (III)). A THF solution (10−15 mL) of *closo-exo*-Li(THF)-1-Na(THF)-2-$(SiMe_3)$-3-(R)-2,3-$C_2B_4H_4$ (1.68 g, 4.3 mmol, R = $SiMe_3$; 2.40 g, 7.2 mmol, R = Me; 1.69 g, 5.3 mmol, R = H) was reacted with anhydrous $HfCl_4$ (0.73 g, 2.28 mmol; 1.15 g, 3.60 mmol; 0.85 g, 2.64 mmol, respectively) in dry benzene, with constant stirring at 0 °C for 4 h, and then at room temperature for an additional 24 h. During this time the solution turned a yellowish brown. Anhydrous diethyl ether (Et_2O) was then added, and the mixture was stirred for a period of 2 h, filtered through a frit *in vacuo* and the residue washed repeatedly with a solvent mixture of hexane (90%) and THF (10%), to collect a clear yellow-orange filtrate. After slow removal of the solvents from the filtrate *in vacuo*, a yellow moisture-sensitive crystalline solid was isolated and identified as 1-Cl-1-(THF)-2,2′-$(SiMe_3)_2$-3,3′-$(R)_2$-4′,5,5′,6-Li$(THF)_n$-[1,1′-*commo*-Hf$(2,3\text{-}C_2B_4H_4)_2$] (R = $SiMe_3$, $n = 2$ (**I**), 1.41 g, 1.76 mmol, 77.2% yield; R = Me, $n = 1$ (**II**), 1.60 g, 2.23 mmol, 65% yield; R = H, $n = 1$ (**III**), 1.23 g, 1.87 mmol, 71% yield). The sandwich hafnacarboranes are reasonably soluble in polar and nonpolar organic solvents and melted at 181 °C (**I**), 167 °C (**II**), and 153 °C (**III**), respectively. Anal. Calcd for $C_{28}H_{68}B_8O_3ClSi_4LiHf$ (**I**): C, 38.54; H, 7.86; Cl, 4.06; Li, 0.79. Found: C, 38.59; H, 7.79; Cl, 4.18; Li, 0.83. Calcd for $C_{20}H_{48}B_8O_2ClSi_2LiHf$ (**II**): C, 35.11; H, 7.07; Cl, 5.18; Li, 1.01. Found: C, 35.00; H, 7.18; Cl, 5.27; Li, 1.04. Calcd for $C_{18}H_{44}B_8O_2ClSi_2LiHf$ (**III**): C, 32.95; H, 6.76; Cl, 5.40; Li, 1.06. Found: C, 33.11; H, 6.88; Cl, 5.47; Li, 1.11. The NMR spectral data of **I**−**III** are listed in Table 1. The IR spectral data of the compounds are contained in the Supporting Information.

Synthesis of 1,1′-$(Cl)_2$-2-$(SiMe_3)$-3-(Me)-4,5-Li(THF)-1,1′-*commo*-Hf[$(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}2,3\text{-}C_2B_4H_4)$] (IV). A 2.38 mmol sample of *closo-exo*-Li(THF)-1-Na(THF)-2-$(SiMe_3)$-3-(Me)-2,3-$C_2B_4H_4$, synthesized from the precursor *nido*-2-$(SiMe_3)$-3-(Me)-2,3-$C_2B_4H_6$, was dissolved in 20 mL of anhydrous benzene and the solution then slowly added to Cp^*HfCl_3 (1 g, 2.38 mmol) at −78 °C *in vacuo*. The reaction mixture was warmed to room temperature over a period of 10−12 h and then stirred at this temperature for an additional 16 h to produce a reddish brown heterogeneous reaction mixture. This mixture was filtered, and the solvent was then removed from the filtrate *in vacuo* to obtain a pale yellow-orange solid (**IV**), identified as the mixed-ligand hafnacarborane sandwich 1,1′-$(Cl)_2$-2-$(SiMe_3)$-3-(Me)-4,5-Li(THF)-1,1′-*commo*-Hf[$(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}2,3\text{-}C_2B_4H_4)$] (1.21 g, 1.94 mmol, mp 130 °C dec) in 82% yield. Anal. Calcd for $C_{20}H_{39}B_4OLiSiCl_2Hf$: C, 38.55; H, 6.31; Cl, 11.38; Hf, 28.64. Found: C, 38.42; H, 6.52; Cl, 11.24; Hf, 28.93. The NMR spectral data of **IV** are listed in Table 1. The IR spectral data of the compound are contained in the Supporting Information.

