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Registry No. 1, 80581-71-1; 2, 111112-81-3; 3a, 111112-80-2; 3b, 111112-82-4; 4, 111112-86-8; 5, 111112-87-9; 6 (BPh_4 salt), 111112-89-1; *cis*-$PtCl_2(PMe_3)_2$, 15630-86-1; *cis*-$PtCl_2(SEt_2)_2$, 15442-57-6; Ph_3SiH, 993-07-7; Ph_3GeH, 2816-43-5; Ph_3SnH, 892-20-6; $[Pt(PMe_3)_2(\mu\text{-}H)_2Pt(PMe_3)_2H][OCH_3]$, 111112-84-6; $CH_2{=}CH_2$, 74-85-1; $Pt(C_2H_4)(PMe_3)_2$, 69547-16-6; $PhC{\equiv}CPh$, 501-65-5; $Pt(PhC{\equiv}CPh)(PMe_3)_2$, 75982-99-9; *tert*-butylethylene, 558-37-2; allyl chloride, 107-05-1.

Supplementary Material Available: Tables of least-squares planes, anisotropic thermal parameters, and bond distances and angles for $Pt(C_2Ph_2)(PMe_3)_2$ and $[PtH(PMe_3)_3][BPh_4]$ and a table of hydrogen coordinates for $Pt(C_2Ph_2)(PMe_3)_2$ and a table of positional parameters for $[PtH(PMe_3)_3][BPh_4]$ (21 pages); listings of structure factors (69 pages). Ordering information is given on any current masthead page.

Synthesis of Metallacarborane Clusters Derived from the Monocarbon Carborane $9\text{-}(CH_3)_2S\text{-}7\text{-}[((CH_3)_3Si)_2CH]CB_{10}H_{11}$

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A single-crystal X-ray study of $9\text{-}Ph_3P\text{-}7\text{-}[((CH_3)_3Si)_2CH]CB_{10}H_{11}$ (I) has confirmed that the compound has a structure based on an 11-vertex nido cage geometry. Crystal data for I: space group $P2_1/n$; $Z = 4$; $a = 17.154$ (3) Å, $b = 11.999$ (2) Å, $c = 17.469$ (4) Å, $\beta = 108.2$ (1)°; $V = 3414.2$ Å^3. The structure was refined to a final $R = 0.061$ and $R_w = 0.073$ for the 2916 reflections having $F_o^2 > 3\sigma(F_o^2)$. The dimethyl sulfide analogue of I, $9\text{-}(CH_3)_2S\text{-}7\text{-}[((CH_3)_3Si)_2CH]CB_{10}H_{11}$, has been shown to be a versatile ligand for transition metals. The reaction of $9\text{-}(CH_3)_2S\text{-}7\text{-}[((CH_3)_3Si)_2CH]CB_{10}H_{11}$ and $(\eta\text{-}C_5H_5)Co(CO)_2$ in refluxing toluene resulted in a complex mixture from which three metallacarborane products could be characterized. Compounds II and III were shown to be the isomeric sandwich complexes $7\text{-}(CH_3)_2S\text{-}2\text{-}(\eta\text{-}C_5H_5)\text{-}1\text{-}[((CH_3)_3Si)_2CH]\text{-}2,1\text{-}CoCB_{10}H_9$ and $12\text{-}(CH_3)_2S\text{-}2\text{-}(\eta\text{-}C_5H_5)\text{-}1\text{-}[((CH_3)_3Si)_2CH]\text{-}2,1\text{-}CoCB_{10}H_9$, respectively. Also isolated in trace amounts was the zwitterionic compound IV, $12\text{-}[(\eta\text{-}C_5H_5)Co(\eta\text{-}C_5H_4)]^+[2\text{-}(\eta\text{-}C_5H_5)\text{-}1\text{-}[((CH_3)_3Si)_2CH]\text{-}2,1\text{-}CoCB_{10}H_9]^-$. Reaction of $[(\eta\text{-}C_5H_5)Ni(CO)]_2$ and $9\text{-}(CH_3)_2S\text{-}7\text{-}[((CH_3)_3Si)_2CH]CB_{10}H_{11}$ gave $2\text{-}(\eta\text{-}C_5H_5)\text{-}1\text{-}[((CH_3)_3Si)_2CH]\text{-}2,1\text{-}NiCB_{10}H_{10}$ (V), while reaction of the carborane with cobalt vapor and toluene gave $2\text{-}(\eta^6\text{-}C_6H_5CH_3)\text{-}1\text{-}[((CH_3)_3Si)_2CH]\text{-}2,1\text{-}CoCB_{10}H_{10}$ (VI). The sandwich structures of compounds of V and VI were confirmed by single-crystal X-ray crystallographic studies. Crystal data for V: space group $P\bar{1}$; $Z = 2$; $a = 8.856$ (1) Å, $b = 17.165$ (5) Å, $c = 8.647$ (1) Å, $\alpha = 103.14$ (1)°; $\beta = 114.51$ (1)°; $\gamma = 85.63$ (2)°; $V = 1164.5$ Å^3. The structure was refined to a final $R = 0.056$ and $R_w = 0.069$ for the 3726 reflections having $F_o^2 > 3\sigma(F_o^2)$. Crystal data for VI: space group $P\bar{1}$; $Z = 2$; $a = 8.803$ (2) Å, $b = 18.007$ (5) Å, $c = 8.663$ (2) Å, $\alpha = 101.09$ (2)°, $\beta = 114.16$ (2)°, $\gamma = 83.07$ (2); $V = 1228.1$ Å^3. The structure was refined to a final $R = 0.087$ and $R_w = 0.096$ for the 2355 reflections having $F_o^2 > 3\sigma(F_o^2)$.

Introduction

We recently reported[1] that the dimethyl sulfide promoted reaction of bis(trimethylsilyl)acetylene with decaborane(14) gives, as one of the major products, the new monocarbon carborane $9\text{-}(CH_3)_2S\text{-}7\text{-}[((CH_3)_3Si)_2CH]CB_{10}H_{11}$. From the spectroscopic data, the compound was proposed to have an 11-vertex nido-cage geometry, based on an icosahedron missing one vertex, with the dimethyl sulfide and bis(trimethylsilyl)methyl groups bound to the 9-boron and 7-carbon, respectively, on the open face. In addition, the ^1H NMR data indicated the presence of two boron–boron bridging hydrogens. We have now found that the dimethyl sulfide group can be readily displaced by triphenylphosphine and a single-crystal X-ray study of the resulting compound $9\text{-}Ph_3P\text{-}7\text{-}[((CH_3)_3Si)_2CH]CB_{10}H_{11}$ has confirmed the proposed structures of these carboranes.

It was also demonstrated[1] that under appropriate conditions the dimethyl sulfide and/or the two bridging hydrogens can be removed from $9\text{-}(CH_3)_2S\text{-}7\text{-}[((CH_3)_3Si)_2CH]CB_{10}H_{11}$. For example, reaction of the compound with lithium triethylborohydride results in hydrogen loss, dimethyl sulfide dissociation, and cage closure to yield the *closo*-$RCB_{10}H_{10}^-$ anion, while thermolysis of the compound results in hydrogen loss and cage closure to give the isoelectronic neutral carborane *closo*-$RCB_{10}H_9{\cdot}SMe_2$. These results suggested that $9\text{-}(CH_3)_2S\text{-}7\text{-}[((CH_3)_3Si)_2CH]CB_{10}H_{11}$ might also function as a versatile transition-metal ligand similar to other known eleven-vertex monocarbon carboranes.[2] Thus, depending on whether the bridge protons and/or the dimethyl sulfide are removed from the cage either of the anions $RCB_{10}H_{10}^{3-}$

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and $RCB_{10}H_9SMe_2^{2-}$ could be formed. Each of these anions should have nido-cage geometries and function as six-electron ligands when bound to transition metals. We report here the synthesis and characterization of a number of such transition-metal sandwich complexes containing these two different anions.

