Cobalt–Hydrogen Metallocarboranes. Synthesis of *closo*-$[(CH_3)_2C_2B_4H_4]_2CoH$ and *nido,closo*-$[(CH_3)_2C_2B_3H_5]CoH[(CH_3)_2C_2B_4H_4]$ and Their Conversion to New Cobalt–Cobalt Bonded Metallocarboranes

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Abstract: The reaction of $Na^+[(CH_3)_2C_2B_4H_5]^-$ with $CoCl_2$ at 25° yields the red neutral *commo*-metallocarborane $[C,C'$-$(CH_3)_2C_2B_4H_4]_2Co^{III}H$. From NMR evidence the hydrogen atom associated with the metal is proposed to be face-bonded to a triangular face on the polyhedral surface. The compound is converted in aqueous acid to a nido,closo species, $[C,C'$-$(CH_3)_2C_2B_3H_5]CoH[C,C'$-$(CH_3)_2C_2B_4H_4]$, which in turn can be metal deprotonated by NaH to give the $[(CH_3)_2C_2B_3H_5]$-$Co[(CH_3)_2C_2B_4H_4]^-$ ion; reaction of the latter species with aqueous HCl regenerates the neutral metal-protonated compound. The reaction of the ion with $CoCl_2$ and NaC_5H_5 produces *nido,closo*-$[(CH_3)_2C_2B_3H_5]CoH[(CH_3)_2C_2B_3H_3]Co(\eta^5$-$C_5H_5)$ in which a Co–Co bond is postulated. Treatment of $[C,C'$-$(CH_3)_2C_2B_4H_4]_2Co^{III}H$ with $(\eta^5$-$C_5H_5)Co(CO)_2$ yields 4,5-$(CH_3)_2$-1,2,4,5-$(\eta^5$-$C_5H_5)_2Co_2C_2B_3H_3$ and $(\eta^5$-$C_5H_5)Co[(CH_3)_2C_2B_3H_3]CoH[(CH_3)_2C_2B_3H_3]Co(\eta^5$-$C_5H_5)$, each species having a proposed Co–Co link. Air oxidation of $[C,C'$-$(CH_3)_2C_2B_4H_4]_2Co^{III}H$ produces the tetracarbon carborane $(CH_3)_4C_4B_8H_8$.

One of the most versatile carborane systems in reactions with metal reagents is 2,3-$C_2B_4H_8$ (*nido*-dicarbahexaborane[8]). The variety of main-group and transition metal compounds obtained from the neutral carborane, its bridge-deprotonated ion $C_2B_4H_7^-$, or C-alkyl derivatives of these includes such diverse species as bridged complexes containing B–M–B three-center bonds,[1] σ-bonded terminally substituted derivatives,[1b,c,f] open-cage (nido) metallocarboranes,[1d,2] and closed polyhedral (closo) mono- and dimetallocarboranes,[1d,2a,b,3] including the triple-decked sandwich complexes 1,7,2,3- and 1,7,2,4-$(\eta^5$-$C_5H_5)_2Co_2C_2B_3H_5$. The present paper describes recent work on the $C_2B_4H_8$ system which led us into systematic studies of metallocarboranes containing metal–hydrogen bonds, produced several new species having adjacent metal atoms in a polyhedral cage, and in addition provided an entry to a previously unknown area of metallocarborane chemistry, the tetracarbon metallocarboranes.

Many of our earlier investigations in this area[1d,2b,4] utilized reactions of the carborane substrate $C_2B_4H_7^-$ with metal ions in the presence of cyclopentadienide ion, $C_5H_5^-$, giving metallocarboranes containing one or more $(\eta^5$-$C_5H_5)M$ moieties in the cage framework, for example, $(\eta^5$-$C_5H_5)CoC_2B_4H_6$. Anticipating a routine extension of this work, we assumed that similar reactions in the *absence* of $C_5H_5^-$ would generate *commo*-metallocarborane anions in which the metal is present simultaneously in two polyhedral cages (or, in the "metal-complex" terminology, the metal atom is face-bound to two carboranyl ligands):