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Table 1. FT NMR Spectral Data for Hafnacarboranes[a]

compd	δ, splitting, assign [$^1J(^{11}B-^1H)$ or $^1J(^{13}C-^1H)$, Hz]	rel area
	200.13 MHz ^1H NMR Data	
I	4.18, br, ill-defined peak, basal H [$J(^{11}B-^1H)$ unresolved]; 3.61, s, THF; 2.1, br, ill-defined peak, apical H [$J(^{11}B-^1H)$ unresolved]; 1.22, s, THF; 0.64, s, Me_3Si; 0.51, s, Me_3Si	3:4:1:4:9:9
II	3.98, s, THF; 3.62, s, THF; 2.75, s, Me; 2.70, s, Me; 1.34, s, THF; 1.21, s, THF; 0.53, s, Me_3Si; 0.48, s, Me_3Si	4:4:3:3:4:4:9:9
III	6.20, s, H; 4.04, br, ill-defined peak, basal H [$J(^{11}B-^1H)$ unresolved]; 3.80, s, THF; 3.64, s, THF; 1.8, br, ill-defined peak, apical H [$J(^{11}B-^1H)$ unresolved]; 1.21, s, THF; 0.86, s, THF; 0.43, s, Me_3Si; 0.38, s, Me_3Si	2:6:4:4:2:4:4:9:9
IV	3.53, s, THF; 2.83, s, Me; 2.26, s, Cp*; 1.57, s, THF; 0.59, s, Me_3Si	4:3:15:4:9
V	3.53, s, THF; 1.59, s, THF; 0.50, s, Me_3Si	4:4:9
	64.21 MHz ^{11}B NMR Data[b,c]	
I	33.69, br, basal BH [$^1J(B-H)$ unresolved]; 24.78, br, basal BH [$^1J(B-H)$ unresolved]; −18.53, br, apical BH [$^1J(B-H)$ unresolved]	1:2:1
II	30.03, br, basal BH [$^1J(B-H)$ unresolved]; 21.90, br, basal BH [$^1J(B-H)$ unresolved]; −16.62, d(br), apical BH [$^1J(B-H) = 127.7$ Hz]	1:2:1
III	27.87, br, basal BH [$^1J(B-H)$ unresolved]; 20.71, br, basal BH [$^1J(B-H)$ unresolved]; −19.75, d(br), apical BH [$^1J(B-H) = 139$ Hz]	1:2:1
IV	28.00, vbr, basal BH [$^1J(B-H)$ unresolved]; 26.09, br, basal BH [$^1J(B-H)$ unresolved]; −19.78, br, apical BH [$^1J(B-H)$ unresolved]	1:2:1
V	30.00, vbr, basal BH [$^1J(B-H)$ unresolved]; 20.13, br, basal BH [$^1J(B-H)$ unresolved]; −19.05, br, apical BH [$^1J(B-H)$ unresolved]	1:2:1
	50.32 MHz ^{13}C NMR Data[a,d]	
I	121.3, s(br), cage C(SiCB); 77.05, t, Hf−THF (152.1); 68.65, t, Li−THF (143.9); 25.42, t, THF (126.4); 3.68, q, Me_3Si (122); 3.28, q, Me_3Si (119.5)	2:1:1:2:3:3
II	122.57, s(br), cage C(SiCB); 121.06, s(br), cage C(SiCB); 118.06, s(br), cage C(CCB); 115.96, s(br), cage C(CCB); 76.55, t, Hf−THF (152.8); 69.03, t, Li−THF (149.1); 25.27, t, THF (128.9); 22.52, q, Me (127.2); 2.20, q, Me_3Si (119.3)	1:1:1:1:2:2:4:2:6
III	110.27, d(br), cage C(SiCB) (113.5); 108.1, s(br), cage C(HCB); 76.87, t, Hf−THF (155.1); 68.9, t, Li−THF (141.1); 25.36, t, THF (127); 0.20, q, Me_3Si(120.6)	1:1:1:1:2:3
IV	119.82, s (br), cage C(SiCB); 119.09, s, ring C (Cp*); 111.61, s (br), cage C (CCB); 67.74, t, THF(144); 25.43, t, THF(133); 22.28, q, CH_3; 12.71, q, CH_3 of Cp* (127); 2.47, q, $SiMe_3$ (118)	1:5:1:2:2:1:5:3
V	121.60, s (br), cage C (SiCB); 67.68, m, THF; 25.34, m, THF; 4.16, q, Me_3Si (120)	2:4:4:6

[a] C_6D_6 was used as solvent and as an internal standard of δ 7.15 ppm (in the ^1H NMR spectra) and δ 128.0 ppm (in the ^{13}C NMR spectra) for compounds, with a positive sign indicating a downfield shift. Legend: s = singlet, d = doublet, t = triplet, q = quartet, v = very, br = broad. [b] C_4D_8O was used as solvent. [c] Shifts relative to external $BF_3{\cdot}OEt_2$. [d] Since relaxations of the quaternary and cage carbons are slower than that of a protonated C, the relative areas of these carbons could not be measured accurately. Unambiguous assignments of the apical BH's in the ^1H NMR spectra of **II** could not be made.