Experimental Section

Materials and Procedures. The monocarbon carborane 9-$(CH_3)_2S$-7-$[((CH_3)_3Si)_2CH]CB_{10}H_{11}$ was prepared by using the previously reported method.[1] Cyclopentadienylcobalt dicarbonyl was purchased from Strem Chemicals and used as received. Cyclopentadienylnickel carbonyl dimer and cobalt powder (50 mesh) were obtained from Alfa Products/Ventron Division. Toluene was obtained from Baker Chemical Co. and dried prior to use. Triphenylphosphine was obtained from Aldrich. All reaction solvents were reagent grade and dried according to literature methods. Preparative thin-layer chromatography was conducted on 0.5 mm (20 × 20 cm) silica gel F-254 plates (Merck).

Proton NMR spectra, at 250 MHz, were obtained on a Bruker WH-250 Fourier transform spectrometer. Boron-11 NMR spectra, at 64.2, 115.5, and 160.5 MHz, were obtained on IBM WP200SY, Bruker WH-360, and Bruker AM-500 Fourier transform spectrometers, respectively. All boron-11 chemical shifts are referenced to $BF_3 \cdot O(C_2H_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift. All proton chemical shifts were measured relative to internal residual solvent from the lock solvents used (99.5% C_6D_6 and 99.8% $CDCl_3$) and are referenced to tetramethylsilane (0.0 ppm) with positive values indicating downfield shifts. High- and low-resolution mass spectra were obtained on a Hitachi Perkin-Elmer RMH-2 mass spectrometer and/or a VG Micromass 7070H mass spectrometer interfaced to a Kratos DS50S data system. Infrared spectra were obtained on a Perkin-Elmer 337 or 1310 spectrophotometer. All melting points are uncorrected.

The metal atom apparatus employed in these studies was based on a design by Klabunde[3] and is described elsewhere.[4]

Reaction of 9-$(CH_3)_2S$-7-$[((CH_3)_3Si)_2CH]CB_{10}H_{11}$ and PPh_3. In a 100-mL flask equipped with a high vacuum stopcock were added 0.75 g (2.13 mmol) of 9-$(CH_3)_2S$-7-$[((CH_3)_3Si)_2CH]CB_{10}H_{11}$ and 0.56 g (2.14 mmol) of PPh_3. The flask was degassed, and 30 mL of dry benzene was condensed in. The resulting solution was then heated at reflux for 3 days, after which the solvent was removed under vacuum. The resulting yellow solid was dissolved in CH_2Cl_2, and then pentane was added dropwise until the solution started to turn turbid. The solution was placed in a refrigerator overnight at −5 °C which then resulted in the precipitation of 0.95 g (1.70 mmol, 80% yield) of crystalline 9-Ph_3P-7-$[((CH_3)_3Si)_2CH]CB_{10}H_{11}$ (I): white; mp 230–232 °C; mass calcd for $^{12}C_{26}{}^{1}H_{45}{}^{11}B_{10}{}^{31}P^{28}Si_2$ 554.3727, found 554.3524.

Reaction of 9-$(CH_3)_2S$-7-$[((CH_3)_3Si)_2CH]CB_{10}H_{11}$ and (η-C_5H_5)$Co(CO)_2$. In a 250-mL, three-neck flask, fitted with a condenser, gas inlet, and bubbler were placed 0.6234 g (1.76 mmol) of 9-$(CH_3)_2S$-7-$[((CH_3)_3Si)_2CH]CB_{10}H_{11}$ along with 100 mL of dry toluene. After the system was flushed for several minutes with nitrogen gas, 0.6333 g (3.52 mmol) of (η-C_5H_5)$Co(CO)_2$ was added to the solution. The mixture was then heated at reflux for 2 h. The resulting black solution was cooled to room temperature, concentrated, filtered through silica gel, and then separated by preparative TLC. Elution in benzene gave six bands.

Two of these bands were identified: 7-$(CH_3)_2S$-2-(η-C_5H_5)-1-$[((CH_3)_3Si)_2CH]$-2,1-$CoCB_{10}H_9$ (II) [R_f 0.24; 0.0808 g, 9.6% based on starting carborane; orange crystals; mp 250 °C dec; mass measurement calcd for $^{12}C_{15}{}^{1}H_{39}{}^{11}B_{10}{}^{32}S^{28}Si_2{}^{59}Co$ 476.2597, found 476.2568] and 12-$(CH_3)_2S$-2-(η-C_5H_5)-1-$[((CH_3)_3Si)_2CH]$-2,1-$CoCB_{10}H_9$ (III) [R_f 0.71; 0.0340 g, 4.1% based on starting carborane; red, oily solid; mass measurement calcd for $^{12}C_{15}{}^{1}H_{39}{}^{11}B_{10}{}^{32}S^{28}Si_2{}^{59}Co$ 476.2597, found 476.2601].

The base line (R_f 0.0) was further purified by TLC, using chloroform as the mobile phase. The second band obtained from this separation (R_f 0.16) was repurified by TLC in ethyl acetate as solvent to give 12-[(η-C_5H_5)Co(η-C_5H_4)]$^+$[2-(η-C_5H_5)-1-$[((CH_3)_3Si)_2CH]$-2,1-$CoCB_{10}H_9$]$^-$ (IV) [R_f 0.10; 0.0097 g, 0.90% based on starting carborane; yellow-orange crystals, mp 285 °C; mass measurement calcd for $^{12}C_{23}{}^{1}H_{42}{}^{11}B_{10}{}^{28}Si_2{}^{59}Co_2$ 602.2420, found 602.2082].

The remaining bands were not obtained in sufficient quantities to allow full characterization.

Reaction of [(η-C_5H_5)Ni(CO)]$_2$ and 9-$(CH_3)_2S$-7-$[((CH_3)_3Si)_2CH]CB_{10}H_{11}$. In a 250-mL, two-neck, round-bottom flask fitted with condenser and gas inlet were placed 0.2500 g (0.71 mmol) of 9-$(CH_3)_2S$-7-$[((CH_3)_3Si)_2CH]CB_{10}H_{11}$ and 0.2100 g (0.71 mmol) of [(η-C_5H_5)Ni(CO)]$_2$ dissolved in 75 mL of dry mesitylene. The solution was flushed with N_2 and then heated at reflux for 2 h. A black precipitate formed during the course of the reaction that was filtered after the solution was cooled to room temperature. The resulting dark red solution was concentrated and separated into six components by preparative TLC using benzene as the

Table I. ^{11}B NMR Data

compd	δ (J, Hz)	rel intensities
I[a,b]	−0.04 (145), −1.73 (155), −5.09,[c] −7.36 (157), −18.96 (123), −23.30 (145), −26.88 (133), −28.63 (144)	1:1:1:2:1:1:2:1
II[d,e]	3.30,[f] 2.07 (144), 1.47,[f] 0.03 (158), −1.90 (151), −10.85 (135), −11.44,[c] −12.68,[f] −14.31 (146)	1:1:1:1:1:1:1:1:2
III[d,e]	−2.00 (125), −3.00 (115), −5.77,[c] −13.64 (137), −14.81 (146)	3:2:1:2:2
IV[d,e]	0.75 (141), −1.05 (121), −6.41,[c], −11.05 (132), −14.38 (147)	4:1:1:2:2
V[b,d]	21.67 (102), 20.98 (121), 13.40 (156), 0.73 (147), −0.65 (135), −5.11 (157)	1:2:2:2:1:2
VI[e,g]	16.09 (169), 13.27 (146), 7.88 (153), −3.69 (142), −8.33 (142)	1:2:2:3:2

[a] 160.5 MHz. [b] C_6D_6 solvent. [c] Singlet. [d] 115.5 MHz. [e] $CDCl_3$ solvent. [f] Coupling constants could not be reliably calculated due to overlapping peaks. [g] 64.2 MHz.

