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Chemistry of *C*-Trimethylsilyl-Substituted Heterocarboranes. 31. New Insights into Reaction Pathways of Carborane Ligand Systems: Synthetic, Structural, Spectroscopic, and Electrochemical Studies on Sandwich and Half-Sandwich Metallacarboranes of Iron, Cobalt, and Nickel

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A series of full- and half-sandwich metallacarboranes were synthesized from the reaction of MCl_2 (M = Co, Fe) and *closo*-*exo*-*y*,*x*-Li(L)-1-Li(L)-2,*n*-$(SiMe_3)_2$-2,*n*-$C_2B_4H_4$ ($y = 4$, $x = 5$, L = 2 THF, $n = 3$ (**1**); $y = 4$, $x = 5$, L = TMEDA, $n = 3$ (**2**); $y = 5$, $x = 6$, L = 2 THF, $n = 4$ (**3**); $y = 5$, $x = 6$, L = TMEDA, $n = 4$ (**4**)) in 1:1 molar ratios in benzene. The metallacarborane complexes *exo*-4,4′,5,5′-Fe(TMEDA)-*commo*-1,1′-Fe[2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$]$_2$ (**5**), M^+[*commo*-1,1′-Co{2,3-$(SiMe_3)_2$-(2,3-$C_2B_4H_4$)}$_2$]$^-$ (M = CoCl (**6a**), $Co_3(TMEDA)_3Cl_5$ (**6b**)), *commo*-1,1′-M[2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$]$_2$ (M = FeH (**7**), CoH (**8**)), and 1-(TMEDA)-*closo*-2,4-$(SiMe_3)_2$-1,2,4-$MC_2B_4H_4$ (M = Co (**9**)) were isolated in yields ranging from 80 to 92%. The reaction of *commo*-1,1′-Ni[2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$]$_2$ (**10**) with carefully dried TMEDA produced the charge-compensated *commo*-1,1′-Ni^{III}-[(2,4-$(SiMe_3)_2$-5,6-B_2-{σ-N(Me)$(CH_2)_2$N$(Me)_2$}-2,4-$C_2B_2H_2$)(2′,4′-$(SiMe_3)_2$-2′,4′-$C_2B_4H_4$)] (**12**) and 1,2-$(SiMe_3)_2$-*closo*-1,2-$C_2B_4H_4$. With the exception of **5** and **12**, all of the *commo*-metallacarboranes involved metal oxidation in addition to ligation, with M^0 as a coproduct. All compounds were characterized by analysis and infrared spectroscopy, and **5**, **6b**, **7**, **9**, and **12** were also characterized by X-ray diffraction analysis. Because of the paramagnetic nature of either the products or their counterions, only **8** could be characterized by ^1H, ^{11}B, and ^{13}C NMR spectroscopy; its ^1H NMR spectrum showed a broad resonance at δ −18.9 attributable to the Co-bound H. The paramagnetic compounds were characterized by EPR spectroscopy. The electrochemical reduction of **10** produced a Ni(III) metallacarborane that was characterized by EPR spectroscopy and found to be a $3d^7$ species related to nickelocenium derivatives. All results are consistent with a mechanism involving the initial formation of a half-sandwich metallacarborane, which can be isolated or can undergo a disproportionation process to give the full-sandwich products.

Introduction

The π complexes formed between transition metals and *nido*-carborane anions have been the subject of extensive synthetic and structural investigations.[1] The earliest, and the most extensively studied, systems have been the icosahedral metallacarboranes derived from the *nido*-$[C_2R_2B_9H_9]^{2-}$ dianion.[1,2] There is also a fairly large body of data on the pentagonal-bipyramidal metallacarboranes of the *nido*-$[C_2R_2B_4H_4]^{2-}$ ligand system (R denotes exo-polyhedral substituent groups on the cage carbons).[1] In these complexes metal−ligand bonding is through a set of π-type orbitals localized on the

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open C_2B_3 pentagonal faces of the nido cages that bear a striking resemblance to the primary metal-bonding orbitals of the cyclopentadienide ion, $[C_5R_5]^-$.[2a] This analogy has proved to be useful in rationalizing the syntheses and structures of the metallacarboranes. There are two isomeric arrangements of the atoms on the C_2B_3 faces, the "carbons adjacent" isomer, where the two carbons are next to one another, and the "carbons apart" isomer, where there is a boron atom between the two carbons.[2b] In general, both seem to bind metals equally well, but, at least in the case of the C_2B_4 cage system, the "carbons apart" isomer is the more stable one and this fact, at times, has dictated different paths for the metallacarboranes derived from the two isomers. It was found that the reactions of anhydrous $NiCl_2$ with the dilithium-complexed "carbons adjacent" *nido*-carborane dianions $[2\text{-}(SiMe_3)\text{-}3\text{-}(R)\text{-}2,3\text{-}C_2B_4H_4]^{2-}$ (R = $SiMe_3$, Me) in *n*-hexane, THF, or TMEDA produced the corresponding *closo*-1,2-carborane derivatives in 40−59% yields along with small quantities of C_4B_8-carborane derivatives; no evidence of a persisting nickelacarborane could be found.[3] On the other hand, the same reaction with the dilithium-complexed "carbons apart" *nido*-carborane dianion $[2,4\text{-}(SiMe_3)_2\text{-}2,4\text{-}C_2B_4H_4]^{2-}$ produced either the *commo*-nickelacarborane (when THF-solvated *closo*-dilithiacarborane was used) or the *closo*-nickelacarborane (when TMEDA-solvated *closo*-dilithiacarborane was used).[4] The presence of other coordinating ligands has also been found to influence the course of the reactions. Grimes reported that the reaction of either $FeCl_2$ or $CoCl_2$ with $[2,3\text{-}(RC)_2B_4H_5]^-$ produced the sandwich compound $(R_2C_2B_4H_4)_2FeH_2$ or $(R_2C_2B_4H_4)_2CoH$, which decomposed to give the cage fusion product $R_4C_4B_8H_8$.[5,6] On the other hand, it was found that, in the presence of good coordinating ligands, the half-sandwich *closo*-metallacarboranes were stabilized.[7,8] Similarly, the structurally and EPR spectroscopically characterized Co(II) half-sandwich complex 1-Co(TMEDA)-$2,4\text{-}(SiMe_3)_2\text{-}2,4\text{-}C_2B_4H_4$ has been isolated exclusively when TMEDA-solvated dilithiacarborane was used as the precursor.[9] However, a full-sandwich complex, [*commo*-1,1′-Co{$2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4$}$_2$]$^-$, was synthesized from the reaction of the THF-solvated "carbons adjacent" trinuclear *closo*-samaracarborane precursor with anhydrous $CoCl_2$ in benzene.[10] In addition, the sequence of reactions leading to the various products is not clear-cut. Hawthorne and co-workers[2a] reported that the reaction of Co(II) with $[C_2B_9H_{11}]^{2-}$ led to the isolation of the monoanionic cobalt(III) sandwich complex $[(1,2\text{-}C_2B_9H_{11})_2Co]^-$ with the concomitant formation of metallic cobalt. When the reaction was run in the presence of NaC_5H_5, the Co(III) mixed-ligand sandwich complex $(C_5H_5)Co(1,2\text{-}C_2B_9H_{11})$ and Co(0) were formed.[2a] This suggests a rapid oxidation, or disproportionation, of an initially formed Co(II) sandwich complex. Likewise, the results for the C_2B_4 cage systems indicate that a similar disproportionation sequence exists in the formation of the Ni(IV) complex *commo*-1,1′-Ni$[2,4\text{-}(SiMe_3)_2\text{-}2,4\text{-}C_2B_4H_4]_2$[4] and the Co(III) full-sandwich complex [*commo*-1,1′-Co{$2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4$}$_2$]$^-$.[10] In both systems the respective M(II) half-sandwich *closo*-metallacarboranes could be trapped as their TMEDA complexes and no evidence of an oxidized full-sandwich metallacarborane could be found.[4,9] A similar reactivity pattern should also exist for other metalla-C_2B_4-carborane systems of the d- and f-block metals. While such a pattern has been found for the lanthanacarborane systems,[11] an unambiguous pattern of reactivity in the late d-block metallacarboranes has yet to be established. The recent suggestion that a Ni(III)/Ni(IV) interconversion in the full-sandwich nickelacarboranes can be used as the basis of a nanorotary machine[12] emphasizes the need to understand the overall nature and role of the ligands in determining the stabilities and properties of the metallacarboranes. It was this incentive that led us to embark on a parallel, systematic study of the syntheses, structures, and reactivities of the metallacarboranes of iron, cobalt, and nickel. Herein we report the results on the ferracarboranes and cobaltacarboranes, as well as an electrochemical study of the known nickelacarboranes. The synthesis, crystal structure, and EPR spectroscopic analysis of a novel paramagnetic zwitterionic nickelacarborane sandwich complex in which nickel exists in the +3 oxidation state is also presented.