Synthesis of the Half-Sandwich Hafnacarborane [Li(THF)$_2$][1,1,1-(Cl)$_3$-*closo*-1-Hf-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$] (V). In a manner similar to that described above, a freshly prepared sample of *closo*-*exo*-Li(THF)-1-Na(THF)-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$ (1.175 g, 3.00 mmol) was reacted with anhydrous $HfCl_4$ (0.96 g, 3.00 mmol) in a 1:1 stoichiometry in dry benzene, with constant stirring at 0 °C. The resulting mixture was stirred overnight at room temperature to give a brown turbid solution. The product mixture was then filtered through a frit *in vacuo*, and the residue was washed repeatedly with dry benzene. The filtrate and washings were combined, and the solvent was removed *in vacuo* to produce a dark residue which was subsequently extracted with hexane. The hexane extract was concentrated, under vacuum, to isolate a pale yellow microcrystalline solid that was later identified as the half-sandwich hafnacarborane [Li(THF)$_2$][1,1,1-(Cl)$_3$-*closo*-1-Hf-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$] (**V**; 1.51 g, 2.31 mmol; mp 110−112 °C) in 77% yield. Anal. Calcd for $C_{16}H_{38}O_2B_4Si_2Cl_3$ LiHf (**V**): C, 29.40; H, 5.86; Cl, 16.27; Li, 1.06. Found: C, 29.49; H, 5.97; Cl, 16.11; Li, 1.01. The NMR spectral data of **V** are listed in Table 1. The IR spectral data of the compound are contained in the Supporting Information.

Preliminary Reactivity Studies of the Hafnacarborane Sandwich Complex I toward Alkyl and Alkoxylating Reagents. In an experiment, a 1.59 mmol (1.39 g) sample of **I** in a 5:1 mixture of Et_2O/THF (30 mL) was reacted with Me_3SiCH_2MgCl (1 M, 3.1 mL) in Et_2O with constant stirring *in vacuo* at −78 °C for 30 min and then at room temperature for 3 days. During this time the color of the resulting solution remained unchanged, as did its ^1H and ^{11}B NMR spectra. When the temperature was increased to 110 °C, the mixture turned dark red and its ^1H and ^{11}B NMR spectra showed a multiplicity of unidentifiable peaks, indicating decomposition of the reactants and/or products occurred during the reaction. Since the mixture could not be further resolved, it was discarded.

In another experiment, a 0.44 mmol (0.384 g) sample of **I** was dissolved in 25 mL of THF and the resulting solution was poured *in vacuo* onto 0.44 mmol (0.024 g) of sodium methoxide, NaOMe, at −196 °C. The mixture was slowly warmed to 0 °C and stirred constantly for 48 h, during which time it turned into a pale yellow suspension. At this point, the suspension was filtered *in vacuo* and the filtrate was concentrated to collect a yellow oily liquid whose ^1H and ^{11}B NMR spectra showed the absence of C_2B_4-carboranes, or any other identifiable polyhedral boron cage, indicating that extensive cage degradation had occurred during the reaction. The solution was discarded without further workup.

Crystal Structure Analyses of 1-Cl-1-(THF)-2,2′-(SiMe$_3$)$_2$-3,3′-(R)$_2$-4′,5,5′,6-Li(THF)$_n$-[1,1′-*commo*-Hf(η^5-C$_2$B$_4$H$_4$)$_2$] (R = SiMe$_3$, *n* = 2 (I); R = Me, *n* = 1 (II); R = H, *n* = 1 (III)). Crystals of the sandwich hafnacarborane complexes **I**−**III** were grown from their solutions of *n*-hexane (90%) and THF (10%) in glass tubes *in vacuo*. The selected crystals were coated with mineral oil and mounted sequentially on an automatic Siemens R3m/V diffractometer under a low-temperature nitrogen stream. The pertinent crystallographic data are summarized in Table 2. The final unit cell parameters were obtained by least-squares fits of 24 accurately centered reflections measured in the range 15° < 2θ < 30°; the intensity data were collected in the ranges 3.50° ≤ 2θ ≤ 44.0°, 3.5° ≤ 2θ ≤ 42.0°, and 3.5° ≤ 2θ ≤ 56.0°at 228, 230, and 230 K, for **I**, **II**, and **III**, respectively. Three standard reflections, monitored after every 150 reflections for compounds **II** and **III**, did not show any significant change in intensity during the data collection. However, a similar monitoring of compound **I** revealed significant decay;

Table 2. Crystallographic Data[a] for Hafnacarboranes I−III

	I	II	III
formula	$C_{28}H_{68}O_3B_8Si_4LiClHf$	$C_{20}H_{48}O_2B_8Si_2LiClHf$	$C_{18}H_{44}O_2B_8Si_2LiClHf$
fw	872.5	684.1	656.1
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a, Å	11.356(2)	16.821(5)	12.127(4)
b, Å	12.095(2)	16.277(5)	10.003(2)
c, Å	17.574(3)	12.131(5)	26.073(7)
α, deg	86.20(1)	90.00	90.00
β, deg	89.58(1)	90.41(3)	89.18(2)
γ, deg	65.26(1)	90.00	90.00
V, Å^3	2186.9(7)	3321(2)	3162.5(15)
Z	2	4	4
D_{calcd}, g cm^{-3}	1.325	1.368	1.378
abs coeff, mm^{-1}	2.582	3.474	3.442
crystal dmns, mm	0.35 × 0.30 × 0.10	0.35 × 0.15 × 0.30	0.15 × 0.30 × 0.05
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
scan sp in ω: min, max	3.50, 35.00	5.00, 25.00	6.00, 30.00
2θ range, deg	3.5−44.0	3.5−42.0	3.5−56.0
T, K	228	230	230
decay, %	59.4	0	0
no. of data collected	5672	3471	8086
no. of obsd rflns ($F > 6.0\sigma(F)$)	4566	2482	2930
no. of params refined	341	298	238
GOF	1.96	2.15	1.23
$\Delta\rho_{max,min}$, e/Å^3	1.51, −1.49	0.99, −1.67	3.42, −0.48
R[b]	0.0541	0.0490	0.0494
R_w[c]	0.0796	0.0650	0.0517