Table II. ^1H NMR Data

compd	δ (assignt)
I[a,b]	7.62 (2, m, C_6H_5P), 7.59 (3, m, C_6H_5P), 0.92 (1, CH), 0.06 (18, Me_3Si)
II[a,b]	5.14 (5, C_5H_5), 2.58 (3, CH_3S), 2.37 (3, CH_3S), 1.35 (1, CH), 0.21 (9, $SiMe_3$), 0.19 (9, $SiMe_3$)
III[a,b]	5.15 (5, C_5H_5), 2.31 (6, $(CH_3)_2S$), 1.44 (1, CH), 0.18 (18, $SiMe_3$)
IV[a,b]	5.41 (5, C_5H_5), 5.32 (2, C_5H_4), 5.17 (2, C_5H_4), 5.08 (5, C_5H_5), 1.54 (1, CH), 0.21 (18, $SiMe_3$)
V[a,c]	4.87 (5, C_5H_5), 1.35 (1, CH), 0.24 (18, $SiMe_3$)
VI[a,b]	7.02 (t, 1, C_6H_5), 6.56 (t, 2, C_6H_5), 6.36 (d, 2, C_6H_5), 1.57 (1, CH), 1.24 (3, $PhCH_3$), 0.27 (18, $SiMe_3$)

[a] 250 MHz. [b] $CDCl_3$ solvent. [c] C_6D_6 solvent.

Table III. IR Data (cm^{-1})[a]

I[b]	3090 (w), 3060 (m), 2980 (m), 2940 (m), 2920 (m), 2900 (m), 2580 (sh), 2545 (s), 1975 (w), 1965 (w), 1920 (w), 1890 (w), 1820 (w), 1590 (m), 1570 (w), 1480 (s), 1430 (s), 1400 (w), 1330 (w), 1310 (w), 1260 (sh), 1245 (s), 1235 (sh), 1210 (m), 1190 (m), 1160 (m), 1110 (s), 1090 (s), 1025 (s), 1000 (s), 985 (m), 935 (m), 900 (m), 865 (sh), 840 (s), 760 (sh), 745 (s), 715 (m), 690 (s), 660 (sh), 640 (m), 620 (m), 600 (w), 560 (w), 510 (s), 490 (sh), 460 (sh), 410 (m), 340 (w), 300 (w)
II[b]	2900 (m), 2600 (m), 2500 (s), 2350 (sh), 1410 (s), 1370 (s), 1270 (s), 1260 (s), 1210 (sh), 1080 (sh), 1020 (sh), 1000 (s), 940 (m), 920 (m), 850 (s, br), 670 (m), 630 (m)
III[c]	2950 (sh), 2900 (m), 2870 (sh), 2600 (sh), 2500 (s), 1620 (w), 1440 (m), 1370 (s), 1240 (s), 1090 (sh), 1010 (s), 960 (sh), 860 (sh), 840 (s), 820 (sh), 800 (sh), 670 (sh), 630 (m)
V[c]	3030 (m), 2920 (m), 2510 (sh), 2470 (s), 1440 (s), 1280 (s), 1250 (s), 1070 (sh), 1020 (s), 930 (sh), 840 (s, br), 750 (sh)
VI[b]	3037 (w), 2990 (m), 2975 (m), 2900 (sh), 2615 (m), 2515 (s), 1470 (m), 1420 (m), 1375 (m), 1250 (s), 1205 (w), 1165 (w), 1085 (w), 1020 (s), 980 (sh), 930 (m), 900 (m), 860 (sh), 840 (s), 750 (w), 680 (m), 650 (sh), 610 (w)

[a] KBr pellet. [b] Perkin-Elmer 1310. [c] Perkin-Elmer 337.

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Table IV. Data Collection and Structure Refinement Information

	I	IV	V
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a, Å	17.154 (3)	8.856 (1)	8.803 (2)
b, Å	11.999 (2)	17.165 (5)	18.007 (5)
c, Å	17.469 (4)	8.647 (1)	8.663 (2)
α, deg		103.14 (1)	101.09 (2)
β, deg	108.2 (1)	114.51 (1)	114.16 (2)
γ, deg		85.63 (2)	83.07 (2)
V, Å^3	3414.2	1164.5	1228.1
Z	4	2	2
ρ(calcd), g cm^{-3}	1.076	1.176	1.192
cryst dimens, mm	0.05 × 0.30 × 0.05	0.125 × 0.40 × 0.36	0.075 × 0.23 × 0.30
mol formula	$C_{26}H_{45}B_{10}PSi_2$	$C_{13}H_{34}B_{10}NiSi_2$	$C_{15}H_{37}B_{10}CoSi_2$
mol wt	552.90	412.40	440.68
λ, Å	Mo Kα, 0.71703	Mo Kα, 0.71703	Mo Kα, 0.71703
scanning range, deg	$4° \le 2\theta \le 50°$	$0° \le 2\theta \le 55°$	$0° \le 2\theta \le 50°$
scan mode	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
$\pm h,\pm k,\pm l$, collected	20,14,±20	11,±22,±11	±10,±21,−10
no. of measured *I*'s	5985	5690	4633
no. of $F_o^2 > 3\sigma(F_o^2)$	2916	3726	2355
no. of variables	352	235	253
abs coeff (μ), cm^{-1}	1.62	9.33	7.93
trans. coeff, %	98.4	83.6	91.8
max, min, %	99.2, 92.2	89.3, 67.3	94.4, 84.9
R	0.061	0.056	0.087
R_w	0.073	0.069	0.096

Table V. Atomic Positional Parameters and Their Estimated Standard Deviations for 9-Ph_3P-7-[$((CH_3)_3Si)_2CH$]$CB_{10}H_{11}$ (I)