Experimental Section

Materials. All manipulations were carried out either under a dry argon atmosphere or on a high-vacuum line. Benzene, tetrahydrofuran (THF), and *n*-hexane were dried over NaH or Na/benzophenone and doubly distilled before use. Prior to use, *N,N,N′,N′*-tetramethylethylenediamine, TMEDA (Aldrich), was distilled in vacuo and stored over sodium metal. All other solvents were dried over 4−8 Å mesh molecular sieves (Aldrich) and were either saturated with dry argon or degassed

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before use. The syntheses of the "carbons adjacent" *closo-exo*-4,5-Li(THF)$_2$-1-Li(THF)$_2$-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$ (**1**) and *closo-exo*-4,5-Li(TMEDA)-1-Li(TMEDA)-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$ (**2**) and the "carbons apart" *closo-exo*-5,6-[(μ-H)$_2$Li(THF)$_2$]-1-Li(THF)$_2$-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$ (**3**) and *closo-exo*-5,6-[(μ-H)$_2$Li(TMEDA)]-1-Li(TMEDA)-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$ (**4**) followed the literature procedures.[13,14] Prior to use, FeCl$_2$, CoCl$_2$, and NiCl$_2$ (Aldrich) were first degassed in vacuo at 130 °C for 24 h and then treated with thionyl chloride (SOCl$_2$) to remove the last traces of moisture present in their crystal lattices.

Spectroscopic Procedures. Proton, boron-11, and carbon-13 NMR spectra were recorded on a Bruker Fourier transform multinuclear NMR spectrometer at 200, 64.2, and 50.3 MHz, respectively. Infrared spectra were recorded on a Perkin-Elmer Model 1600 FT-IR spectrophotometer and Nicolet Magna 550 FT-IR spectrophotometer. Elemental analyses were determined in-house at Northern Illinois University using a Perkin-Elmer 2400 CHN elemental analyzer.

EPR Spectra. Electron paramagnetic resonance (EPR) spectra were recorded in the X-band on a Bruker System ESP 300 equipped with a Bruker ER035 M gauss meter and an HP 5350B microwave counter.

Electrochemical Studies. Cyclic voltammetry measurements were carried out in CH$_2$Cl$_2$/0.1 M Bu$_4$NPF$_6$ solutions at a scan rate of 100 mV/s. A three-electrode configuration (glassy-carbon working electrode, Pt counter electrode, and Ag/AgCl reference) and an EG&G M273 potentiostat and function generator were used. The ferrocene/ferrocenium couple, Fc$^{0/+}$, served as an internal reference. A two-electrode capillary was used for intra muros generation of the Ni(III) complex for EPR spectra.

Synthetic Procedures. All experiments were carried out in 100 mL Pyrex glass round-bottom flasks, equipped with magnetic stirring bars and high-vacuum Teflon valves. After their initial purifications, nonvolatile substances were manipulated in either a drybox or a glovebag, under an atmosphere of dry nitrogen or argon. All known compounds were verified by comparing their IR and/or ^{1}H NMR spectra with those of authentic samples.

A. Reaction of *closo-exo*-4,5-Li(TMEDA)-1-Li(TMEDA)-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$ (2) with Iron(II) Chloride: Synthesis of *exo*-4,4′,5,5′-Fe(TMEDA)-*commo*-1,1′-Fe[2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$]$_2$ (5). A 8.04 mmol (3.73 g) sample of TMEDA-solvated dilithiacarborane (**2**) in a mixture of benzene (20 mL) and hexane (10 mL) was allowed to react with anhydrous FeCl$_2$ (1.02 g, 8.05 mmol) with constant stirring at 0 °C for 4 h, and the stirring was continued at room temperature for 2 days. During this time the heterogeneous mixture changed to dark green with the formation of a precipitate that settled to the bottom of the flask on standing at room temperature. At this point, the mixture was filtered through a glass frit in vacuo to collect a clear green filtrate. An off-white solid product (not measured), remaining on the frit, was identified as LiCl and, therefore, was discarded. The filtrate was then slowly concentrated in vacuo, and after several days of standing at room temperature, a purple reddish crystalline solid was isolated that was later identified as the paramagnetic (low-spin/high-spin) wedged-sandwich diferracarborane complex *exo*-4,4′,5,5′-Fe(TMEDA)-*commo*-1,1′-Fe[2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$]$_2$ (**5**; 2.40 g, 3.62 mmol, 90%, mp 170−171 °C). Anal. Calcd (found) for C$_{22}$H$_{60}$B$_8$N$_2$Fe$_2$Si$_4$ (**5**): C, 39.84 (39.91); H, 9.12 (9.34); N, 4.22 (4.31). IR (cm^{-1}, KBr pellet): 2952 (vs), 2900 (sh), 2860 (ws) (ν(C−H)), 2683 (ws), 2657 (ws), 2530 (ms) (ν(B−H)), 2216 (ws), 1961 (ms), 1820 (ms), 1590 (wsh), 1488 (ws), 1373 (ms) (δ(C−H)$_{\text{asym}}$), 1283 (ms) (δ(C−H)$_{\text{sym}}$), 1180 (ms), 1079 (ss), 1040 (ss), 898 (vs) (ρ(C−H)), 676 (ss).

Identical results were obtained when a large excess (in 5:1 ratio) of anhydrous FeCl$_2$ was reacted with the TMEDA-solvated dilithiacarborane (**2**).

B. Reaction of *closo-exo*-4,5-Li(THF)$_2$-1-Li(THF)$_2$-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$ (1) with a Stoichiometric Quantity of Cobalt(II) Chloride: Synthesis of [CoCl]$^+$[*commo*-1,1′-Co{2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$}$_2$]$^-$ (6a). A 10.00 mmol (5.20 g) sample of THF-solvated dilithiacarborane (**1**) was dissolved in dry benzene (30 mL), the resulting clear solution was allowed to react with anhydrous CoCl$_2$ (1.30 g, 10.01 mmol) with constant stirring at 0 °C for 4 h, and the stirring was continued at room temperature for 2 days. During this time the heterogeneous mixture changed to dark green with the formation of a precipitate that remained at the bottom of the flask after standing at room temperature. The mixture was filtered through a glass frit, and the solvent was removed from the filtrate in vacuo. An off-white solid product remaining on the frit was identified as a mixture of LiCl and the metallic cobalt (not measured) and was discarded. On evaporation of the solvent of the filtrate, a yellowish green residue formed, which was redissolved in a mixture of 5% THF and 95% hexane; slow evaporation of the solvent yielded a pale greenish solid, identified as [CoCl]$^+$[*commo*-1,1′-Co{2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$}$_2$]$^-$ (**6a**) (2.56 g, 4.35 mmol, 87%; mp >191 °C dec) after thorough drying in vacuo. Anal. Calcd (found) for C$_{16}$H$_{44}$B$_8$ClCo$_2$Si$_4$ (**6a**): C, 32.64 (33.11); H, 7.53 (7.34); Cl, 6.02 (5.93). IR (cm^{-1}, KBr pellet) 2950 (s), 2920 (sh), 2890 (m), 2859 (m) (ν(C−H)), 2530 (ms) (ν(B−H)), 1600 (ws), 1510 (ms), 1470 (mw), 1393 (ss) (δ(C−H)$_{\text{asym}}$), 1360 (ms), 1263 (vs) (δ(C−H)$_{\text{sym}}$), 1180 (ms), 1069 (ss), 1020 (br), 848 (vs,br) (ρ(C−H)), 799 (ms), 636 (ms).

The paramagnetic nature of **6a** precluded obtaining useful NMR data. The EPR spectrum of this species could not be resolved properly to provide any meaningful interpretation.

C. Reaction of *closo-exo*-4,5-Li(TMEDA)-1-Li(TMEDA)-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$ (1) with an Excess Quantity of Cobalt(II) Chloride: Synthesis of [Co$_3$(TMEDA)$_3$Cl$_5$]$^+$-[*commo*-1,1′-Co{2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$}$_2$]$^-$ (6b). In a procedure identical with that described above for the preparation of **6a**, a 5.02 mmol (2.33 g) sample of TMEDA-solvated dilithiacarborane (**2**) in dry benzene (30 mL) was allowed to react with a large excess of anhydrous CoCl$_2$ (3.29 g, 25.34 mmol) with constant stirring at 0 °C for 4 h and then at room temperature for 2 days, to isolate a yellowish green crystalline solid, identified as [Co$_3$(TMEDA)$_3$Cl$_5$]$^+$[*commo*-1,1′-Co{2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$}$_2$]$^-$ (**6b**) (2.41 g, 2.01 mmol, 80%; mp >210 °C dec). Anal. Calcd (found) for C$_{34}$H$_{92}$B$_8$N$_6$Cl$_5$Co$_4$Si$_4$ (**6b**): C, 34.12 (33.98); H, 7.75 (7.71); N, 7.02 (7.11), Cl, 14.81 (14.62). IR (cm^{-1}, KBr pellet) 2957 (s), 2887 (m), 2861 (sh) (ν(C−H)), 2533 (ms) (ν(B−H)), 1610 (ws), 1510 (ms), 1470 (mw), 1399 (s) (δ(C−H)$_{\text{asym}}$), 1360 (ms), 1241 (vs) (δ(C−H)$_{\text{sym}}$), 1179 (w), 1140 (w), 1113 (w), 1024 (s), 831 (vs,br) (ρ(C−H)), 786 (m), 691 (m), 631 (m).

The paramagnetic nature of **6b** precluded obtaining useful NMR data. The EPR spectrum of this species could not be resolved properly to provide any meaningful interpretation.