[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] $w = 1/[\sigma^2(F_o) + 0.0005(F_o)^2]$.

the intensity data for **I** were corrected for this decay. The data were corrected for Lorentz and polarization effects, and semiempirical absorption corrections (based on ψ scans) were applied. The structures were solved by heavy-atom methods and subsequent difference Fourier syntheses using the SHELXTL-Plus package of programs.[16] The scattering factors, with anomalous dispersion corrections for the heavy atoms, were taken from ref 17. The carbon atoms of one THF molecule (C(72)−C(75)) in compound **I** were statistically disordered, having an occupancy factor of 53.8% for the major sites (C(72) through C(75)) and 46.2% for the minor ones (C(72′) through C(75′)). The disordered THF molecule was elastically constrained during the final stages of refinement. While the difference Fourier maps of **I** did not reveal any meaningful peaks for the carborane-cage H atoms, the cage H atoms of **II** and **III** were recognized from the respective DF maps. Methyl and methylene H atoms, except for the disordered THF of compound **I**, were calculated at idealized positions with fixed isotropic temperature factors ($U = 0.08$ Å^2) and on the "ride-mode" during refinement. The final cycles of refinements of **I**, **II**, and **III** converged at $R = 0.0541$, 0.0490, and 0.0494, $R_w = 0.0796$, 0.0650, and 0.0517, and GOF = 1.96, 2.15, and 1.23, respectively. Selected bond distances and bond angles are listed in Table 3.

Results and Discussion

Syntheses. The hafnacarboranes **I**−**V** were synthesized from the reaction of the sodium/lithium compounds *closo-exo*-Li(THF)-1-Na(THF)-2-($SiMe_3$)-3-(R)-2,3-$C_2B_4H_4$ (R = $SiMe_3$, Me, H) with the appropriate hafnium reagent, as outlined in Scheme 1. The products of the reactions with $HfCl_4$ were dictated by the beginning stoichiometry used in the synthesis. When a 2:1 molar ratio of carborane to hafnium chloride is used, the full-sandwich chlorohafnacarboranes 1-Cl-1-(THF)-2,2′-($SiMe_3$)$_2$-3,3′-(R)$_2$-4′,5,5′,6-Li(THF)$_n$-[1,1′-*commo*-Hf-(2,3-$C_2B_4H_4$)$_2$] (R = $SiMe_3$ (**I**), Me (**II**), H (**III**)) were produced in yields of 77, 65, and 71%, respectively. On the other hand, a 1:1 molar ratio of carborane to $HfCl_4$ gave the trichlorohafnium half-sandwich metallacarborane [Li(THF)$_2$][1,1,1-(Cl)$_3$-*closo*-1-Hf-2,3-($SiMe_3$)$_2$-2,3-$C_2B_4H_4$] (**V**) in 77% yield. Both 2:1 and 1:1 molar ratios of carborane to Cp*$HfCl_3$ produced exclusively the mixed sandwich complex 1,1′-(Cl)$_2$-2-($SiMe_3$)-3-(Me)-4,5-Li(THF)-1,1′-*commo*-Hf[(η^5-C_5Me_5)(η^5-2,3-$C_2B_4H_4$)] (**IV**) in 82% yield. The similarities in yields could argue for a common driving force in the reactions, with the formation of the NaCl and LiCl coproducts being the likely candidates. However, the stability (or inertness) of the resulting hafnacarboranes must also be considered. The formulas of all these compounds show that they all contain the elements of LiCl, with the Cl's coordinated to the Hf metals and the Li's being present as exopolyhedrally bound Li(THF)$_n^+$ cations; however, they show little inclination to eliminate LiCl. It is an open question as to whether the three chlorides in the half-sandwich complex **V** are equally coordinated to the hafnium to give a trichlorohafnium capping group, similar to those found in the MCl_3Cp* (M = Zr, Hf) complexes,[18] or whether one Cl is more loosely bound to give an aggregate of a dichlorohafnacarborane and a LiCl. Since the X-ray-quality crystals of **V** could not be obtained and spectroscopic analysis could not resolve this question, there is no way at present to ascertain the exact nature of the capping group; the formulation of **V** as [Li(THF)$_2$][1,1,1-(Cl)$_3$-*closo*-1-Hf-2,3-($SiMe_3$)$_2$-2,3-$C_2B_4H_4$] must be considered as tentative. Preliminary evidence indicates that **I** does not undergo facile ligand substitution, in that there was no evidence of a room-temperature reaction with the Grignard reagent Me$_3$-

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

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

(18) Blenkers, J.; Meijer, H. J. de L.; Teuber, J. H. *J. Organomet. Chem.* **1981**, *218*, 383.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for Hafnacarboranes I−III