$$C_2B_4H_7^- + CoCl_2 \xrightarrow[-H_2,Co^0]{} (C_2B_4H_6)_2Co^-$$

Analogous commo species derived from higher carboranes are well known.[5] However, our investigation of reactions of the $C_2B_4H_7^-$ ion with $FeCl_2$ and $CoCl_2$ gave no isolable metallocarborane products. The corresponding reactions of the C,C'-$(CH_3)_2C_2B_4H_5^-$ ion, in contrast, gave good yields of metallocarboranes which somewhat surprisingly proved to be neutral molecues rather than salts. In this paper we describe the chemistry of the cobalt species, which differed substantially from that of the iron systems presented elsewhere.[6]

Results and Discussion

Reaction of the C,C'-$(CH_3)_2C_2B_4H_5^-$ Ion with $CoCl_2$. The $(CH_3)_2C_2B_4H_5^-$ ion reacts with cobalt(II) chloride at room temperature in tetrahydrofuran (THF) to give the neutral *commo*-metallocarborane $[C,C'$-$(CH_3)_2C_2B_4H_4]_2Co^{III}H$ (I) in up to 34% yield, obtained as a moderately air-sensitive tomato red crystalline solid. The synthesis of I from $CoCl_2$ is accompanied by the formation of a dark ferromagnetic solid assumed to be cobalt metal, but no evolution of gas is observed. The assignment of a formal cobalt +3 oxidation state in I is consistent with its diamagnetism as evidenced by its normal ^{11}B and ^1H NMR spectra.

The gross structures proposed for I (depicted in Figure 1) and all other new compounds reported herein are based on ^{11}B and ^1H pulse Fourier transform nuclear magnetic resonance (FTNMR) spectra obtained at 32.1 and 100 MHz, respectively, as well as infrared, electron impact and chemical ionization mass spectra (see Tables I–IV). The location of the "extra" hydrogen in I has not been definitively established, but hydrogens producing unusually high-field[7] ^1H NMR resonances in metallocarboranes[8,9] and metalloboranes[10] have been shown via x-ray diffraction studies[9,10b] or assumed[8] to be bonded to the metal atoms. Furthermore, in the case of I it is observed that the Co–H ^1H resonance sharpens on ^{11}B decoupling, implying that this unique hydrogen is not bound exclusively to the metal but is associated partially with nearby boron atoms in a face-bonded arrangement. In earlier papers from this laboratory[1d,8] a similar proposal was advanced for the related compounds 1,2,3- and 1,2,4-$(\eta^5$-$C_5H_5)$-$Fe^{II}HC_2B_4H_6$. Recently, the elusive face-bonded hydrogen in the octahedral CB_5H_7 system has been located by an electron-diffraction study,[11] following a microwave investigation[12] which had given indirect evidence of four-center H–B_3 bonding. The electron diffraction results confirm that the extra hydrogen in CB_5H_7 is located above the center of a triangular B_3 face; earlier NMR work by Onak[13] had strongly suggested that at room temperature the face-bridging proton rapidly tautomerizes around the molecule, rendering the four equatorial boron atoms equivalent on the NMR time scale. Similar tautomeric behavior is likely in I, and the high symmetry evident from the FTNMR spectra (Tables I and II) is consistent