D. Reaction of *closo-exo*-4,5-Li(L)$_n$-1-Li(L)$_n$-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$ (1, L = THF, n = 2; 2, L = TMEDA, n = 1) with a Stoichiometric Quantity of Nickel(II) Chloride. In an attempt to synthesize the half-sandwich *closo*-nickelacarborane complex, *closo-exo*-4,5-Li(L)$_n$-1-Li(L)$_n$-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$ (**1**, L = THF, n = 2; **2**, L = TMEDA, n = 1) was reacted with a stoichiometric quantity of nickel(II) chloride, as described elsewhere.[3,16,17] An oxidative cage closure reaction took

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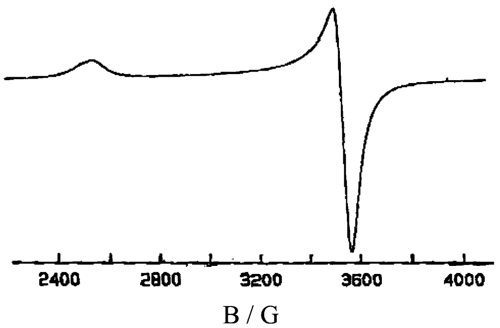


Figure 1. EPR spectrum of **7**.

place to form the corresponding "carbons adjacent" *closo*-carborane 1,2-$(SiMe_3)_2$-1,2-$C_2B_4H_4$ in 59−64% yields, along with a cage fusion product, the "carbons apart" *nido*-C_4B_8-carborane 2,4,7,9-$(SiMe_3)_4$-2,4,7,9-$C_4B_8H_8$, in 11% yield.

E. Reaction of *closo-exo*-5,6-[(μ-H)$_2$Li(TMEDA)]-1-Li-(TMEDA)-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$ (4) with Iron(II) Chloride. A 5.05 mmol (2.34 g) sample of *closo-exo*-5,6-[(μ-H)$_2$Li-(TMEDA)]-1-Li[(TMEDA)]-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$ (**4**) was dissolved in vacuo in 30 mL of benzene at room temperature. The resulting clear solution was slowly poured in vacuo onto anhydrous $FeCl_2$ (0.65 g, 5.13 mmol) at 0 °C, and the resulting heterogeneous mixture was stirred at this temperature for 4 h and then at room temperature overnight, during which time the solution turned dark brown with the formation of some black precipitate that was subsequently filtered through a glass frit in vacuo to collect the reddish brown filtrate. After benzene was removed from this filtrate at room temperature in vacuo, the reaction flask containing a dark brown residue was attached to a detachable U-trap held at 0 °C. Upon vacuum sublimation of the dark brown residue at 200 °C overnight, a red crystalline solid, identified as *commo*-1,1′-FeH[2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$]$_2$ (**7**) (1.09 g, 2.21 mmol; 88% yield; mp 196 °C), was collected in the detachable U-trap held at 0 °C. The sidearms of both the reaction flask and the U-trap were maintained at 140−150 °C with heating tape during the sublimation. The gray-black residue that remained in the reaction flask after isolating **7** was identified as a mixture of LiCl and iron metal (not measured) and was therefore discarded. The new neutral *commo*-ferracarborane complex is highly soluble in THF and slightly soluble in benzene and *n*-hexane. Anal. Calcd (found) for $C_{16}H_{45}B_8Si_4Fe$ (**7**): C, 39.04 (38.56); H, 9.21 (8.88). The paramagnetic nature of **7** precluded obtaining useful NMR data. However, in frozen THF solution at 90 K, **7** exhibits an intense EPR signal with $g_1 = 2.745$ and $g_{2,3} = 1.979$ (Figure 1). IR (cm^{-1}, KBr pellet): 2957 (s), 2887 (m), 2543 (m) (ν(B−H)), 1399 (s), 1241 (s), 1179 (w), 1140 (w), 1113 (w), 1024 (s), 831 (vs), 786 (m), 691 (m), 631 (m).

F. Reaction of *closo-exo*-5,6-[(μ-H)$_2$Li(THF)$_2$]-1-Li(THF)$_2$-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$ (3) with Cobalt(II) Chloride. In a procedure identical with that described above for the synthesis of **7**, an 8.15 mmol (4.24 g) sample of *closo-exo*-5,6-[(μ-H)$_2$Li-(THF)$_2$]-1-Li[(THF)$_2$]-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$ (**3**) was allowed to react overnight with 9.01 mmol (1.17 g) of anhydrous $CoCl_2$ in 30 mL of dry benzene at room temperature to isolate an orange-red sublimable solid, identified as the diamagnetic *commo*-1,1′-CoH[2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$]$_2$ (**8**) (1.67 g, 3.38 mmol; 83% yield; mp 201 °C), that was collected in the detachable high-vacuum U-trap held at 0 °C. The gray-brown residue that remained in the reaction flask after isolating **8** was identified as a mixture of LiCl and cobalt metal (not measured) and was therefore discarded. The new neutral *commo*-cobaltacarborane complex is highly soluble in THF and slightly soluble in benzene and *n*-hexane. Anal. Calcd (found) for $C_{16}H_{45}B_8Si_4Co$ (**8**): C, 38.80 (38.45); H, 9.16 (9.08). IR (cm^{-1}, KBr pellet): 2945 (s), 2918 (s), 2852 (s), 2575 (s) (ν(B−H)), 1455 (s), 1402 (s), 1248 (s), 1109 (m), 1023 (m), 838 (vs), 691 (m), 622 (m), 543 (m). NMR data for compound **8**: ^{1}H NMR (C_6D_6, external Me_4Si) δ 0.21 (36H, s (br), −Si(CH_3)$_3$), −18.9 (vbr, Co−H); ^{13}C NMR (C_6D_6, external Me_4Si) δ −0.01 (Si−(CH_3)$_3$), 99.89 (Si−C_{cage}); ^{11}B NMR (C_6D_6, relative to external $BF_3 \cdot OEt_2$) δ 2.08 (d(br), 2 B, basal BH), −3.72 (d(br), 1B, unique BH), −11.91 (d, 1B, apical BH,$^1J(^{11}B-^1H) = 158$ Hz).

G. Reaction of *closo-exo*-5,6-[(μ-H)$_2$Li(TMEDA)]-1-Li-(TMEDA)-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$ (4) with Cobalt(II) Chloride: Synthesis of a Half-Sandwich "Carbons Apart" TMEDA-Stabilized Cobaltacarborane Complex (9). As described in our preliminary report,[9] a 3.24 mmol (1.50 g) sample of **4** in a 30 mL mixture of dry benzene (50%) and dry *n*-hexane (50%) was allowed to react with 3.24 mmol (0.42 g) of anhydrous $CoCl_2$ in vacuo at 0 °C for 3 h and then at 25 °C for 5 h, during which time the solution turned dark green with the formation of a precipitate. The mixture was then filtered through a frit in vacuo to collect a dark green filtrate. The solid on the frit (not measured), identified by qualitative analysis as LiCl, was discarded. The solvents and the liberated TMEDA (not measured) were then removed from the filtrate to collect a deep green solid, which was then recrystallized in vacuo from a solution of benzene (25%) and *n*-hexane (75%) to collect extremely air-sensitive deep green crystals, identified as *closo*-1-(TMEDA)-1-Co-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$ (**9**), in 92% yield (1.17 g, 2.98 mmol; mp >250 °C; reasonably soluble in polar and slightly soluble in nonpolar organic solvents). Anal. Calcd (found) for $C_{14}H_{38}N_2B_4Si_2Co$ (**9**): C, 42.75 (43.41); H, 9.67 (8.60); N, 7.12 (6.16). IR (cm^{-1}, C_6D_6 vs C_6D_6): 3013 (ms), 2955 (ss), 2886 (ss), 2839 (ss), 2793 (ws) (ν(CH)), 2492 (vs) (ν(BH)), 1463 (ss), 1434 (sh), 1405 (ws) ($\delta(CH)_{asym}$), 1278 (ms), 1237 (ss) ($\delta(CH)_{sym}$), 1174 (ss), 1139 (ws), 1121 (ws), 1058 (ms), 1017 (ms), 994 (ws), 948 (ms), 895 (m, br), 837 (vs, br) (ρ(CH)), 756 (ms), 681 (ms), 623 (ms), 495 (ss). In frozen toluene solution at 4 K, **9** exhibits a well-resolved rhombic EPR signal with $g_1 = 2.549$, $g_2 = 2.108$, and $g_3 = 1.976$. The corresponding ^{59}Co coupling constants ($I = 7/2$) are $a_1 = 2.9$, $a_2 = 2.7$, and $a_3 = 3.5$ mT.[9]

When 5.82 mmol of **4** was reacted with 2.91 mmol of $CoCl_2$, under similar reaction conditions, 2.62 mmol (1.03 g, 90% yield) of **9** was isolated as deep green crystals after recrystallization from a solution of benzene (25%) and *n*-hexane (75%), and nearly all of the unreacted **4** (1.43 g, 3.08 mmol) was recovered. It should be noted that compound **9** is extremely air sensitive and difficult to handle. This results in less than ideal analytical results for the compound. However, the successful crystal structure determination (vide infra) leaves little doubt as to the formula of compound **9**.