atom	*x*	*y*	*z*	*B*, Å^2
P	0.36213 (7)	0.0243 (1)	0.76287 (7)	2.92 (2)
Si1	0.71249 (9)	−0.3432 (1)	0.7216 (1)	4.80 (4)
Si2	0.5692 (1)	−0.2227 (2)	0.5838 (1)	5.77 (4)
B1	0.5556 (4)	−0.2258 (6)	0.9015 (4)	5.1 (2)
B2	0.5839 (4)	−0.3063 (6)	0.8308 (4)	4.5 (2)
B3	0.6113 (3)	−0.1676 (5)	0.8430 (3)	3.9 (1)
B4	0.5292 (3)	−0.0891 (5)	0.8595 (3)	3.9 (1)
B5	0.4515 (4)	−0.1904 (6)	0.8581 (4)	5.1 (2)
B6	0.4850 (4)	−0.3233 (5)	0.8396 (4)	5.3 (2)
B8	0.5403 (3)	−0.0955 (5)	0.7603 (3)	3.5 (1)
B9	0.4377 (3)	−0.0986 (5)	0.7768 (3)	3.1 (1)
B10	0.4073 (3)	−0.2485 (5)	0.7629 (4)	4.5 (2)
B11	0.4965 (3)	−0.3140 (5)	0.7404 (4)	4.2 (1)
C7	0.5716 (3)	−0.2228 (4)	0.7492 (3)	3.1 (1)
C1	0.6282 (3)	−0.2333 (4)	0.6948 (3)	3.8 (1)
C11	0.3010 (2)	0.0097 (4)	0.8297 (3)	3.1 (1)
C12	0.3375 (3)	0.0164 (5)	0.9131 (3)	4.2 (1)
C13	0.2908 (3)	0.0031 (5)	0.9639 (3)	5.0 (1)
C14	0.2082 (3)	−0.0181 (6)	0.9320 (3)	5.9 (2)
C15	0.1715 (3)	−0.0270 (5)	0.8502 (3)	5.4 (1)
C16	0.2172 (3)	−0.0127 (4)	0.7976 (3)	3.9 (1)
C17	0.4151 (3)	0.1575 (4)	0.7811 (3)	3.3 (1)
C18	0.4090 (3)	0.2318 (5)	0.8398 (3)	5.1 (1)
C19	0.4539 (4)	0.3298 (5)	0.8523 (3)	6.2 (2)
C20	0.5034 (3)	0.3552 (5)	0.8062 (3)	5.6 (2)
C21	0.5090 (3)	0.2812 (5)	0.7474 (3)	5.3 (1)
C22	0.4650 (3)	0.1834 (4)	0.7337 (3)	4.4 (1)
C23	0.2918 (2)	0.0302 (4)	0.6614 (2)	3.4 (1)
C24	0.2527 (3)	0.1306 (5)	0.6313 (3)	4.8 (1)
C25	0.1940 (3)	0.1341 (6)	0.5560 (3)	6.3 (2)
C26	0.1757 (3)	0.0378 (7)	0.5105 (3)	7.1 (2)
C27	0.2147 (4)	−0.0622 (6)	0.5389 (3)	6.5 (2)
C28	0.2725 (3)	−0.0654 (5)	0.6146 (3)	4.9 (1)
CA	0.7734 (3)	−0.3317 (6)	0.6500 (4)	6.8 (2)
CB	0.7884 (3)	−0.3209 (6)	0.8236 (4)	6.6 (2)
CC	0.6733 (4)	−0.4894 (5)	0.7168 (4)	7.6 (2)
CD	0.5400 (5)	−0.3608 (7)	0.5341 (4)	10.1 (2)
CE	0.6336 (4)	−0.1483 (8)	0.5310 (4)	10.0 (2)
CF	0.4712 (4)	−0.1442 (7)	0.5632 (4)	8.5 (2)

eluent. The first band, which was the major product, was identified as 2-(η-C_5H_5)-1-[$((CH_3)_3Si)_2CH$]-2,1-$NiCB_{10}H_{10}$ (V) [R_f 0.81; 0.1004 g (0.24 mmol), 34%; red crystals; mp 212 °C dec; mass measurement calcd for $^{12}C_{13}{}^{1}H_{34}{}^{11}B_{10}{}^{28}Si_2{}^{60}Ni$ 416.2438, found 416.2328].

The third band was identified as unreacted carborane, by comparison of its ^{11}B NMR spectrum to that of an authentic sample.[1] The remaining bands were not present in sufficient amounts (<1 mg) to allow complete characterization.

Reaction of [(η-C_5H_5)Ni(CO)]$_2$ and [2-($((CH_3)_3Si)_2CH$)C$B_{10}H_{10}$]$^-$. The Na^+ salt of [2-($((CH_3)_3Si)_2CH$)$CB_{10}H_{10}$]$^-$ was prepared according to the published procedure.[1] A 100-mL, round-bottom flask equipped with a high vacuum stopcock was charged with 0.35 g (1.11 mmol) of Na^+[2-($((CH_3)_3Si)_2CH$)-$CB_{10}H_{10}$]$^-$ and 0.33 g (1.08 mmol) of [(η-C_5H_5)Ni(CO)]$_2$. The flask was degassed, and 30 mL of dry THF was condensed in. The solution was then heated at reflux for 3 h. The bright red solution was filtered through a medium frit and the filtrate evaporated to dryness.

The resulting bright red solid was dissolved in 5 mL of dry CH_2Cl_2 and chromatographed by preparative TLC using benzene as the eluent. The major product was identified by its ^{11}B NMR and ^{1}H NMR spectra to be compound V and was obtained in 25% yield (0.11 g).

Reaction of Cobalt Vapor, Toluene and 9-$(CH_3)_2S$-7-[$((CH_3)_3Si)_2CH$]$CB_{10}H_{11}$. Approximately 1.5 g of cobalt powder was placed in an integral tungsten alumina crucible in a static metal atom reactor.[4] In the bottom of the reactor was placed 2.500 g (7.1 mmol) of 9-$(CH_3)_2S$-7-[$((CH_3)_3)Si)_2CH$]$CB_{10}H_{11}$. The flask was evacuated and cobalt vapor condensed with 15 mL of dry toluene over a ~2-h period onto the walls of the reactor. Following metal deposition, the matrix was warmed to room temperature and stirred for 1 h. The excess toluene was evaporated in vacuo and the resulting black residue dissolved in CH_2Cl_2. The resulting solution was treated with silica gel, filtered, and separated into two bands by TLC using a 60:40 benzene/hexane mixture.

The first band (R_f 0.31) was identified as 2-(η^6-$C_6H_5CH_3$)-1-[$((CH_3)_3Si)_2CH$]-2,1-$CoCB_{10}H_{10}$ (VI) [0.020 g, 6.4% based on starting carborane; red-green crystals]. The second band (R_f 0.59) was identified as unreacted 9-$(CH_3)_2S$-7-[$((CH_3)_3Si)_2CH$]$CB_{10}H_{11}$ by comparison of its ^{11}B NMR spectrum to that of an authentic sample.[1]

Crystallographic Data for 9-Ph_3P-7-[$((CH_3)_3Si)_2CH$]-$CB_{10}H_{11}$ (I), 2-(η-C_5H_5)-1-[$((CH_3)_3Si)_2CH$]-2,1-$NiCB_{10}H_{10}$ (V), and 2-(η^6-$C_6H_5CH_3$)-1-[$((CH_3)_3Si)_2CH$]-2,1-$CoCB_{10}H_{10}$ (VI). Single crystals of I, V, and VI were grown overnight by slow evaporation in air of methylene chloride/heptane solutions. In each case, a suitably sized crystal was mounted and transferred to the diffractometer. Refined cell dimensions and their standard deviations were obtained from least-squares refinement of 20–25 accurately centered reflections. See Table IV for crystal data.

Collection and Reduction of the Data. Diffraction data were collected at 295 K on an Enraf-Nonius four-circle CAD-4 dif-

Table VI. Atomic Positional Parameters and Their Estimated Standard Deviations for 2-(η-C_5H_5)-1-[$((CH_3)_3Si)_2CH$]-2,1-$NiCB_{10}H_{10}$ (V)