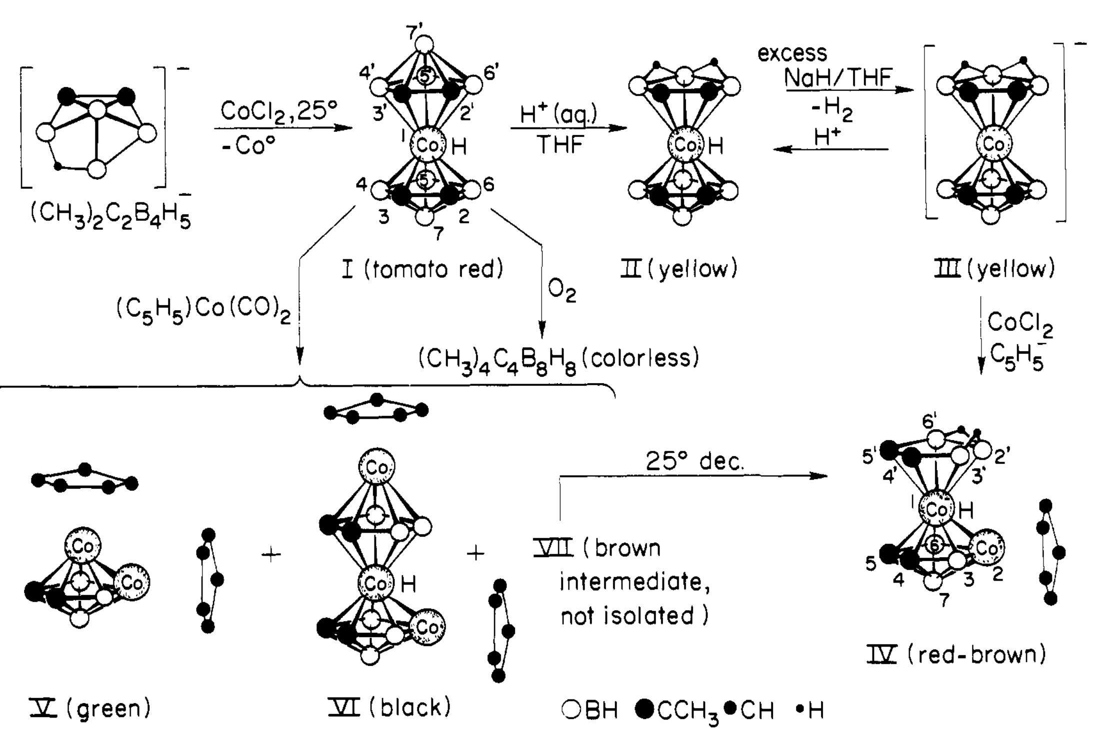

Figure 1. Reaction scheme showing proposed structures of new metallocarboranes I-VI. Metal-bound hydrogens are shown schematically.

Table I. 32.1-MHz ^{11}B FTNMR Data[a]

Compound	δ,[b] ppm (J, Hz)	Rel. areas
$[(CH_3)_2C_2B_4H_4]_2CoH$ (I)	−6.9(168), −1.7(156)	1, 3
$[(CH_3)_2C_2B_4H_4]CoH[(CH_3)_2C_2B_3H_5]$ (II)	−5.5(128),[c] −2.4(128),[c] +0.9(172), +11.4(168)	2,[c] 1,[c] 3, 1
$(CH_3)_4N^+\{[(CH_3)_2C_2B_4H_4]Co[(CH_3)_2C_2B_3H_5]\}^-$ (III)[d]	−4.9(136),[c] −1.8(140),[c] +1.8(144)[c]	3,[c] 2,[c] 2[c]
$(C_5H_5)Co[(CH_3)_2C_2B_3H_3]CoH[(CH_3)_2C_2B_3H_5]$ (IV)	−30.8(157), −8.4(161), −3.7(146),[c] −0.8(160)[c]	2, 1, 2, 1
1,2,4,5-$(C_5H_5)_2Co_2[(CH_3)_2C_2B_3H_3]$ (V)	−45.7(156), −16.8(167)	2, 1
$(C_5H_5)Co[(CH_3)_2C_2B_3H_3]CoH[(CH_3)_2C_2B_3H_3]Co(C_5H_5)$ (VI)	−61.6,[e,f] −30.0(150), −9.3[e,g]	1, 2, 3