H. Reaction of *closo-exo*-5,6-[(μ-H)$_2$Li(THF)$_2$]-1-Li(THF)$_2$-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$ (3) and *closo-exo*-5,6-[(μ-H)$_2$Li-(TMEDA)]-1-Li(TMEDA)-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$ (4) with Nickel(II) Chloride: Syntheses of a "Carbons Apart" Neutral Full-Sandwich *commo*-Ni(IV)-Carborane Complex (10) and Neutral Half-Sandwich "Carbons Apart" TMEDA-Stabilized *closo*-Ni(II)-Carborane Complex (11). In separate experiments, the THF-solvated "carbons apart" dilithiacarborane **3** and the corresponding TMEDA-solvated precursor **4** were allowed to react with anhydrous $NiCl_2$ in a 1:1 molar ratio in dry benzene to produce *commo*-1,1′-Ni[2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$]$_2$ (**10**) as a neutral and sublimable solid and the neutral half-sandwich complex *closo*-1-(TMEDA)-l-Ni-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$ (**11**), in 37 and 59% yields, respectively. The details of these syntheses and the crystal structures of **10** and **11** have already been published elsewhere.[4]

I. Reaction of the *commo*-Nickelacarborane Complex 10 with TMEDA: Synthesis of the Charge-Compensated *commo*-Ni(III)-Carborane Complex 12. A 2.54 g (5.14 mmol) yellow crystalline diamagnetic sample of *commo*-1,1′-Ni[2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$]$_2$ (**10**) was dissolved in 20 mL of anhydrous TMEDA, and the resulting clear pale yellow solution was stirred constantly at room temperature over a period of 8 days, during which time the solution became turbid green. The unreacted TMEDA was then slowly removed from

Table 1. Crystal Data[a] and Structure Refinement Details for 5 and 7

	5	7
empirical formula	$C_{22}H_{60}B_8N_2Si_4Fe_2$	$C_{16}H_{44}B_8Si_4Fe$
formula weight	663.26	491.20
crystal system	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_12_12_1$
a, Å	12.574(1)	10.932(2)
b, Å	16.472(1)	12.939(3)
c, Å	18.362(2)	22.815(5)
α, deg	90	90
β, deg	92.06(1)	90
γ, deg	90	90
V, Å^3	3800.9(6)	3227(1)
Z	4	4
ρ_{calcd}, g/cm^3	1.159	1.011
μ, mm^{-1}	0.905	0.619
extinction coeff[15]	0.0014(2)	n/a
R1 ($I > 2\sigma(I)$)[b]	0.037	0.097
wR2 (all data)[b]	0.090	0.246
Flack param		0.33(15)

[a] Graphite-monochromated Mo Kα radiation, $\lambda = 0.710\ 73$ Å. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + F_o^2]/3$.

Table 2. Crystal Data[a] and Structure Refinement Details for 6b, 9, and 12

	6b	9	12
empirical formula	$[C_{34}H_{92}B_8N_6Cl_5Si_4Co_4]\cdot{}^1/_2C_6H_6$	$C_{14}H_{38}B_4N_2Si_2Co$	$C_{21}H_{55}B_8N_2Si_4Ni$
formula weight	1236.00	392.81	593.22
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a, Å	11.562(2)	8.329(2)	17.788(5)
b, Å	15.644(4)	19.648(6)	10.130(2)
c, Å	17.925(4)	14.570(4)	21.049(5)
α, deg	89.85(2)	90	90
β, deg	76.21(2)	94.38(2)	112.33(2)
γ, deg	86.52(2)	90	90
V, Å^3	3142(1)	2377(1)	3508(1)
Z	2	4	4
$\rho_{cald,}$ g/cm^3	1.306	1.097	1.123
μ, mm^{-1}	1.357	0.821	0.704
extinction coeff[15]	0.0029(2)	0.0002(4)	n/a
R1 ($I > 2\sigma(I)$)[b]	0.030	0.041	0.034
wR2 (all data)[b]	0.076	0.101	0.089

[a] Graphite-monochromated Mo Kα radiation, $\lambda = 0.710\ 73$ Å. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + F_o^2]/3$.

the solution in vacuo to collect a green residue that was washed with anhydrous *n*-pentane, and the resulting green solid was recrystallized from a hot solution of benzene (20 mL) and TMEDA (20 mL) to isolate pale green crystals, later identified as the charge-compensated zwitterionic *commo*-1,1′-Ni^{III}-[(2,4-$(SiMe_3)_2$-5,6-B_2-{σ-N(Me)$(CH_2)_2$N$(Me)_2$}-2,4-$C_2B_2H_2$)(2′,4′-$(SiMe_3)_2$-2′,4′-$C_2B_4H_4$)] (**12**), in 89% yield (2.71 g, 4.57 mmol). The removal of *n*-pentane from the washings in vacuo recovered the unreacted starting Ni(IV)-carborane complex **10** (0.25 g, 0.51 mmol). Anal. Calcd (found) for $C_{21}H_{55}N_2B_8Si_4Ni$ (**12**): C, 42.52 (43.01); H, 9.35 (9.51); N, 4.72 (4.56). IR (cm^{-1}, C_6D_6 vs C_6D_6): 3021 (ms), 2956 (ss), 2889 (ss), 2836 (ss), 2799 (ws) (ν(CH)), 2502 (vs) (ν(BH)), 1461 (ss), 1415 (ws) ($\delta(CH)_{asym}$), 1276 (ms), 1233 (ss) ($\delta(CH)_{sym}$), 1175 (ss), 1139 (ws), 1122 (ws), 1055 (ms), 1023 (ms), 994 (ws), 953 (ms), 890 (m, br), 841 (vs, br) (ρ(CH)), 760 (ms), 680 (ms), 621 (ms), 491 (ss). In CH_2Cl_2/0.1 M Bu_4NPF_6, measured at 4 K, the *commo*-nickelacarborane **12** exhibits a rhombic *g* component pattern in the EPR spectrum with $g_1 = 2.153$, $g_2 = 2.029$, and $g_3 = 1.989$ which is compatible with the formulation of a nickel(III) = $3d^7$ species related to nickelocenium derivatives.

X-ray Analyses of 5, 6b, 7, 9, and 12. The data for structures were collected on Siemens P3 and P4 diffractometers. The crystals used in the experiments were coated with mineral oil under a low-temperature nitrogen stream. Crystallographic data are summarized in Table 1 for the iron complexes and in Table 2 for the cobalt and nickel complexes. All structures were solved by direct methods and subsequent difference Fourier syntheses and were refined by full-matrix least-squares methods against F^2.[15] Benzene molecules of crystallization were found in the crystal lattice of **6b**. All non-hydrogen atoms were refined anisotropically, while H atoms were constrained with a riding model. Selected bond distances and angles are given in Table 3. Further details regarding the crystal data and refinement, as well as full tables of bond lengths and angles for each structure, are presented in the Supporting Information as CIF files.

Results and Discussion

Synthesis. The metallacarboranes *exo*-4,4′,5,5′-Fe-(TMEDA)-*commo*-1,1′-Fe[2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$]$_2$ (**5**), M^+[*commo*-1,1′-Co{2,3-$(SiMe_3)_2$-(2,3-$C_2B_4H_4$)}$_2$]$^-$ (M = CoCl (**6a**), $Co_3(TMEDA)_3Cl_5$ (**6b**)), *commo*-1,1′-M[2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$]$_2$ (M = FeH (**7**), CoH (**8**), Ni (**10**)), and 1-(TMEDA)-*closo*-2,4-$(SiMe_3)_2$-1,2,4-$MC_2B_4H_4$ (M = Co (**9**), Ni (**11**)) were formed as products of the 1:1 molar ratio reactions of the respective MCl_2 salts with *closo-exo*-4,5-Li$(THF)_2$-1-Li$(THF)_2$-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ (**1**), *closo-exo*-4,5-Li(TMEDA)-1-Li(TMEDA)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ (**2**), *closo-exo*-5,6-[(μ-H)$_2$Li$(THF)_2$]-1-Li$(THF)_2$-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$ (**3**), and *closo-exo*-5,6-[(μ-H)$_2$Li(TMEDA)]-1-Li(TMEDA)-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$ (**4**), in yields ranging from 80 to 92%, as outlined in Schemes 1 and 2. The exceptions were the nickelacarboranes **10** and **11**, which were obtained in 37 and 59% yields, respectively.[4] In the case of *commo*-1,1′-Ni[2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$]$_2$ (**10**), the nickel is present in a formal oxidation state of +4, with the concomitant formation of Ni(0). Therefore, a 50% yield would be the maximum expected for this reaction. Reaction of $NiCl_2$ with the "carbons adjacent" carborane dianions **1** and **2** led directly to oxidative cage closure (**13**) or cage fusion (**14**) with no detectable metallacarborane products.[3] Reference to Schemes 1 and 2 shows that, with the exception of *exo*-4,4′,5,5′-Fe(TMEDA)-*commo*-1,1′-Fe[2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$]$_2$ (**5**), all *commo*-metallacarboranes were the results of a redox reaction in addition to a ligation process; the coproduct in all these reactions was the respective zerovalent metal. The only other redox-free ligation processes were found in the formations of the "carbons apart" *closo*-metallacarboranes 1-(TMEDA)-*closo*-2,4-$(SiMe_3)_2$-1,2,4-$MC_2B_4H_4$ (M = Co (**9**), Ni (**11**)). In both complexes the metal ions are coordinated to bidentate TMEDA molecules, as well as the more oxidation resistant "carbons apart" carboranes. On the other hand, the "carbons apart" carboranes favored a disproportion of Fe(II) in the formation of *commo*-1,1′-FeH[2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$]$_2$ (**7**) and Fe(0), even in the presence and absence of TMEDA. At present, there is no ready explanation as to why the "carbons adjacent" carborane gives the Fe(II) commo complex **5** while the "carbons apart" isomer supports Fe oxidation. It is tempting to envision a compound similar to **5**, which contains two Fe(II)'s, as a possible intermediate to **7**, which has an Fe(III), together with an Fe(0) coproduct. The proximity of the two iron atoms in **5** would facilitate electron transfer between them. This would be consistent with the results of Grimes and co-workers, who