Bond Lengths (Å)							
Compound **I**							
Hf−Cnt(1)	2.142	Hf−C(21)	2.550(13)	C(11)−B(15)	1.508(17)	B(14)−B(16)	1.705(23)
Hf−Cnt(2)	2.122	Hf−C(22)	2.526(13)	C(11)−B(16)	1.720(16)	B(14)−Li	2.635(26)
Hf−Cl	2.447(2)	Hf−B(23)	2.541(14)	C(12)−B(13)	1.541(16)	B(15)−B(16)	1.804(21)
Hf−C(11)	2.484(14)	Hf−B(24)	2.493(14)	C(12)−B(16)	1.699(17)	B(23)−Li	2.481(21)
Hf−C(12)	2.539(13)	Hf−B(25)	2.417(21)	B(13)−B(14)	1.650(20)	B(24)−Li	2.437(24)
Hf−B(13)	2.537(16)	Hf−O(51)	2.253(8)	B(13)−B(16)	1.709(22)	O(61)−Li	1.887(21)
Hf−B(14)	2.531(14)	C(11)−C(12)	1.455(15)	B(14)−B(15)	1.649(17)	Li−O(71)	1.936(22)
Hf−B(15)	2.508(15)						
Compound **II**							
Hf−Cnt(1)	2.146	Hf−C(11)	2.552(13)	C(l)−B(6)	1.741(24)	B(4)−B(6)	1.702(26)
Hf−Cnt(2)	2.161	Hf−C(12)	2.534(13)	C(2)−B(3)	1.550(24)	B(5)−B(6)	1.745(24)
Hf−Cl	2.437(3)	Hf−B(13)	2.560(17)	C(2)−B(6)	1.720(23)	Li−B(3)	2.376(37)
Hf−C(1)	2.503(14)	Hf−B(14)	2.555(18)	C(2)−C(7)	1.555(20)	Li−B(4)	2.337(37)
Hf−C(2)	2.510(14)	Hf−B(15)	2.540(16)	B(3)−B(4)	1.630(24)	Li−B(14)	2.323(34)
Hf−B(3)	2.526(16)	Hf−O(21)	2.199(8)	B(3)−B(6)	1.751(28)	Li−B(15)	2.363(34)
Hf−B(4)	2.522(15)	C(l)−C(2)	1.471(19)	B(4)−B(5)	1.603(25)	Li−O(26)	1.817(32)
Hf−B(5)	2.547(16)	C(l)−B(5)	1.527(19)				
Compound **III**							
Hf−Cnt(l)	2.141	Hf−O(21)	2.206(7)	C(2)−B(6)	1.723(22)	Hf−C(11)	2.492(12)
Hf−Cnt(2)	2.131	Hf−Li	3.415(27)	B(3)−B(6)	1.720(26)	B(5)−B(6)	1.758(25)
Hf−Cl	2.453(3)	Hf−C(1)	2.471(12)	B(4)−B(6)	1.712(24)	B(5)−Li	2.307(28)
Hf−C(12)	2.472(14)	Hf−C(2)	2.433(13)	B(4)−Li	2.354(32)	B(13)−Li	2.429(34)
Hf−B(13)	2.564(15)	Hf−B(3)	2.557(18)	Hf−B(4)	2.598(17)	B(14)−Li	2.294(34)
Hf−B(14)	2.542(14)	C(l)−C(2)	1.477(19)	Hf−B(5)	2.573(16)	Li−O(26)	1.866(29)
Hf−B(15)	2.481(12)	C(l)−B(6)	1.735(22)				
Bond Angles (deg)							
Compound **I**							
Cnt(1)−Hf−Cl	107.8	Cnt(1)−Hf−Cnt(2)	131.3	B(14)−Hf−O(51)	113.9(4)	Hf−B(24)−Li	102.1(8)
Cnt(1)−Hf−O(51)	105.4	Cl−Hf−B(14)	136.1(3)	B(24)−Hf−O(51)	88.0(4)	B(25)−B(24)−Li	170.4(13)
Cnt(2)−Hf−Cl	109.2	Cl−Hf−B(24)	138.5(3)	Hf−B(23)−Li	99.6(7)	B(26)−B(24)−Li	119.8(9)
Cnt(2)−Hf−O(51)	105.6	Cl−Hf−O(51)	89.5(2)				
Compound **II**							
Cnt(l)−Hf−Cl	106.4	Cnt(2)−Hf−O(21)	105.5	B(3)−Li−B(14)	96.7(12)	B(3)−Li−B(15)	77.9(11)
Cnt(l)−Hf−O(21)	106.1	Cnt(l)−Hf−Cnt(2)	134.1	B(4)−Li−B(14)	88.2(12)	B(4)−Li−B(15)	96.3(12)
Cnt(2)−Hf−Cl	106.2	Cl−Hf−O(21)	89.7(2)				
Compound **III**							
Cnt(l)−Hf−Cl	108.2	Cnt(2)−Hf−Cl	107.0	Cnt(l)−Hf−Cnt(2)	132.2	B(6)−B(4)−Li	126.9(13)
Cnt(l)−Hf−O(21)	104.8	Cnt(2)−Hf−O(21)	107.0	Cl−Hf−O(21)	89.2	B(16)−B(14)−Li	129.2(12)

[a] Definitions: Cnt(l), the centroid of C(l), C(2), B(3), B(4), and B(5); Cnt(2), the centroid of C(11), C(12), B(13), B(14), and B(15) (see Figure 2 for example).