[a] All spectra run in $CDCl_3$ solution except where otherwise indicated. [b] Chemical shifts relative to externally referenced $BF_3{\cdot}O(C_2H_5)_2$. [c] Estimated from overlapped resonances. [d] Spectrum measured in CD_3CN solution. [e] Very broad resonance, ^{11}B–H coupling not measurable. [f] $w_{1/2}$ = 360 Hz (undecoupled specrum); $w_{1/2}$ = 164 Hz (proton-decoupled spectrum). [g] $w_{1/2}$ = 520 Hz (undecoupled spectrum); $w_{1/2}$ = 320 Hz (proton-decoupled spectrum).

with this hypothesis. However, a "fixed" (nontautomerizing) hydrogen located on a mirror plane cannot be ruled out, nor can one eliminate the possibility that a bridging hydrogen in an unsymmetrical fixed position might have so small an effect on the NMR chemical shifts as to be undetectable. The resolution of this question in the solid-state structures of I and related molecules may be possible with low-temperature x-ray analysis, but is not crucial to the present discussion which concerns reactions in solution in which rapid proton tautomerism is assumed.

Formation of $(CH_3)_4C_4B_8H_8$ from $[C,C'\text{-}(CH_3)_2C_2B_4H_4]_2CoH$ (I). The bright red solid I is thermally stable in vacuo at room temperature but decomposes slowly on exposure to air, forming in 35–40% yield a colorless crystalline air-stable solid which has been characterized as $(CH_3)_4C_4B_8H_8$, a new carborane system.[14] The same product is formed in higher yield on air oxidation of the ferracarborane $[C,C'\text{-}(CH_3)_2C_2B_4H_4]_2Fe^{II}H_2$ as described in a separate publication,[6] and the properties of $(CH_3)_4C_4B_8H_8$ are presented in that context.

Conversion of $[C,C'\text{-}(CH_3)_2C_2B_4H_4]_2CoH$ (I) to Nido,Closo Cobaltacarboranes. The treatment of I with acidified aqueous THF gives in high yield the yellow species $[(CH_3)_2C_2B_3H_5]CoH[(CH_3)_2C_2B_4H_4]$ (II), as shown in Figure 1. The removal of an apex BH group and its replacement, in effect, with two bridging hydrogens is analogous to the conversion of $(C_5H_5)CoC_2B_4H_6$ to $(C_5H_5)CoC_2B_3H_7$ as reported earlier.[2b] The proposed structure of II is consistent with the FTNMR data (Tables I and II) and contains a cobalt atom which resides in both a nido and a closo cage framework. The high-field band at τ 16.0 in the ^{1}H FTNMR spectrum appears as a broad singlet and fails to distinguish the B–H–B bridging protons from the unique hydrogen associated with the cobalt atom. However, on ^{11}B decoupling this signal is resolved into a low-field doublet of doublets, attributed to coupling of each of the B–H–B bridging protons with its neighboring terminal B–H protons, and a separate broad singlet at higher field assigned to the Co–H group (Figure 2). This observation indicates that the B–H–B and Co–H protons are *not* undergoing rapid tautomeric exchange on the NMR time scale, although exchange at a much slower rate cannot be ruled out.

The planar cyclocarboranyl ligand in II is a C,C'-dimethyl derivative of the formal $C_2B_3H_7^{2-}$ system as found in $(\eta^5\text{-}C_5H_5)CoC_2B_3H_7$[2b] and $(CO)_3FeC_2B_3H_7$,[2a] the latter structure having been established in an x-ray study.[15] The $C_2B_3H_7^{2-}$ ligand is a doubly bridge-protonated analogue of the cyclic planar $C_2B_3H_5^{4-}$ ring found in the triple-decked sandwich metallocarboranes[3b,2b] 1,7,2,4- and 1,7,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$. Both the $C_2B_3H_7^{2-}$ and $C_2B_3H_5^{4-}$ systems are isoelectronic with cyclopentadienide ion, $C_5H_5^-$,