atom	*x*	*y*	*z*	*B*, Å^2
Ni	0.19610 (5)	0.12981 (3)	0.36612 (5)	3.445 (9)
Si1	0.6258 (1)	0.30458 (8)	0.7735 (2)	5.52 (3)
Si2	0.2721 (2)	0.37691 (8)	0.6185 (2)	5.87 (4)
B3	0.4468 (5)	0.1247 (3)	0.4337 (5)	3.9 (1)
B4	0.5391 (5)	0.1972 (3)	0.3846 (6)	4.7 (1)
B5	0.3821 (6)	0.2573 (3)	0.2718 (6)	4.8 (1)
B6	0.1898 (5)	0.2192 (3)	0.2435 (5)	4.0 (1)
B7	0.3188 (5)	0.0582 (3)	0.2240 (5)	4.2 (1)
B8	0.5069 (5)	0.0993 (3)	0.2591 (6)	5.0 (1)
B9	0.4669 (6)	0.1807 (4)	0.1569 (6)	5.8 (1)
B10	0.2508 (6)	0.1955 (3)	0.0706 (5)	5.3 (1)
B11	0.1538 (6)	0.1188 (3)	0.1054 (5)	4.4 (1)
B12	0.3322 (6)	0.0973 (3)	0.0606 (5)	5.2 (1)
C1	0.3716 (4)	0.2220 (2)	0.4344 (4)	3.34 (8)
C1A	0.3989 (4)	0.2813 (2)	0.6102 (4)	3.73 (8)
C11	0.0161 (6)	0.0494 (3)	0.3128 (6)	7.8 (1)
C12	−0.0463 (5)	0.1259 (4)	0.3431 (6)	7.5 (1)
C13	0.0551 (5)	0.1615 (3)	0.5141 (5)	6.6 (1)
C14	0.1726 (6)	0.1087 (3)	0.5833 (5)	6.8 (1)
C15	0.1528 (6)	0.0398 (3)	0.4639 (6)	7.3 (1)
CA	0.7411 (6)	0.2140 (4)	0.8316 (7)	8.0 (2)
CB	0.6296 (8)	0.3635 (4)	0.9852 (7)	8.4 (2)
CC	0.7429 (6)	0.3634 (4)	0.7026 (8)	8.9 (2)
CD	0.2234 (6)	0.3909 (4)	0.8108 (7)	8.7 (2)
CE	0.3819 (8)	0.4663 (3)	0.6323 (7)	8.5 (2)
CF	0.0631 (8)	0.3810 (4)	0.447 (1)	12.9 (2)

Table VII. Atomic Positional Parameters and Their Estimated Standard Deviations for 2-(η^6-$C_6H_5CH_3$)-1-[$((CH_3)_3Si)_2CH$]-2,1-$CoCB_{10}H_{10}$ (VI)

atom	*x*	*y*	*z*	*B*, Å^2
Co	0.8514 (2)	0.65006 (8)	0.8315 (2)	2.73 (3)
Si1	0.3939 (4)	0.8095 (2)	0.5630 (4)	5.01 (9)
Si2	0.7346 (4)	0.8855 (2)	0.7792 (5)	5.6 (1)
B3	0.599 (1)	0.6419 (6)	0.762 (1)	2.9 (3)
B4	0.490 (1)	0.7073 (7)	0.857 (2)	4.1 (3)
B5	0.640 (1)	0.7667 (7)	1.022 (1)	3.8 (3)
B6	0.840 (1)	0.7340 (7)	1.027 (1)	3.5 (3)
B7	0.730 (1)	0.5821 (7)	0.912 (1)	3.4 (3)
B8	0.531 (1)	0.6157 (7)	0.906 (1)	3.7 (3)
B9	0.558 (1)	0.6934 (8)	1.070 (2)	4.4 (3)
B10	0.775 (2)	0.7116 (7)	1.173 (1)	4.2 (3)
B11	0.880 (1)	0.6401 (6)	1.076 (1)	3.1 (3)
B12	0.704 (1)	0.6141 (8)	1.015 (1)	4.0 (3)
C1	0.658 (1)	0.7342 (5)	0.834 (1)	2.7 (2)
C1A	0.622 (1)	0.7912 (5)	0.704 (1)	3.5 (3)
C11	0.875 (1)	0.5650 (6)	0.630 (1)	4.2 (3)
C12	0.850 (1)	0.6371 (5)	0.576 (1)	3.4 (2)
C13	0.956 (1)	0.6946 (6)	0.685 (1)	3.9 (3)
C14	1.081 (1)	0.6832 (6)	0.840 (1)	4.3 (3)
C15	1.105 (1)	0.6146 (6)	0.891 (1)	4.2 (3)
C16	1.000 (1)	0.5550 (6)	0.788 (1)	4.9 (3)
C7	0.767 (2)	0.5013 (7)	0.518 (2)	6.1 (4)
CA	0.261 (1)	0.8616 (8)	0.672 (2)	8.4 (5)
CB	0.383 (2)	0.8649 (8)	0.402 (2)	6.9 (4)
CC	0.293 (1)	0.7206 (7)	0.426 (2)	6.9 (4)
CD	0.604 (2)	0.9671 (7)	0.832 (2)	8.3 (5)
CE	0.780 (1)	0.9016 (7)	0.598 (2)	8.0 (4)
CF	0.937 (2)	0.8952 (8)	0.963 (3)	14.1 (7)

Table VIII. Selected Interatomic Distances (Å) for I

P–B9	1.928 (5)	B5–B9	1.755 (9)
B1–B2	1.75 (1)	B5–B10	1.742 (9)
B1–B3	1.75 (1)	B6–B10	1.804 (8)
B1–B4	1.795 (9)	B6–B11	1.81 (1)
B1–B5	1.760 (8)	B8–B9	1.871 (8)
B1–B6	1.785 (8)	B8–C7	1.651 (7)
B2–B3	1.724 (9)	B9–B10	1.868 (8)
B2–B6	1.76 (1)	B10–B11	1.870 (9)
B2–B11	1.808 (7)	B11–C7	1.660 (7)
B2–C7	1.701 (8)	C7–C1	1.562 (7)
B3–B4	1.791 (9)	Si1–C1	1.903 (5)
B3–B8	1.792 (7)	Si1–CA	1.870 (7)
B3–C7	1.699 (7)	Si1–CB	1.867 (6)
B4–B5	1.799 (9)	Si1–CC	1.871 (6)
B4–B8	1.804 (9)	Si2–C1	1.889 (5)
B4–B9	1.722 (7)	Si2–CD	1.864 (9)
B5–B6	1.76 (1)	Si2–CE	1.874 (8)
		Si2–CF	1.861 (7)

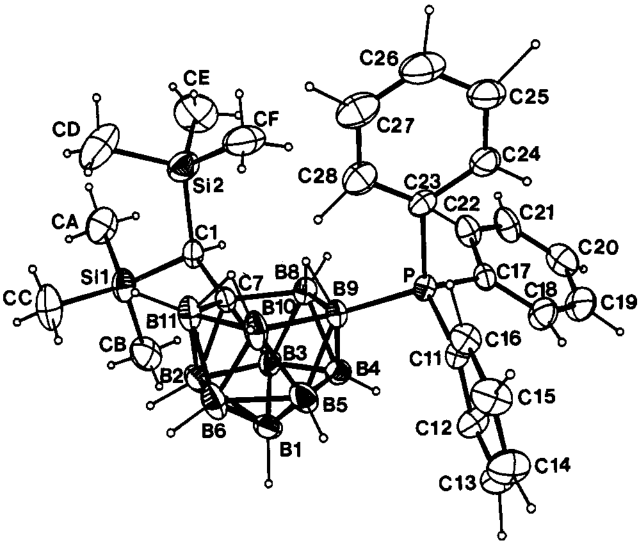

Figure 1. ORTEP drawing of the molecular structure of 9-Ph_3P-7-[$((CH_3)_3Si)_2CH$]$CB_{10}H_{11}$ (I). Non-hydrogen atoms are shown as 30% thermal ellipsoids. The hydrogen atoms have been arbitrarily assigned artificially small thermal parameters.

fractometer employing Mo Kα radiation from a highly oriented graphite-crystal monochromator. The intensities of three standard reflections measured at intervals of 100 reflections showed no systematic change during collection. The raw intensities were corrected for Lorentz and polarization effects by using the Enraf-Nonius program BEGIN.