$SiCH_2MgCl$; higher temperatures (110 °C) resulted in decomposition. There may be some suitable intermediate temperature where thermally activated Cl substitution takes place with a minimum of cage decomposition. Other forms of activation, such as photochemical,[18] may prove more advantageous and are currently under investigation in our laboratories. The ease of preparation of both the full- and half-sandwich hafnacarboranes will allow a systematic investigation of the effects of changing the other ligands or pendant groups on the substitution reactions of these d^0 metallacarboranes.

Structure and Spectra. The single-crystal X-ray structures of the hafnacarboranes **I**, **II**, and **III** are shown in Figures 1−3, respectively. Selected bond distances and bond angles are listed in Table 3. A more complete listing of distances and angles, as well as the atomic coordinates, can be found in the Supporting Information. The structures show that in each complex a Hf metal in a formal +4 state is sandwiched between two carborane (CB) ligands and is also bonded to a Cl and a THF molecule, to give an approximately tetrahedral environment around the metal. The average CB−Hf−CB angle is 132.5 ± 1.0°, which is significantly larger than the value of 89.5 ± 0.2° for the Cl−Hf−THF bond angles.[19] An inspection of the interatomic distances between the Hf atoms and their nearest neighbors shows that equivalent distances are essentially the same in the three complexes; the average distances are Hf−Cl = 2.446 ± 0.006 Å, Hf−O(THF) = 2.219 ± 0.022 Å, and Hf−Cnt(1) = 2.137 ± 0.009 Å (see Table 3). This average Hf−Cl bond distance is similar to the value of 2.417 Å found for $[(\eta^5\text{-}C_5H_4CH_2)_2CH_2]HfCl_2$.[20] Specifically, there is no evidence of any systematic changes in the values of these parameters that are consistent with an increase in steric strain around the metal center as the cage-carbon substituents change from H (**III**) to Me (**II**) to $SiMe_3$ (**I**). The structures of **I** and **II** are quite similar to those of the respective zirconacarboranes 1-Cl-1-(THF)-2,2′-$(SiMe_3)_2$-3,3′-$(R)_2$-4,4′,5,5′-Li$(THF)_n$-1,1′-*commo*-Zr$(2,3\text{-}C_2B_4H_4)_2$ (R = $SiMe_3$, n = 2; R = Me, n = 1).[11] The metal−ligand bond distances in the zirconacarboranes are as follows: Zr−Cl = 2.461 Å (R = $SiMe_3$), 2.450 Å (R = Me); Zr−O(THF) = 2.296 Å (R = $SiMe_3$), 2.240 Å (R = Me); Zr−Cnt = 2.174 ± 0.002 Å (R = $SiMe_3$), 2.174 ± 0.005 Å (R = Me). A comparison of these values with those listed in Table 3 shows that the Hf−Cl bond distances are slightly smaller than the corre-

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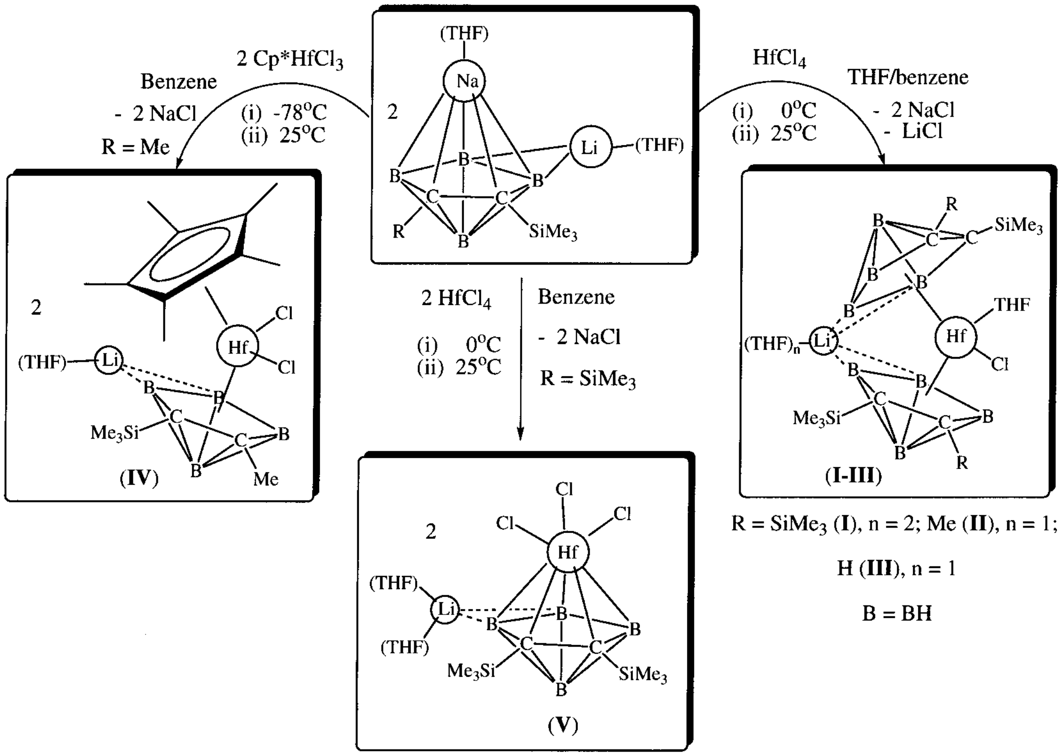
(19) Whenever the average value of a quantity is given, the indeterminations listed are the average deviations.