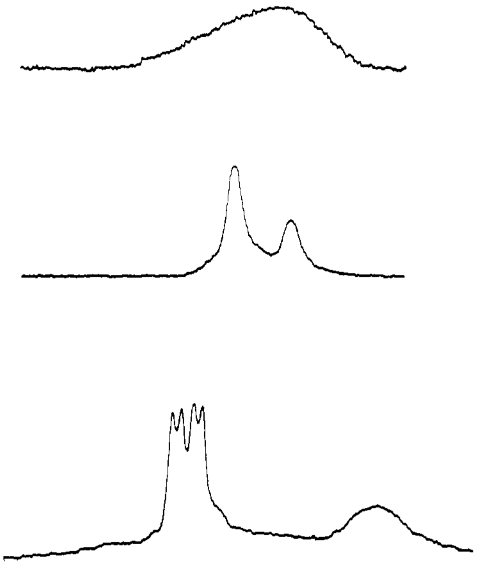

Figure 2. The 100-MHz proton FTNMR spectra of $[C,C'\text{-}(CH_3)_2\text{-}C_2B_3H_5]CoH[C,C'\text{-}(CH_3)_2C_2B_4H_4]$ (II): top spectrum, undecoupled; middle, partially ^{11}B-decoupled; bottom, fully ^{11}B-decoupled, showing B-H-B multiplet and Co-H singlet (see text). The bottom spectrum is shown in an enlarged horizontal scale.

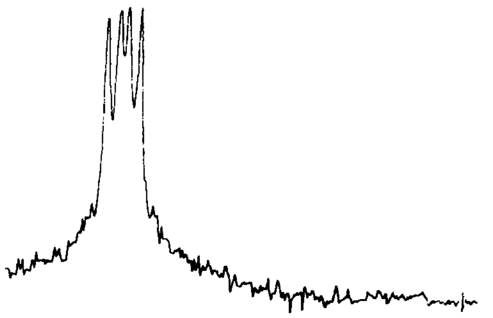

Figure 3. The 100-MHz proton FTNMR spectrum of $[(CH_3)_4\text{-}N]^+[C,C'\text{-}(CH_3)_2C_2B_3H_5]Co[C,C'\text{-}(CH_3)_2C_2B_4H_4]^-$ (III). Multiplet is due to B-H-B protons; note absence of resonance in Co-H region (compare with Figure 2).

Table II. 100-MHz ^1H FTNMR Data[a]

Compound	Resonance, τ^b (rel. area)^c	Assignment
I	7.78(12)	CH_3
	18.7(1),^{d} $w_{1/2}$ = 50 Hz	Co-H
II	7.82(6)	CH_3
	8.21(6)	CH_3
	16.0(3),^{d} $w_{1/2}$ = 144 Hz	Co-H, B-H-B
	15.59(2)^{e,f}	B-H-B
	16.3(1)^{e,g}	Co-H
III (CH_3CN)	8.34(3)	CH_3
	8.03(3)	CH_3
	6.92(6)^h	$(CH_3)_4N^+$
	16.72(1)^i	B-H-B
IV	4.95(5)	C_5H_5
	7.95(6)	CH_3
	8.27(6)	CH_3
	15.80(2)^{j,k}	B-H-B
	24.3(1)^{l,k}	Co-H
	15.78(2)^{m,n}	B-H-B
	24.3(1)^{m,o}	Co-H
V	5.17(5)	C_5H_5
	5.52(5)	C_5H_5
	7.85(6)	CH_3
VI	5.01(5)	C_5H_5
	5.63(5)	C_5H_5
	7.34(6)	CH_3
	8.13(6)	CH_3
	25.8(1)^p	Co-H