Solution and Refinement of the Structure. All calculations were performed on a VAX 11/750 computer using the Enraf-Nonius structure package.[5] The full-matrix least-squares refinement was based on *F*, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights (*w*) were taken as $4F_o^2/(\sigma(F_o^2))^2$ where $|F_o|$ and $F_c|$ are the observed and calculated structure factor amplitudes. The neutral-atom scattering factors and complex anomalous dispersion corrections were taken from ref 6 and 7. Agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

Direct methods, using the 11/82 version of Multan, yielded the location of all non-hydrogen atoms in I. Three-dimensional Patterson syntheses gave the coordinates of the metal atoms in V and VI. Subsequent Fourier maps led to the location of the remaining heavy atoms. Anisotropic refinements followed by difference Fourier syntheses resulted in the location of all the cage hydrogens, along with some hydrogens of the cyclopentadienyl ring in the case of V and some hydrogens of the toluene ring in the case of VI. The remaining hydrogens in I, V, and VI were calculated (C–H distance = 0.95 Å) by using the SDP program HYDRO and included (but not refined) in the structure factor calculations with thermal parameters of 6.0 Å^2. Final refinements included numerical absorption corrections along with anisotropic thermal parameters for non-hydrogen atoms and fixed isotropic thermal parameters for the hydrogen atoms. A final difference Fourier synthesis for I was featureless with the largest peak being 0.29 e/Å^3. The final difference Fourier syntheses for V and VI

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(5) B. A. Frenz and Assoc. Inc., College Station, TX 77840, and Enraf-Nonius, Delft, Holland.

(6) (a) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B. (b) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–87.

(7) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

Table IX. Interatomic Distances (Å) for V and VI

Metallacarborane Cages

bond[a]	V	VI
M-B3	2.048 (4)	2.07 (1)
M-B6	2.039 (5)	2.07 (1)
M-B7	2.102 (5)	2.09 (1)
M-B11	2.091 (5)	2.07 (1)
M-C1	2.112 (4)	2.143 (9)
B3-B4	1.755 (8)	1.73 (2)
B3-B7	1.851 (5)	1.78 (1)
B3-B8	1.757 (7)	1.74 (2)
B3-C1	1.751 (6)	1.72 (1)
B4-B5	1.750 (6)	1.77 (1)
B4-B8	1.752 (7)	1.74 (2)
B4-B9	1.760 (7)	1.75 (2)
B4-C1	1.708 (6)	1.70 (2)
B5-B6	1.772 (7)	1.77 (2)
B5-B9	1.777 (7)	1.77 (2)
B5-B10	1.782 (5)	1.74 (2)
B5-C1	1.690 (7)	1.68 (2)
B6-B10	1.747 (8)	1.72 (2)
B6-B11	1.825 (6)	1.78 (2)
B6-C1	1.758 (4)	1.77 (1)
B7-B8	1.740 (7)	1.77 (2)
B7-B11	1.810 (6)	1.76 (1)
B7-B12	1.744 (8)	1.76 (2)
B8-B9	1.757 (8)	1.76 (2)
B8-B12	1.766 (5)	1.78 (1)
B9-B10	1.763 (7)	1.79 (2)
B9-B12	1.750 (7)	1.79 (2)
B10-B11	1.769 (8)	1.78 (2)
B10-B12	1.780 (8)	1.84 (2)
B11-B12	1.771 (8)	1.80 (2)
C1-C1A	1.559 (5)	1.58 (1)
Si1-C1A	1.924 (3)	1.900 (8)
Si2-C1A	1.922 (4)	1.94 (1)
Si1-CA	1.843 (6)	1.86 (2)
Si1-CB	1.868 (6)	1.83 (2)
Si1-CC	1.854 (8)	1.87 (1)
Si2-CD	1.846 (7)	1.86 (1)
Si2-CE	1.833 (7)	1.85 (2)
Si2-CF	1.840 (6)	1.84 (2)

Ni-(η-C_5H_5)		Co-(η^6-$C_6H_5CH_3$)	
Ni-C11	2.024 (5)	Co-C11	2.15 (1)
Ni-C12	2.077 (5)	Co-C12	2.17 (1)
Ni-C13	2.097 (5)	Co-C13	2.15 (1)
Ni-C14	2.085 (5)	Co-C14	2.15 (1)
Ni-C15	2.050 (6)	Co-C15	2.117 (9)
C11-C12	1.397 (8)	Co-C16	2.10 (1)
C11-C15	1.398 (6)	C11-C7	1.50 (1)
C12-C13	1.391 (5)	C11-C12	1.42 (2)
C13-C14	1.359 (7)	C11-C16	1.39 (1)
C14-C15	1.349 (6)	C12-C13	1.41 (1)
		C13-C14	1.37 (1)
		C14-C15	1.36 (2)
		C15-C16	1.41 (1)

[a] M = Ni for V and Co for VI.

exhibited larger peaks in the vicinity of the nickel and cobalt atoms but no peaks greater than 0.34 and 0.52 e/Å^3, respectively, elsewhere.

Results and Discussion

A single-crystal X-ray investigation of 9-Ph_3P-7-[((CH_3)$_3$Si)$_2$CH]$CB_{10}H_{11}$ (I) has shown that the compound has a structure similar to that proposed[1] for its dimethyl sulfide analogue. Thus, as can be seen in the ORTEP drawing given in Figure 1, the cage structure is based on an 11-vertex nido structure having the triphenylphosphine bound to the 9-boron on the open face and bridging hydrogens between the B8–B9 and B10–B11 borons. The distances and angles within the cage are normal and similar to those recently reported by Todd[8] for the compound 3-Me_2S-9-C_6H_{11}-7-$Me_3CN(H)CB_{10}H_{10}$. The bis(trimethylsilyl)methane group, which is bound to the cage carbon, is oriented such that one of the trimethylsilyl groups extends over the open face of the carborane suggesting that the coordination at that face may be hindered.

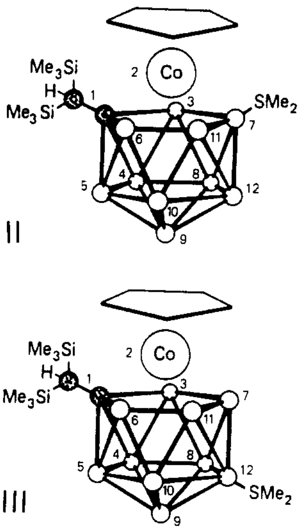

Figure 2. Proposed structures for 7-(CH_3)$_2$S-1-(η-C_5H_5)-1-[((CH_3)$_3$Si)$_2$CH]-2,1-$CoCB_{10}H_9$ (II) and 12-(CH_3)$_2$S-2-(η-C_5H_5)-1-[((CH_3)$_2$Si)$_2$CH]-2,1-$CoB_{10}H_9$ (III).

The reactions of 9-(CH_3)$_2$S-7-[((CH_3)$_3$Si)$_2$CH]$CB_{10}H_{11}$ with several metal reagents were explored, and it was found that sandwich complexes containing either the $RCB_{10}H_9{\cdot}SMe_2{}^{2-}$ or $RCB_{10}H_{10}{}^{3-}$ ligands could be formed. All complexes were isolated as air-stable materials, and their proposed structures are supported by the spectroscopic and crystallographic data discussed below.

The thermal reaction of 9-(CH_3)$_2$S-7-[((CH_3)$_3$Si)$_2$CH]-$CB_{10}H_{11}$ with (η-C_5H_5)Co(CO)$_2$ resulted in hydrogen loss and the direct insertion of a (η-C_5H_5)Co unit into the carborane cage yielding the isomeric complexes II and III as the major isolated products. The proposed compositions of II and III, (η-C_5H_5)Co[((CH_3)$_3$Si)$_2$CH]$CB_{10}H_9{\cdot}S(CH_3)_2$, are supported by exact mass determinations of the parent ions, but the NMR data clearly indicate that the compounds have different molecular symmetries. The ^{11}B and ^{1}H NMR spectra of II indicate the absence of a molecular mirror plane while that obtained for III suggest the presence of such symmetry. Both compounds contain singlets in their ^{11}B NMR spectra which can be attributed to a cage boron substituted by a dimethyl sulfide group.