(20) Saldarriaga-Molina, C. H.; Clearfield, A.; Bernal, I. *Inorg. Chem.* **1974**, *13*, 2880.

Scheme 1. Synthetic Scheme for Sandwich and Half-Sandwich Hafnacarboranes



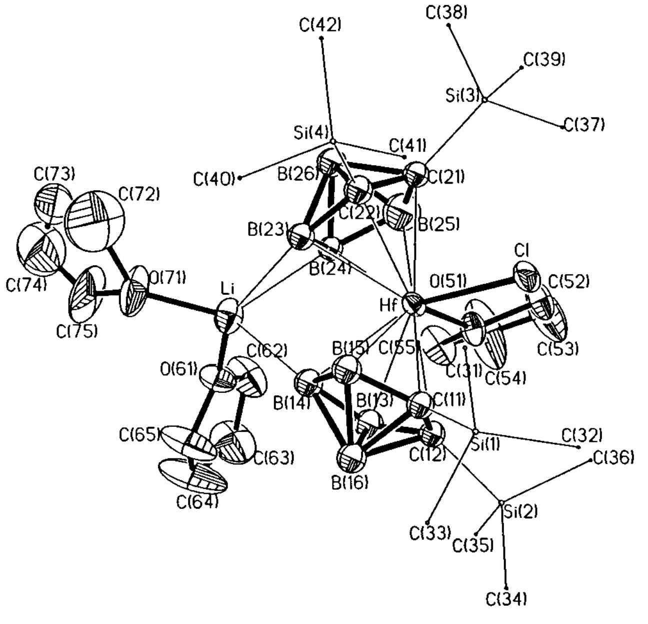


Figure 1. Crystal structure of the hafnacarborane sandwich complex 1-Cl-1-(THF)-2,2′,3,3′-$(SiMe_3)_4$-4′,5,5′,6-Li-$(THF)_2$-[1,1′-*commo*-Hf(η^5-$C_2B_4H_4$)$_2$] (**I**), showing the atom-numbering scheme. The thermal ellipsoids are drawn at the 40% probability level. For clarity, the H atoms of the cage and of the metal-bound THF molecules are omitted and the cage-bound $SiMe_3$ groups are drawn with circles of arbitrary radii.

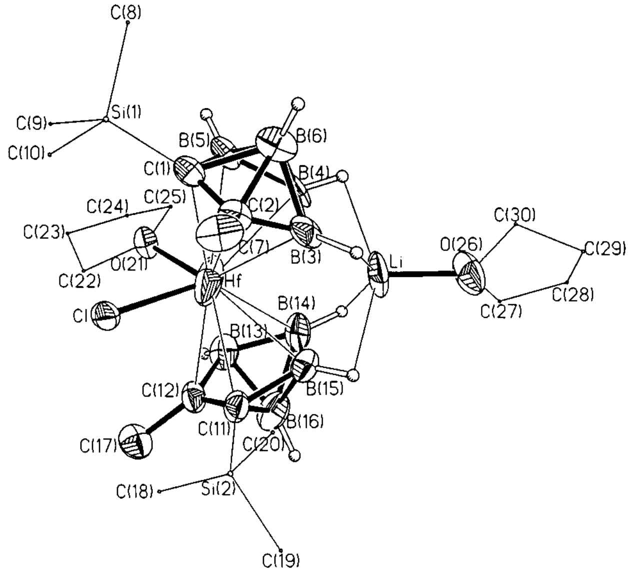


Figure 2. Perspective view of the hafnacarborane sandwich complex 1-Cl-1-(THF)-2,2′-$(SiMe_3)_2$-3,3′-$(Me)_2$-4′,5,5′,6-Li(THF)-[1,1′-*commo*-Hf(η^5-$C_2B_4H_4$)$_2$] (**II**), showing the atom-numbering scheme. The thermal ellipsoids are drawn at the 40% probability level. The cage-bound $SiMe_3$ groups and the carbon atoms of THF's are drawn with circles of arbitrary radii.

sponding distances in the zirconacarboranes; this is in agreement with the results found in the metallocene sandwich complexes of the two metals.[21]

The solution ^1H, ^{13}C, and ^{11}B NMR spectra of compounds **I**–**V** are listed in Table 1. They all show peaks that are consistent with the formulations given in the Experimental Section and, in the case of compounds **I**–**III**, with the structures shown in Figures 1–3. The ^{11}B NMR spectra of **I** and **II** are almost identical with those of the corresponding zirconacarboranes. The ^{11}B NMR spectrum of the zirconium analogue of **I** has three peaks at δ 33.16, 25.48, and −16.32 ppm with peak area ratios of 1:2:1, while the analogue of **II** has a similar three-peak pattern at δ 30.08, 22.65, and −14.04 ppm.