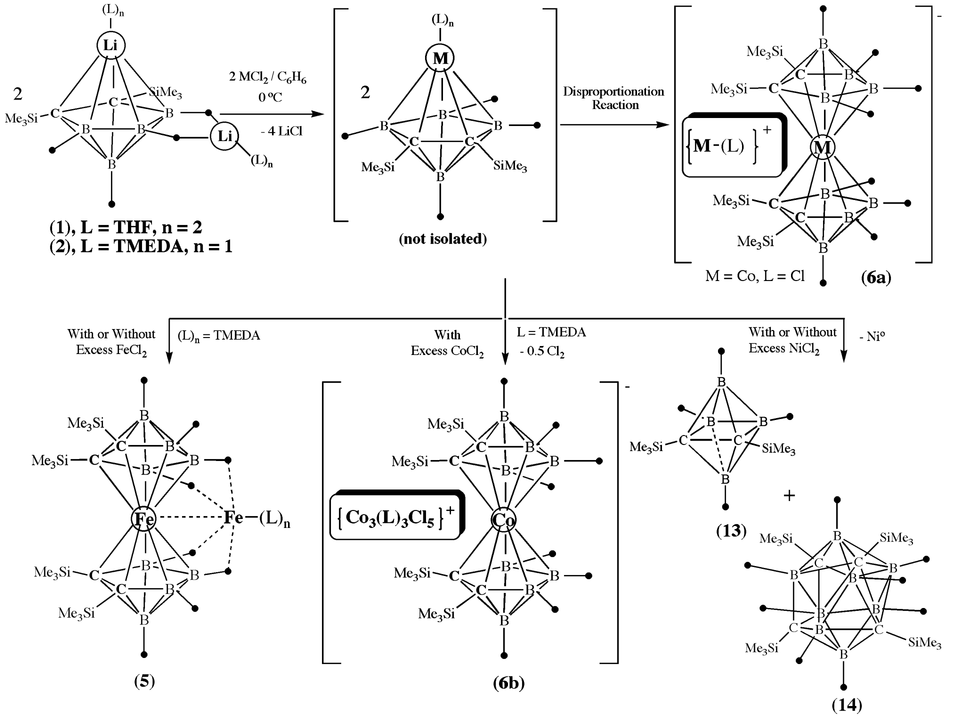
Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 5, 6b, 7, 9, and 12

		Compound **5**			
Fe(1)−Cnt1	1.643	Fe(1)−C(1)	2.079(4)	Fe(1)−C(2)	2.138(4)
Fe(1)−B(3)	2.136(4)	Fe(1)−B(4)	2.175(4)	Fe(1)−B(5)	2.128(4)
Fe(1)−Cnt2	1.647	Fe(1)−C(11)	2.053(4)	Fe(1)−C(12)	2.141(4)
Fe(1)−B(13)	2.179(4)	Fe(1)−B(14)	2.192(4)	Fe(1)−B(15)	2.108(5)
Fe(2)−N(41)	2.215(3)	Fe(2)−B(14)	2.224(4)	Fe(1)−Fe(2)	2.6450(7)
Fe(2)−B(4)	2.234(4)	Fe(2)−B(5)	2.425(4)	Fe(2)−B(15)	2.439(4)
Cnt1−Fe(1)−Cnt2	174.4	N(42)−Fe(2)−B(4)	120.91(14)	B(4)−Fe(1)−Fe(2)	54.16(11)
B(5)−Fe(1)−Fe(2)	59.92(12)	N(41)−Fe(2)−N(42)	81.10(11)	B(14)−Fe(2)−B(4)	104.71(15)
C(2)−Fe(1)−Fe(2)	125.08(10)	C(1)−Fe(1)−Fe(2)	103.59(10)	N(41)−Fe(2)−Fe(1)	138.03(9)
N(41)−Fe(2)−B(4)	116.94(14)	B(3)−Fe(1)−Fe(2)	96.99(13)	N(41)−Fe(2)−B(5)	93.73(13)
		Compound **6b**			
Co(1)−Cnt2	1.580	Co(1)−Cnt1	1.577	Co(2)−N(41)	2.130(4)
Co(1)−C(11)	2.012(3)	Co(1)−C(1)	2.016(3)	Co(2)−N(42)	2.155(4)
Co(1)−C(12)	2.016(3)	Co(1)−C(2)	2.006(3)	Co(2)−Cl(1)	2.4565(12)
Co(1)−B(13)	2.099(4)	Co(1)−B(3)	2.083(4)	Co(2)−Cl(2)	2.4740(12)
Co(1)−B(14)	2.167(4)	Co(1)−B(4)	2.157(4)	Co(2)−Cl(5)	2.4930(12)
Co(1)−B(15)	2.094(4)	Co(1)−B(5)	2.105(4)	Co(2)−Cl(4)	2.5120(13)
Co(3)−N(51)	2.135(3)	Co(4)−N(61)	2.172(3)	Co(4)−Cl(3)	2.4271(12)
Co(3)−N(52)	2.156(3)	Co(4)−Cl(2)	2.4680(13)	Co(4)−Cl(4)	2.4967(13)
Co(3)−Cl(3)	2.4380(12)	Co(4)−Cl(5)	2.5297(11)	Co(4)−N(62)	2.135(3)
Co(3)−Cl(1)	2.4511(12)	Co(3)−Cl(4)	2.5442(12)	Co(3)−Cl(5)	2.5393(12)
Cnt1−Co(1)−Cnt2	178.9	N(42)−Co(2)−Cl(4)	179.30(11)	N(41)−Co(2)−Cl(5)	178.18(1)
N(41)−Co(2)−Cl(1)	97.53(12)	Cl(2)−Co(2)−Cl(4)	81.93(4)	Cl(1)−Co(2)−Cl(5)	82.63(4)
N(41)−Co(2)−Cl(2)	97.22(12)	N(41)−Co(2)−N(42)	84.40(16)	N(41)−Co(2)−Cl(4)	95.49(13)
Cl(1)−Co(2)−Cl(2)	159.24(4)	N(42)−Co(2)−Cl(1)	98.51(11)	Cl(1)−Co(2)−Cl(4)	82.19(4)
N(42)−Co(2)−Cl(5)	93.79(11)	N(42)−Co(2)−Cl(2)	97.39(11)	Cl(5)−Co(2)−Cl(4)	86.32(4)
Cl(2)−Co(2)−Cl(5)	83.09(4)				
		Compound **7**			
Fe−Cnt1	1.642	Fe−Cnt2	1.618	Fe−B(5)	2.06(3)
Fe−B(2)	2.19(3)	Fe−B(12)	2.13(4)	Fe−B(15)	2.10(4
Fe−C(3)	2.14(2)	Fe−C(13)	2.16(2)	Fe−B(14)	2.09(3)
Fe−B(4)	2.08(3)				
Cnt1-Fe−Cnt2	175.1				
		Compound **9**			
Co−Cnt1	1.624	Co−C(1)	2.124(4)	Co−B(2)	2.084(5)
Co−C(3)	2.145(4)	Co−B(4)	2.084(5)	Co−B(5)	2.088(5)
Co−N(21)	2.049(4)	Co−N(22)	2.006(4)	N(21)−C(23)	1.459(7)
Cnt1−Co−N(21)	135.4	N(22)−Co−C(1)	139.10(18)	N(22)−Co−B(2)	176.3(2)
N(22)−Co−N(21)	85.75(17)	Cnt1−Co−N(22)	138.8	B(4)−Co−B(2)	75.5(2)
N(21)−Co−B(4)	156.0(2)	N(22)−Co−B(4)	101.84(19)	N(21)−Co−C(1)	113.97(17)
N(21)−Co−B(2)	95.65(19)				
		Compound **12**			
Ni−Cnt1	1.670	Ni−B(2)	2.150(4)	Ni−C(3)	2.116(3)
Ni−B(4)	2.132(4)	Ni−B(5)	2.105(4)	Ni−Cnt2	1.699
Ni−C(11)	2.225(3)	Ni−B(12)	2.096(4)	Ni−C(13)	2.238(3)
Ni−B(14)	2.070(3)	Ni−B(15)	2.213(4)	B(14)−N(41)	1.559(4)
B(15)−N(42)	1.422(4)	N(41)−C(46)	1.486(4)	N(42)−C(44)	1.447(4)
N(41)−C(45)	1.495(4)	N(41)−C(43)	1.512(4)	N(42)−C(47)	1.455(4)
Cnt1−Ni−Cnt2	179.2				