On the basis of these data the asymmetric isomer II is proposed to be 7-(CH_3)$_2$S-(η-C_5H_5)-1-[((CH_3)$_3$Si)$_2$CH]-2,1-$CoCB_{10}H_9$ and the symmetric isomer III to be 12-(CH_3)$_2$S-(η-C_5H_5)-1-[((CH_3)$_3$Si)$_2$CH]-2,1-$CoCB_{10}H_9$, as shown in Figure 2. Both compounds are sandwich-type complexes containing the η^5-$RCB_{10}H_9{\cdot}SMe_2{}^{2-}$ ligand. The carborane cage is thus an analogue of the $R_3NCB_{10}H_{10}{}^{2-}$ anion that has been previously used to form a variety of metal complexes.[2c-f,h]

Since the carborane 9-(CH_3)$_2$S-7-[((CH_3)$_3$Si)$_2$CH]-$CB_{10}H_{11}$ has the dimethyl sulfide bound to a boron on the open face, complex II is probably formed initially in the reaction. This could occur by the simple dehydroinsertion of a (η-C_5H_5)Co unit onto the open nido face of the carborane. Complex III could then be formed from II by the migration of the dimethyl sulfide ligand from its position on the open face to the 12-position on the lower belt of

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[8] Hernandez, D. M.; Huffman, J. C.; Todd, L. J. *Inorg. Chem.* **1987**, *26*, 213–15.

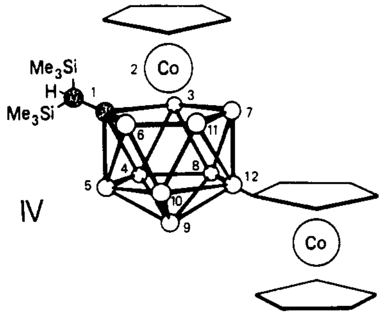

Figure 3. Proposed structure for 12-[(η-C_5H_5)Co(η-C_5H_4)]$^+$[2-(η-C_5H_5)-1-[((CH_3)$_3$Si)$_2$CH]-2,1-CoC$B_{10}H_9$]$^-$ (IV).

borons in III. Similar migration reactions of dimethyl sulfide groups have been observed in the $C_2B_9H_{11}$·S$(CH_3)_2$ system.[9]

Compound IV was isolated from the reaction in only trace amounts. Its composition was again established by exact mass measurements, and the spectral data support the cobaltaceniun–cobaltacarborane zwitterionic structure shown in Figure 3. The ^1H NMR spectrum is characteristic of the proposed structure showing two singlet resonances each of intensity five, due to the two η^5-bound cyclopentadienyl rings, and multiplets at 5.32 and 5.17 ppm attributable to the protons on the substituted C_5H_4 ring. The ^{11}B NMR spectrum indicates that there is a molecular mirror plane, which supports substitution at the 12-position on the carborane cage.

In compounds II and III the carborane cage is present as the $RCB_{10}H_9$·SMe_2^{2-} ligand; however, in IV the dimethyl sulfide has been removed from the cage resulting in the formation of the $RCB_{10}H_{10}^{3-}$ ligand. Thus, if the cobalt has a 3+ charge, then the cobaltacarborane unit has an overall charge of 1–. This charge is balanced by the 1+ charge of the cobaltacenium unit. Other zwitterionic cobaltacenium complexes of carboranes have previously been reported, including (η-C_5H_5)Co(η-C_5H_4–)$^+$(–$B_9C_2H_{11}$)$^-$ [10] and (η-C_5H_5)Co(η-C_5H_4–)$^+$(–$(CH_3)_4C_4B_8H_8$)$^-$.[11]

Hawthorne has previously reported[2a] the synthesis of 2-(η-C_5H_5)Ni-1-$CB_{10}H_{11}$ via the reaction of $B_{10}CH_{11}^{3-}$ with $NiBr_2$ and $Na^+C_5H_5^-$. The compound can also be formed by reaction of the anion with [(η-C_5H_5)$_3$$Ni_2$]$^+$$BF_4^-$ followed by oxidation. We were able to prepare the corresponding bis(trimethylsilyl)methane C-substituted analogue by the direct reaction of 9-$(CH_3)_2$S-7-[((CH_3)$_3$Si)$_2$CH]$CB_{10}H_{11}$ or [2-(((CH_3)$_3$Si)$_2$CH)$CB_{10}H_{10}$]$^-$ with [(η-C_5H_5)Ni(CO)]$_2$ in refluxing mesitylene.[12] The ^{11}B NMR spectrum of the product 2-(η-C_5H_5)-1-[((CH_3)$_3$Si)$_2$CH]-2,1-Ni$CB_{10}H_{10}$ (V) is similar to that of 2-(η-C_5H_5)Ni-1-$CB_{10}H_{11}$, suggesting that the gross cage geometries of the two compounds are similar. However, it was expected on the basis of the structure of I that the large size of the bis(trimethylsilyl)methane group substituted at the cage carbon on the open face should result in significant steric interactions with the cyclopentadienyl ring. This expectation was confirmed by a single-crystal X-ray study of V, the results of which are depicted in Figure 4.

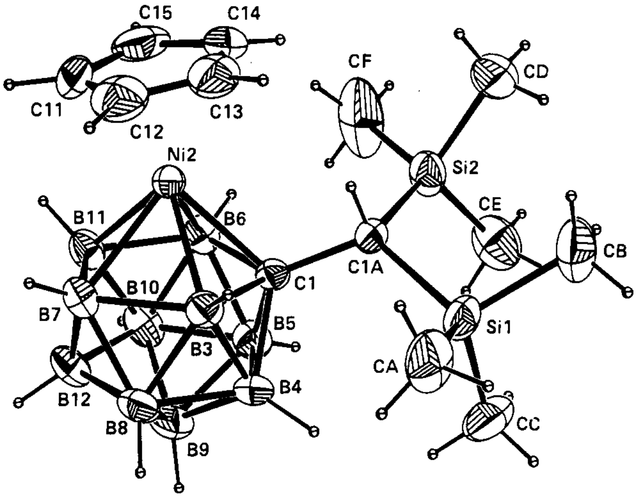

Figure 4. ORTEP drawing of the molecular structure of 2-(η-C_5H_5)-1-[((CH_3)$_3$Si)$_2$CH]-2,1-Ni$CB_{10}H_{10}$ (V). Non-hydrogen atoms are shown as 50% thermal ellipsoids. The hydrogen atoms have been arbitrarily assigned artificially small thermal parameters.

As can be seen in the ORTEP drawing, the cyclopentadienyl ligand is tilted away from the bis(trimethylsilyl)methyl side of the carborane cage, reflecting the steric interactions between these two groups. The plane of the cyclopentadienyl ring and that of the carborane face, C1, B3, B7, B11, and B6, are not parallel, having a dihedral angle of 9.5°. The shortest bonding interaction between the nickel and the cyclopentadienyl ring is on the side away from the bis(trimethylsilyl)methyl group, Ni–C11 = 2.024 (5) Å whereas the longest interaction is Ni–C13 = 2.097 (5) Å.

The C1–B3 and C1–B6 distances are lengthened, while those for B3–B7, B7–B11, and B11–B6 are shortened relative to the analogous distances in I, reflecting the delocalized metal to carborane bonding. The Ni–B and Ni–C distances appear normal as do the remaining cage bonding interactions.

While there is now a fairly wide variety of known (η^6-arene)iron substituted carboranes and boranes, there has been only one previous report of a (η^6-arene)cobalt boron cluster, 2-(η^6-$C_{10}H_8$)-2-Co-1-$CB_{10}H_{11}$.[13] We have previously demonstrated that metal atom techniques can be used to prepare a wide variety of (η^6-arene) metallaboranes,[14] carboranes,[15-17] and thiaboranes.[18] We therefore explored the use of these techniques for the synthesis of such complexes derived from 9-$(CH_3)_2$S-7-[((CH_3)$_3$Si)$_2$CH]$CB_{10}H_{11}$.