[a] All spectra were run in $CDCl_3$ solution except where otherwise indicated. [b] Chemical shifts relative to $(CH_3)_4Si = \tau$ 10.00. [c] Singlet resonance except where otherwise indicated. [d] Undecoupled spectrum. [e] ^{11}B-decoupled spectrum. [f] Doublet of doublets: primary splitting, $J' \simeq 8$ Hz; secondary splitting, $J \simeq 3$ Hz. [g] Singlet, $w_{1/2} = 24$ Hz. [h] Triplet, $J = 0.6$ Hz. [i] Doublet of doublets: $J' \simeq 7$ Hz, $J \simeq 4$ Hz. [j] Broad resonance, $w_{1/2} = 126$ Hz. [k] Undecoupled spectrum. [l] Broad resonance, $w_{1/2} = 32$ Hz. [m] ^{11}B-decoupled spectrum. [n] Doublet of doublets: $J' \simeq 7.2$ Hz, $J = 4.0$ Hz. [o] $w_{1/2} = 21$ Hz. [p] Singlet, $w_{1/2} = 40$ Hz in undecoupled spectrum, 19 Hz in the ^{11}B-decoupled spectrum.

Table III. High Resolution Mass Measurements[a]

Compound	Formula	Calcd mass	Obsd mass
I	$^{59}Co^{12}C_8{}^{11}B_7{}^{10}B^1H_{22}{}^+$	264.1834	264.1828
II	$^{59}Co^{12}C_8{}^{11}B_7{}^1H_{23}{}^+$	255.1784	255.1786
IV	$^{59}Co_2{}^{12}C_{13}{}^{11}B_4{}^{10}B_2\text{-}{}^1H_{26}{}^{+\,b}$	364.1329	364.1325
V	$^{59}Co_2{}^{12}C_{14}{}^{11}B_3{}^1H_{20}{}^+$	339.0508	339.0495
VI	$^{59}Co_3{}^{12}C_{18}{}^{11}B_6{}^1H_{30}{}^+$	489.0902	489.0885

[a] Mass of P + 1 (protonated parent ion) species obtained in methane under chemical ionizing conditions. [b] Parent ion (not protonated). Peaks corresponding to both protonated (P + 1) and parent (P) ions were observed in all spectra; in each case, the choice of peaks employed for exact-mass determination by peak matching against a known standard was dependent on shape and freedom from overlap with other peaks.

although unlike the latter species they have not been detected as free ions.

Structure II can be viewed in another sense, recognizing that the open portion is analogous to *nido*-2,3-$C_2B_4H_8$, while the 7-vertex polyhedral cage is electronically equivalent to *closo*-2,3-$C_2B_5H_7$, with cobalt replacing the apex BH group in both cases. Since 2,3-$C_2B_4H_8$[16] and the analogous molecule 1,2,3-$(\eta^5\text{-}C_5H_5)CoC_2B_3H_7$[2b] each lose a bridge proton on reaction with hydride ion, similar behavior might have been anticipated for II. Treatment of II with excess NaH or KOH liberates 1 equiv of H_2; however, proton loss occurs not at a B-H-B bridging location but rather at the Co-H group. The resulting yellow $[(CH_3)_2C_2B_3H_5]Co[(CH_3)_2C_2B_4H_4]^-$ anion, which can be precipitated in aqueous media as a yellow tetramethylammonium salt (III) exhibits a ^1H FTNMR spectrum (Figure 3) which clearly shows that both B-H-B bridges are retained while the proton which was associated with the metal in the neutral species is no longer present.

The Co-H proton abstraction is reversible, since treatment of III with aqueous or anhydrous HCl regenerates II quantitatively. These results, together with similar findings on the $[(CH_3)_2C_2B_4H_4]_2Fe^{II}H_2$ system[6] and on $(\eta^5\text{-}C_5H_5)\text{-}Fe^{II}HC_2B_4H_6$,[1d] show that the metal-bound hydrogen atoms in these species are protonic rather than hydridic in character. In this respect these metal-hydrogen metallocarboranes are formally distinct from the hydrido metallocarborane family exemplified by $[(C_6H_5)_3P]_2HRhC_2B_9H_{11}$,[17] which contains a formal H^- ligand coordinated to the metal atom.[18] On the other hand, the $[(C_2B_9H_{11})_2Fe^{II}H]^-$ ion, obtained by direct protonation of $[(C_2B_9H_{11})_2Fe^{II}]^{2-}$, may contain a metal-bound proton although the ^1H NMR spectrum of this species contained no resonance in the high-field region associated with metal-hydrogen groups.[19]