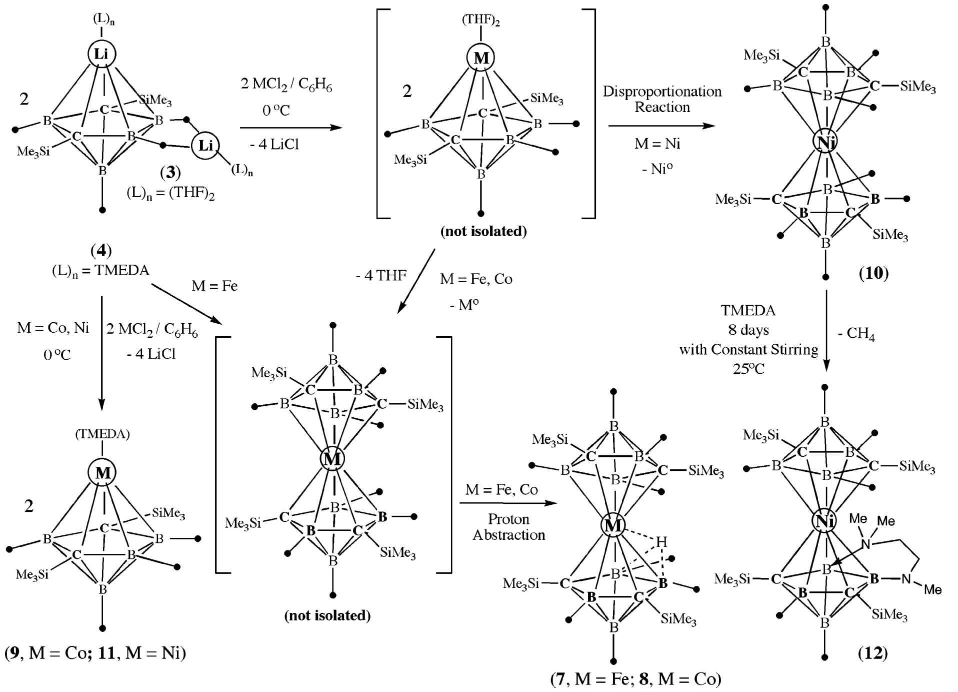
have identified the diiron compound $[2,3\text{-}(CH_3)_2\text{-}2,3\text{-}C_2B_4H_4]_2Fe\cdot Fe(L)_2$ (L = TMEDA, THF)[5c] as an intermediate to the *commo* compound $[(CH_3)_2C_2B_4H_4]_2FeH_2$, in the oxidative cage fusion to give $(CH_3)_4C_4B_8H_8$. However, compound **5** was produced in 90% yield and showed no tendency to react further in the absence of air. We find no evidence of a compound similar to **5** in the synthesis of **7**.

The results of the carborane/$CoCl_2$ reactions to a large extent parallel those of $FeCl_2$ in that, irrespective of the starting stoichiometry, both the THF (**1**) and TMEDA (**2**) solvated "carbons adjacent" carborane dianions produced the sandwich cobaltacarboranes **6a**,**b**. The structure of **6b** was unambiguously determined by X-ray diffraction to be a salt with a $[Co_3(TMEDA)_3Cl_5]^+$ cation and a $[$*commo*$\text{-}1,1'\text{-}Co\{2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4\}_2]^-$ anion. The structure of **6a** is postulated on the basis of **6b**. In the absence of structural data, it is not possible to ascertain the nature of the interaction of the $CoCl^+$ "cation" with the $[$*commo*$\text{-}1,1'\text{-}Co\{2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4\}_2]^-$ "anion"; a wedged complex similar to **5** might well exist. Unfortunately, no interpretable EPR spectra of either **6a** or **6b** could be obtained. The THF-solvated "carbons apart" dianion **3** reacted with $CoCl_2$, in a 1:1 molar ratio, to give the hydrido cobaltacarborane *commo*-$1,1'\text{-}CoH[2,4\text{-}(SiMe_3)_2\text{-}2,4\text{-}C_2B_4H_4]_2$ (**8**), similar to that found in the analogous $FeCl_2$ reaction. However, the reaction of $CoCl_2$ with the TMEDA solvated "carbons apart" dianion **4** produced *closo*-1-(TMEDA)-l-Co-$2,4\text{-}(SiMe_3)_2\text{-}2,4\text{-}C_2B_4H_4$ (**9**), even when excess **4** was available.[9]

While there is a parallel between the reactions of $CoCl_2$ and $FeCl_2$, the reactions of the carborane dianions with $NiCl_2$ produced quite different products.[4] The



Scheme 1. Proposed Reaction Pathways of "Carbons-Adjacent" *closo-exo*-4,5-Li(L)$_n$-1-Li(L)$_n$-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$ with MCl$_2$ (L = THF, n = 2; L = TMEDA, n = 1; M = Fe, Co, Ni)



Scheme 2. Plausible Reaction Pathways of "Carbons-Apart" *closo-exo*-5,6-[(μ-H)$_2$Li(L)$_n$]-1-Li(L)$_n$-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$ (L = THF, n = 2; L = TMEDA, n = 1; M = Fe, Co, Ni)

reaction of either the THF-solvated or the TMEDA-solvated "carbons adjacent" carborane **1** or **2** with NiCl$_2$ produced the oxidative cage closure product *closo*-1,2-(SiMe$_3$)$_2$-1,2-C$_2$B$_4$H$_4$ (**13**) and cage fusion product (SiMe$_3$)$_4$C$_4$B$_8$H$_8$ (**14**), in yields of 59−64% and 11%, respectively (see Scheme 1).[3,16,17] A similar oxidative cage closure/fusion was reported by Grimes and coworkers in the reactions of the alkyl-substituted carboranes [2,3-(R)$_2$-*nido*-2,3-C$_2$B$_4$H$_4$]$^{2-}$ with FeCl$_2$ or CoCl$_2$, followed by oxidation, except that the cage fusion product was dominant.[5−7] In these reactions, the fusion products were shown to arise from the intramolecular oxidation of (R$_2$C$_2$B$_4$H$_4$)$_2$FeH$_2$ or (R$_2$C$_2$B$_4$H$_4$)$_2$CoH intermediates.[5b] It could well be that the products **13** and **14** were the results of two different oxidation processes, one involving an intermediate of the form 1-L-2,3-(SiMe$_3$)$_2$-*closo*-1,2,3-NiC$_2$B$_4$H$_4$, leading to **13**, and another involving a *commo*-nickelacarborane, producing the fusion product **14**. The fact that **13** and **14** were formed by a disproportionation process, rather than reaction with an outside oxidizing agent, might also be important in determining the distribution of products. As was the case with $CoCl_2$ (vide supra),[9] the reaction of the "carbons apart" TMEDA-solvated dilithiacarborane **4** with $NiCl_2$ produced the half-sandwich species 1-(TMEDA)-2,4-$(SiMe_3)_2$-*closo*-1,2,4-$NiC_2B_4H_4$ in 59% yield.[4] On the other hand, the THF-solvated dilithiacarborane **3** produced the Ni^{IV} complex *commo*-1,1′-Ni[2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4]_2$ (**10**) in 37% yield, along with nickel metal.[4] The unusual charge-compensated nickelacarborane *commo*-1,1′-Ni^{III}-[(2,4-$(SiMe_3)_2$-5,6-B_2-{σ-N(Me)$(CH_2)_2$N$(Me)_2$}-2,4-$C_2B_2H_2$)(2′,4′-$(SiMe_3)_2$-2′,4′-$C_2B_4H_4$)] (**12**) was the product of the reaction of the Ni^{IV} complex **10** with carefully dried TMEDA. The high yield (89%) indicates that **12** is the main product of the reaction, rather than the result of an interesting side reaction. It is of interest to note that when the reaction was carried out in the presence of moisture, 1-(TMEDA)-*closo*-2,4-$(SiMe_3)_2$-1,2,4-$NiC_2B_4H_4$ (**11**) was formed in addition to 1,2-$(SiMe_3)_2$-*closo*-1,2-$C_2B_4H_4$ (**13**); this is the only example of an oxidative cage closure reaction of a "carbons apart" carborane encountered in our studies. Ni^{II}, Ni^{III}, and Ni^{IV} carborane complexes have all been reported in the larger, C_2B_9, cage system; Ni^{II} is involved in *closo*-metallacarboranes and the two higher oxidation states in commo complexes.[18,19] Hawthorne has recently proposed that the geometric changes accompanying the *commo*-Ni^{III}/Ni^{IV}-carborane interconversions could be used as a basis for constructing molecular gates.[12]

All results indicate that the reactions of the metal halides with either the "carbons adjacent" or "carbons apart" dianions proceed through the initial formation of a half-sandwich *closo*-metallacarborane, which may be sufficiently stabile to be isolated, as in the case of **9** and **11**, or could undergo further reaction, yielding full-sandwich *commo*-metallacarboranes and/or redox products. In this regard, it should be noted that the solvents used are all nonpolar (benzene, hexane) so that the reactions are most likely between ion clusters and aggregates. Under such conditions metal proximity is likely, which should facilitate metal−metal electron transfer. Thus, the large number of disproportionation processes described in the Experimental Section should not be surprising.