The reaction of 9-$(CH_3)_2$S-7-[((CH_3)$_3$Si)$_2$CH]$CB_{10}H_{11}$ with cobalt vapor and toluene resulted in the low-yield production of the new complex 2-(η^6-$C_6H_5CH_3$)-1-[((CH_3)$_3$Si)$_2$CH]-2,1-Co$CB_{10}H_{10}$ (VI). As in compound V, the carborane is bound as the $RCB_{10}H_{10}^{3-}$ ligand resulting in a 3+ charge for the cobalt atom.

The ^{11}B NMR spectrum of VI is similar to that of the isoelectronic compound V and to that of 2-(η^6-$C_{10}H_8$)-2-Co-1-$CB_{10}H_{11}$. The ^1H NMR spectrum shows the characteristic peaks attributable to the η^6-toluene unit and the bis(trimethylsilyl)methyl groups. A single-crystal X-ray investigation of VI confirmed the sandwich structure of the compound as shown in the ORTEP drawing in Figure 5.

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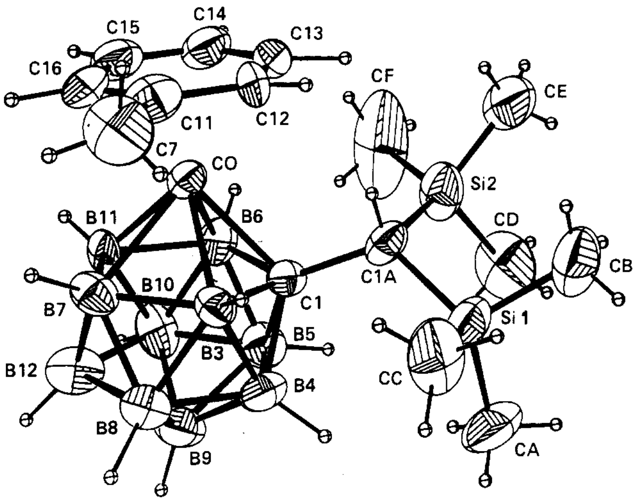

Figure 5. ORTEP drawing of the molecular structure of 2-(η^6-$C_6H_5CH_3$)-1-[$((CH_3)_3Si)_2CH$]-2,1-$CoCB_{10}H_{10}$ (VI). Non-hydrogen atoms are shown as 50% thermal ellipsoids. The hydrogen atoms have been arbitrarily assigned artifically small thermal parameters.

As was observed in V, the planes of the two ligands are tilted with respect to each other (7.6°) in order to minimize the repulsions between the bis(trimethylsilyl)methyl group and the η^6-toluene unit. The average of the cobalt to ring-carbon distances (2.14 Å) is the same as that observed in, for example, (η^6-$C_6H_5CH_3$)$Co(C_6F_5)_2$;[19] however, the carbons near the bis(trimethylsilyl)methyl group have longer Co–C distances, C12–Co = 2.17 (1) Å and C13–Co = 2.15 (1) Å, than those on the opposite side of the toluene ring, C16–Co = 2.10 (1) Å and C15–Co = 2.117 (1) Å.

In general, the carborane interatomic distances are again found to be within the normal ranges and are similar to those in V; however, the distances between the atoms on the bonding face of the carborane (C1, B3, B7, B11 and B6) are somewhat shortened compared to the analogous distances in V.

In summary, the results reported herein have demonstrated that the carborane 9-$(CH_3)_2S$-7-[$((CH_3)_3Si)_2CH$]-$CB_{10}H_{11}$ can function as a versatile ligand by coordinating to transition metals as either the [$((CH_3)_3Si)_2CH$]$CB_{10}H_{10}{}^{3-}$ or $(CH_3)_2S$–[$((CH_3)_3Si)_2CH$]$CB_{10}H_9{}^{2-}$ anions. Steric interactions between the other ligands on the metal and the cage-bound bis(trimethylsilyl)methyl group, however, can lead to significant geometric distortions. We are presently investigating the development of new synthetic routes to the parent carborane *nido*-$(CH_3)_2S$–$CB_{10}H_{12}$ so that the chemistry of this potentially useful ligand can be more fully explored.

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Registry No. I, 110717-83-4; II, 110743-51-6; III, 110717-84-5; IV, 110717-85-6; V, 110743-52-7; VI, 110743-53-8; PPh_3, 603-35-0; 9-$(CH_3)_2S$-7-[$((CH_3)_3Si)_2CH$]$CB_{10}H_{11}$, 105335-10-2; (η-C_5H_5)$Co(CO)_2$, 12078-25-0; [(η-C_5H_5)$Ni(CO)$]$_2$, 12170-92-2; Na[2-$(((CH_3)_3Si)_2CH)CB_{10}H_{10}$]$^-$, 105309-51-1.

Supplementary Material Available: Tables of general temperature factors, intermolecular angles, molecular planes, and hydrogen positions for I, V and VII (29 pages); listings of observed and calculated structure factors for I, V, and VI (28 pages). Ordering information on any current masthead page.

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Alkyl and η^2-Acyl Complexes of Iron(II)

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The reduction with sodium amalgam in acetonitrile (MeCN) of [$Fe(CO)_2L_2X_2$] (X = Cl, Br, I; L = PMe_3, PMe_2Ph, $P(n\text{-}Bu)_3$, $PMePh_2$, $P(i\text{-}Bu)_3$, $P(i\text{-}Pr)_3$, $PEtPh_2$, PPh_3) gives a mixture of two different complexes in equilibrium. One is probably the cluster complex [$Fe(CO)_2L_2$]$_3$, isoelectronic with [$Fe_3(CO)_{12}$]; the other is the complex [$Fe(CO)_2L_2(MeCN)$]. The mixture in equilibrium reacts with RI (R = CH_3, C_2H_5) to give oxidative addition products. With L = PMe_3, PMe_2Ph, and $P(n\text{-}Bu)_3$ the products are the alkyl complexes [$Fe(CO)_2L_2(R)I$]. With L = $PMePh_2$, $PEtPh_2$, $P(i\text{-}Bu)_3$, and PPh_3 the reaction products are the η^2-acyl complexes [$Fe(CO)L_2(\eta^2\text{-}COR)I$]. Complex [$Fe(CO)(PMePh_2)_2(\eta^2\text{-}COCH_3)I{\cdot}2CH_2Cl_2$] was analyzed by the single-crystal X-ray diffraction method. It crystallizes in the monoclinic space group $P2_1/n$ with lattice parameters a = 23.603 (4) Å, b = 12.256 (3) Å, c = 12.318 (3) Å, and β = 97.08 (2)°; it contains four molecules per cell. The structure was solved by using 2642 observed reflections and refined to R_w = 0.062. The electronic and steric features of the phosphine ligands, which stabilize the η^2-acyl structure, are discussed, the steric hindrance appearing to be the most important factor for the same metal. The effect of the nature of the metal is also discussed, the stability of the η^2-acyl structure being correlated with the number of the d electrons on the metal in its formal oxidation state.

Introduction

The study of the synthesis and characterization of alkyl complexes of transition metals is valuable, since their reactivity with carbon monoxide can yield information about the mechanism and stereochemistry of the insertion of this ligand in the metal–alkyl bond.[1] Much information on the stereochemistry of the insertion of carbon monoxide has been obtained in the study of the octahedral complexes of Mn.[2] The alkyl cyclopentadienyl complexes of iron(II) have also been extensively studied,[3] but, due to their

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