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[21] See ref 1e, Chapter 4, for examples.

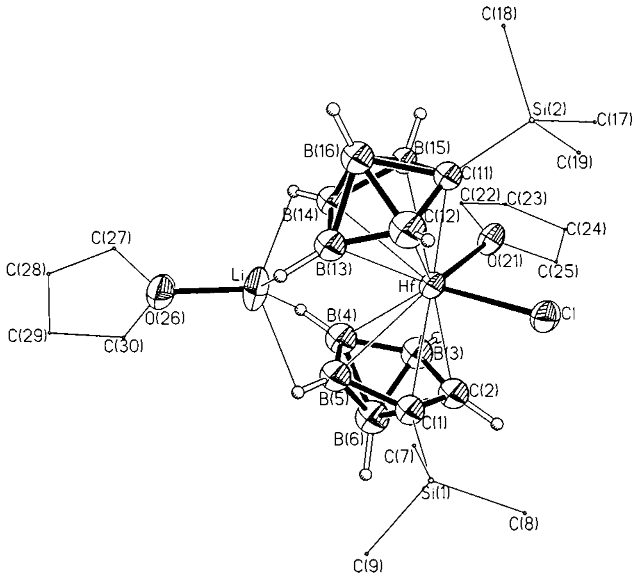

Figure 3. Perspective view of the structure of the hafnacarborane sandwich complex 1-Cl-1-(THF)-2,2′-$(SiMe_3)_2$-3,3′-$(H)_2$-4′,5,5′,6-Li(THF)-[1,1′-*commo*-Hf(η^5-$C_2B_4H_4$)$_2$] (**III**), showing the atom-numbering scheme. The thermal ellipsoids are drawn at the 40% probability level. The cage-bound $SiMe_3$ groups and the carbon atoms of THF's are drawn with circles of arbitrary radii.

In view of the similarities in the charges, sizes, and bonding characteristics of Hf and Zr,[1e] the agreement between their NMR spectra is not surprising. A comparison of the ^{11}B NMR spectra of these metallacarboranes with their *closo*-*exo*-Li(THF)-1-Na(THF)-2-$(SiMe_3)$-3-(R)-2,3-$C_2B_4H_4$ (R = $SiMe_3$, Me, H) precursors shows that, on complexation of the carborane with the group 4 metal, the apical and unique borons are significantly deshielded, resulting in downfield shifts of 25−35 ppm, while the basal boron shifts are more moderate (~5 ppm). For example, the ^{11}B NMR spectrum of *closo*-*exo*-Li(THF)-1-Na(THF)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ shows a 2:1:1 peak area pattern at δ 20.85, 2.39, and −44.53 ppm, while **I** has a 1:2:1 pattern at δ 33.69, 24.78, and −18.53 ppm, respectively. The similarities in the ^{11}B NMR spectra of **I** and **II** with those of **IV** and **V**, whose structures have not been determined, lend support to the respective mixed-ligand and half-sandwich structures proposed for the latter two complexes. It is of interest to note that the ^{11}B NMR spectrum of a coordinated carborane is insensitive to the nature of the other ligands on the group 4 metal; although ^1H and ^{13}C NMR spectra show more variation, they are difficult to interpret. Therefore, NMR spectroscopy is of limited use in resolving the more detailed structural question regarding **IV** and **V**.

Conclusions. The mixed-ligand sandwich and full- and half-sandwich chloro complexes of hafnium could be synthesized, in good yields, from the reaction of the sodium/lithium compounds *closo*-*exo*-Li(THF)-1-Na-(THF)-2-$(SiMe_3)$-3-(R)-2,3-$C_2B_4H_4$ (R = $SiMe_3$, Me, H), with the appropriate hafnium reagent. Structural studies show very little distortion around the Hf atom resulting from changing R from H to $SiMe_3$. These results agree with those found for the group 4 metallocenes $[C_5H_x(SiMe_3)_{5-x}][C_5H_y(SiMe_3)_{5-y}]TiCl_2$ ($x = 2, 3$; $y = 3-5$)[22] and $[C_5H_2(SiMe_3)_3]_2ZrCl_2$,[23] in which increasing $SiMe_3$ substitution produced no great effect on the structures of the complexes. Our results also agree with the observation that, while $SiMe_3$ substitution produces no marked change in the geometry of the metallocenes, it does affect their reactivities. This attenuation in reactivity is presumably due to the shielding of the other metal-bound ligands by the pendant $SiMe_3$ groups, although other factors may also be of importance.[22,23] The ease of syntheses of the monomeric mixed-ligand sandwich (**IV**) and the half-sandwich (**V**) hafnacarboranes leads us to conclude that it should be possible to synthesize a number of different hafnacarboranes, some of which could undergo facile ligand exchange reactions. These studies are currently underway in our laboratories.

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Supporting Information Available: Tables of 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**−**III** and the IR spectral data for **I**−**V** (Table S-5). This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) Choukroun, R.; Dahan, F. *Organometallics* **1994**, *13*, 2097.