EPR Spectra and Electrochemistry. The ferracarborane obtained from the reaction of the "carbons apart" dilithium compound **1** or **2** was formulated as *commo*-1,1′-FeH[2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4]_2$ (**7**). Although the commo structure has been established by X-ray diffraction, the presence of the hydrido atom is inferred, primarily through EPR spectroscopy. Figure 1 shows the EPR spectrum of compound **7** in frozen THF at 90 K. The compound exhibits an intense EPR signal with $g_1 = 2.745$ and $g_{2,3} = 1.979$. This type of axial splitting is characteristic for low-spin d^5 sandwich compounds; the prototypical ferrocenium ion Fc^+ has $g_1 = 4.36$ and $g_{2,3} = 1.28$.[20] Whereas the average g values of 2.23 (**7**) and 2.31 (Fc^+) are not that different, the g anisotropy $\Delta g = g_1 - g_3$ is much larger for ferrocenium with 3.08 than for **7** with $\Delta g = 0.766$. The high symmetry of Fc^+ with the resulting near-degeneracy of spin-bearing orbitals is responsible for the unusually large deviations of the g components from the free-electron value of $g_e = 2.0023$, thus causing large g-anisotropies of substituted and especially unsubstituted ferrocenium.[20,21] In contrast, the low symmetry of **7** as confirmed by structure determination should lead to the lifting of orbital degeneracies and thus smaller Δg values. Despite these differences, based on symmetry, the EPR data clearly identify compound **7** as a ferrocenium-analogous iron(III) species. Therefore, charge balance requires the addition of H in the formulation of **7**.

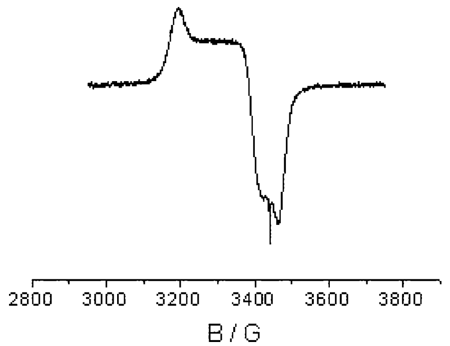


Figure 2. EPR spectrum of the reduction product of **10**.

The characteristics of a Ni^{III}-carborane complex were investigated by a combined study of the electrochemical/EPR spectra of the complex *commo*-1,1′-Ni[2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4]_2$ (**10**). Electrochemical reduction of the yellow Ni^{IV} complex in CH_2Cl_2/0.1 M Bu_4NPF_6 produced a green solution (λ_{max} 700 nm), which exhibits a rhombic g component pattern in its EPR spectrum measured at 4 K (see Figure 2). The values of $g_1 = 2.153$, $g_2 = 2.029$, and $g_3 = 1.989$ are compatible with the formulation of a Ni^{III} ($3d^7$) species related to nickelocenium derivatives.[22] The higher values for the Ni^{III}-carborane complex in comparison to the Jahn−Teller distorted decamethylnickelocenium cation in various environments[22] are in agreement with the lower symmetry and thus more extensive d-orbital splitting of the metallacarborane species.

NMR and IR Spectra. The infrared spectra of all new compounds were recorded and are given in the Experimental Section. The spectra show B−H stretching in the 2500 cm^{-1} region, as well as C−H stretching at their expected values. The spectra are all compatible with, but not diagnostic of, the formulations given in Schemes 1 and 2. Due to the paramagnetic nature of either the cations or anions of the compounds studied, only compound **8**, *commo*-1,1′-CoH[2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4]_2$, gave fully interpretable NMR spectra. The ^{11}B NMR spectra show resonances at δ 2.08, −3.72, and −11.91 ppm in a 2:1:1 peak area ratio, which is typical of the metallacarboranes in the C_2B_4 cage systems.[4,23] The most significant aspect of the ^1H NMR spectrum is the broad peak at δ −18.9 ppm assigned to the cobalt-

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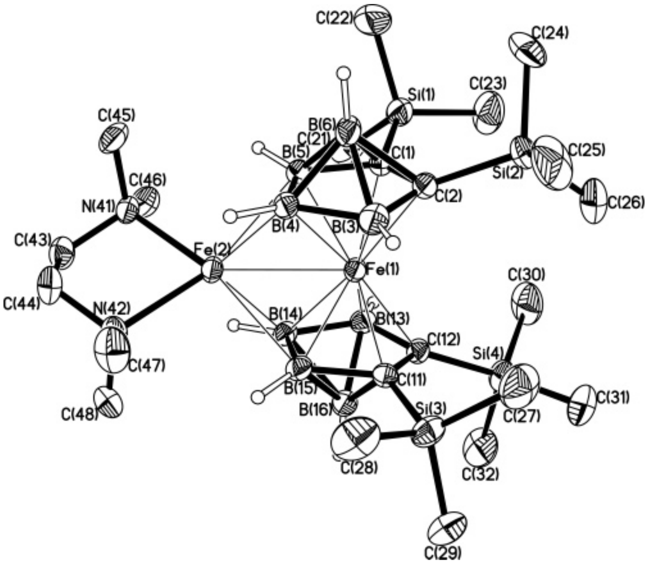

Figure 3. Perspective view of **5**. Thermal ellipsoids are drawn at the 50% probability level. The methyl and methylene hydrogens are omitted for clarity.

bound hydrogen, thereby confirming the formulation of **8** as having a CoH unit. The ^{1}H NMR spectrum of compound **7** showed a very broad resonance peak, ranging from δ −18 to −24 ppm, that could be attributed to a hydrogen in rapid equilibrium between a cage site and the Fe metal.

Crystal Structures. The solid-state structures of *exo*-4,4′,5,5′-Fe(TMEDA)-*commo*-1,1′-Fe-[2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4]_2$ (**5**), $[Co_3(TMEDA)_3Cl_5]^+$[*commo*-1,1′-Co-{2,3-$(SiMe_3)_2$-(2,3-$C_2B_4H_4$)}$_2]^-$ (**6b**), *commo*-1,1′-FeH[2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4]_2$ (**7**), 1-(TMEDA)-*closo*-2,4-$(SiMe_3)_2$-1,2,4-$CoC_2B_4H_4$ (**9**), and *commo*-1,1′-Ni^{III}-[(2,4-$(SiMe_3)_2$-5,6-B_2-{σ-N(Me)$(CH_2)_2$N$(Me)_2$}-2,4-$C_2B_2H_2$)(2′,4′-$(SiMe_3)_2$-2′,4′-$C_2B_4H_4$)] (**12**) were determined and are given in Figures 3−7, with Figure 4 showing both the anion and cation of **6b**. Tables 1 and 2 give the pertinent crystallographic data, and Table 3 lists some relevant bond distances and angles. The structures of the four full-sandwich compounds **5**, **6b**, **7**, and **12** show that each metal is bound symmetrically to the open C_2B_3 faces of the carboranes. The Co−Cnt1 and Co−Cnt2 distances in **6b** are 1.577 and 1.580 Å, with a Cnt1−Co−Cnt2 angle in **6b** of 178.9° showing the metal is symmetrically bound to two parallel carborane ligands. Compound **12** shows a similar symmetry with Ni−Cnt1 and Ni−Cnt2 distances of 1.670 and 1.699 Å, respectively, and a Cnt1−Ni−Cnt2 angle of 179.2°. These Ni−Cnt distances are longer than the 1.597 Å reported for the full-sandwich Ni(IV) complex **10**. The nearly equivalent Ni−carborane bonding in **12** is somewhat surprising in that the carborane with centroid Cnt2 is formally −1, due to the presence of the cationic boron-bound $-N(CH_3)_2$-$CH_2CH_2N(CH_3)-$ group; the only difference is the slightly longer Ni−Cnt2 distance.

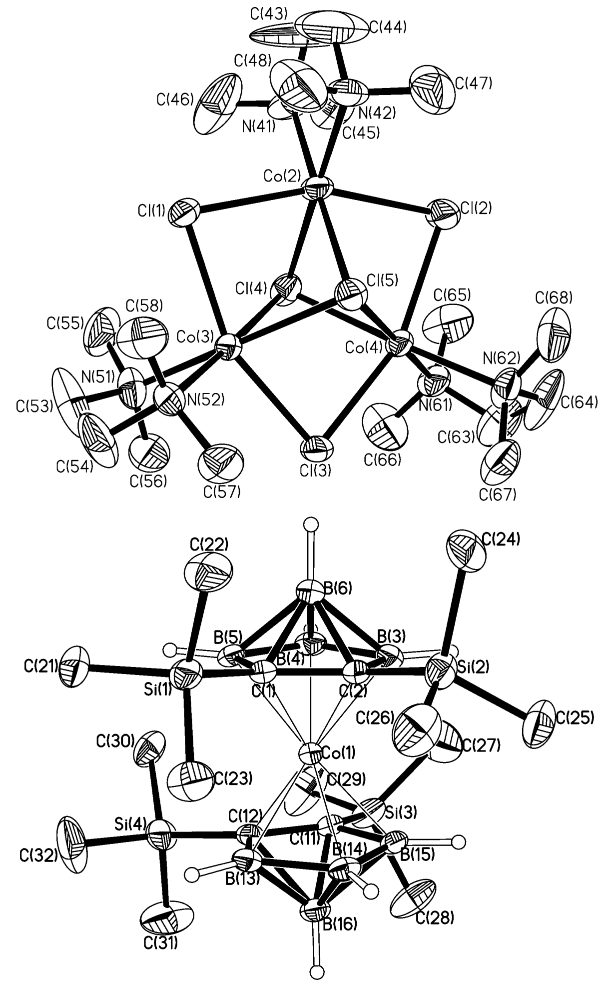

Figure 4. Perspective view of **6b**. Thermal ellipsoids are drawn at the 50% probability level. The methyl and methylene hydrogens are omitted for clarity.

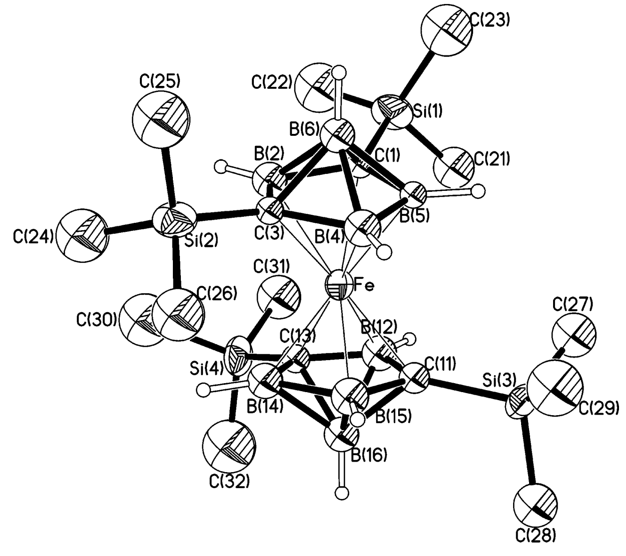

Figure 5. Perspective view of **7**. Thermal ellipsoids are drawn at the 50% probability level. The methyl hydrogens are omitted for clarity.

The structure of *exo*-4,4′,5,5′-Fe(TMEDA)-*commo*-1,1′-Fe-[2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4]_2$ (**5**), given in Figure 3, shows that one iron is equivalently bonded to the C_2B_3 open faces of two carborane cages (Fe(1)−Cnt(1) = 1.643 Å, Fe(1)−Cnt(2) = 1.647 Å) and the other occupies an exo-polyhedral position between the cages. This is structurally similar to the wedged diiron complex [2,3-$(CH_3C)_2B_4H_4]_2Fe_2(OCH_3)_2C_2H_4$, reported by Grimes and

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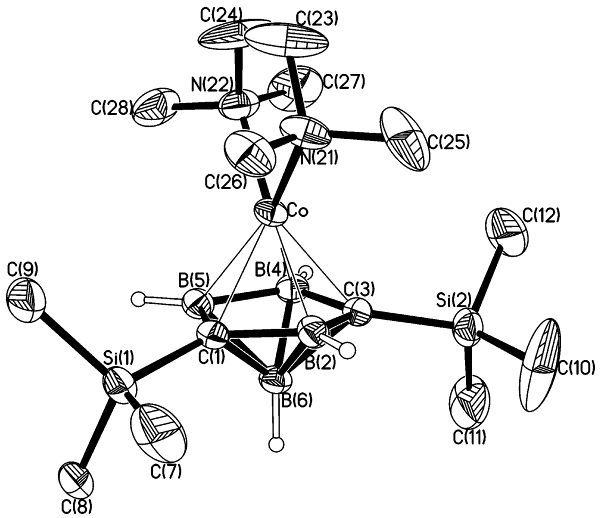

Figure 6. Perspective view of **9**. Thermal ellipsoids are drawn at the 50% probability level. The methyl and methylene hydrogens are omitted for clarity.

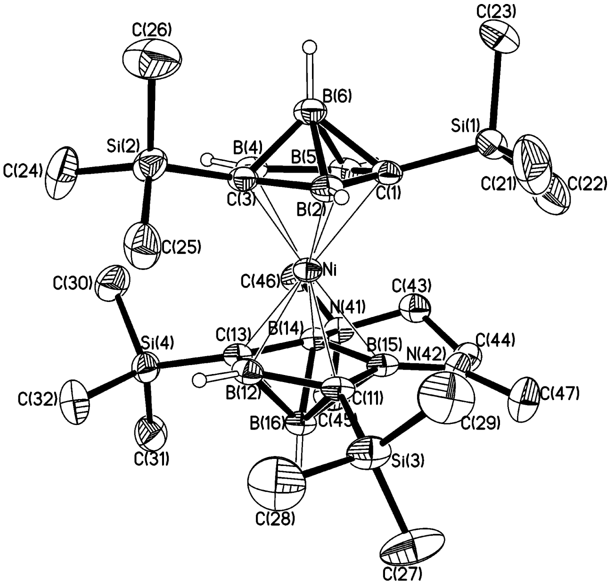

Figure 7. Perspective view of **12**. Thermal ellipsoids are drawn at the 50% probability level. The methyl and methylene hydrogens are omitted for clarity.

co-workers.[5c] The Fe(1)−Fe(2) distance in **5** is equal to 2.645 Å, which is substantially longer than the 2.414 Å reported by Grimes for the equivalent distance in the diiron wedged complex and the Fe−Fe distance of 2.571 Å found in 1,6-(η^5-C_5H_5)$_2$-1,6,2,3-$Fe_2C_2B_6H_8$.[24] In view of the long interiron distance in **5** there should be little direct Fe−Fe interaction; the exo-polyhedral Fe would be better described as being η^2-bonded by each of the two cages. Such bonding is commonly found in many metallacarboranes.[25]

One of the full-sandwich complexes, *commo*-1,1′-FeH-[2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$]$_2$ (**7**), has a hydrogen that is, presumably, metal-bound. The structure of the compound, given in Figure 5, shows no distortions that can be directly attributable to the presence of the hydrogen. The Fe seems symmetrically bonded to the two carborane ligands with an average Fe−[C(1),B(2), C(3), B(4), B(5)] length of 2.13 ± 0.05 Å and an average Fe−[C(11), B(12), C(13), B(14), B(15)] length of 2.11 ± 0.02 Å. The faces are not exactly parallel; the Cnt1−Fe−Cnt2 angle is 175.1°. An inspection of the differences in the distances between the atoms of the two rings reveals that the tilt is one favoring a shorter B(4)−B(15) distance (2.932 Å) compared to either the C(1)−B(12) (3.534) or the B(2)−C(13) (3.453 Å) distance. Although these differences are substantial, they are in the direction expected from the relative orientations of the bulky $SiMe_3$ groups and cannot be attributable to the presence of a hydrogen atom. Therefore, the presence of the extra hydrogen is inferred from the fact that the ESR spectrum of **7** clearly shows the presence of Fe(III) and the requirement of electrical neutrality with the two dianionic carborane ligands; there is no direct evidence for the hydrogen being directly bound to the metal. However, the requirement of electrical neutrality, coupled with the broad peak in the ^1H NMR spectrum of **7** (δ −18 to −24 ppm) which is in the region of the metal-bound hydrogen in *commo*-1,1′-CoH[2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$]$_2$ (**8**) and in [$(CH_3)_2C_2B_4H_4$]$_2$$FeH_2$,[5] forms the basis for the formulation of **7** as *commo*-1,1′-FeH[2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$]$_2$.

Conclusions. A series of both full- and half-sandwich metallacarboranes have been prepared from the reaction of MCl_2 (M = Fe, Co, Ni) with either the "carbons adjacent" or "carbons apart" dianion [2,*n*-$(SiMe_3)_2$-*nido*-2,*n*-$C_2B_4H_4$]$^{2-}$(n = 3, 4). In benzene solvent, the full-sandwich complexes *exo*-4,4′,5,5′-Fe(TMEDA)-*commo*-1,1′-Fe[2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$]$_2$ (**5**), [$Co_3(TMEDA)_3Cl_5$]$^+$-[*commo*-1,1′-Co{2,3-$(SiMe_3)_2$-(2,3-$C_2B_4H_4$)}$_2$]− (**6b**), *commo*-1,1′-FeH[2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$]$_2$ (**7**), and *commo*-1,1′-Ni[2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$]$_2$ (**10**) were obtained. With the exception of **5**, the syntheses of the *commo* products were the result of a tandem complexation/disproportionation process in which M^0 was also produced. On the other hand, the presence of good metal coordinating agents, such as TMEDA, could lead to the synthesis of half-sandwich metallacarboranes, such as 1-(TMEDA)-*closo*-2,4-$(SiMe_3)_2$-1,2,4-$CoC_2B_4H_4$ (**9**) and *closo*-1-(TMEDA)-l-Ni-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$ (**11**). These observations are consistent with the assumption that all the reactions proceed through an initial formation of a half-sandwich *closo*-metallacarborane, which, depending on the metal, carborane, and other ligands present, could be sufficiently stable to be isolated or could undergo further reaction, yielding full-sandwich, *commo*-metallacarborane, and/or redox products.

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Supporting Information Available: Tables of crystallographic data, including fractional coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates, of **5**, **6b, 7**, **9,** and **12** through combined CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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