Cobalt Insertion into the Nido,Closo Monocobalt Anion (III). The nido,closo species III undergoes reaction with $CoCl_2$ and

Table IV. Infrared Absorptions, cm^{-1}

I[a]	2960(w), 2925(m), 2885(w), 2578(vs), 1438(m), 1380(m), 1110(w), 1045(m), 900(w), 865(m), 812(m)
II[b]	2960(m), 2930(m), 2860(w), 2580(vs), 2545(sh,s), 1890(sh,w), 1865(m), 1655(w), 1585(m), 1455(m), 1375(m), 1118(w), 1075(w), 1032(w), 1000(m), 985(sh,w), 945(m), 908(w), 885(m), 855(w), 820(w), 798(m), 740(m), 702(m), 620(w)
III[b]	3030(m), 2950(m), 2912(m), 2880(m), 2518(vs), 1845(m), 1510(w), 1482(m), 1448(w), 995(m), 945(m), 870(m), 775(m), 738(w)
IV[a]	2950(sh), 2925(s), 2858(w), 2538(vs), 1862(m), 1735(m), 1570(w), 1435(m,br), 1370(w), 1245(w), 1150(m), 1100(m), 1003(m), 945(w), 900(m), 825(s)
V[c]	2958(sh,w), 2920(m), 2850(w), 2485(s), 1732(m), 1430(w), 1100(w), 1000(w), 895(w), 820(m), 725(m)
VI[a]	2922(m), 2870(m), 2512(s), 1738(w)

[a] CH_2Cl_2 solution vs. CH_2Cl_2. [b] KBr pellet. [c] Thin film, solid state.

NaC_5H_5 followed by aqueous HCl to give neutral, red-brown $(\eta^5\text{-}C_5H_5)Co[(CH_3)_2C_2B_3H_3]CoH[(CH_3)_2C_2B_3H_5]$ (IV) in low yield; the same compound is also obtained from I (vide infra). The proposed structure depicted in Figure 1 is based on the following considerations. Assuming that the cage carbon atoms in each carboranyl unit remain adjacent (elevated temperatures normally being required to effect carbon–carbon separation in metallocarboranes[20,21]) and taking into account the synthetic route as well as the symmetry indicated from ^{11}B and ^1H NMR spectra (e.g., only two distinct methyl group environments are evident), only two structures seem plausible for IV: that indicated in Figure 1, and a triple-decked sandwich geometry produced by interchanging the $(C_5H_5)Co$ and apex BH groups in the structure shown. A clear preference for the adjacent-cobalt geometry given in the figure is afforded by the ^{11}B FTNMR spectrum which closely resembles that of the structurally analogous species 1,2,4,5-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$,[21] a molecule differing from IV (except for the methyl groups) only by replacement of the $[(CH_3)_2C_2B_3H_5]CoH$ moiety with an electronically equivalent $(\eta^5\text{-}C_5H_5)Co$ group. In contrast, the ^{11}B spectra[2b,22] of the structurally defined[3b] triple-decked sandwich 1,7,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ and its C-substituted derivatives are very different from that of IV; in particular, the 1,7,2,3 species each exhibit an area 1 resonance at very low field (δ −50 to −60 ppm) arising from the unique equatorial boron in the ring. The spectrum of IV contains no such feature, its lowest-field resonance being an *area 2* signal at δ −30.8 which can be assigned to the pair of equivalent boron atoms in the CoB_2C_2 ring. The ^{11}B spectra of 1,2,4,5-$(\eta^5\text{-}C_5H_5)CoC_2B_3H_5$[21] and its *C,C′*-dimethyl derivative (compound V in this paper) exhibit low-field doublets of area 2 at δ −44.7 and −45.7, respectively; the apex boron resonances in all three cases appear at much higher field, separated by approximately 30 ppm from the low-field doublet.

The ^{11}B and ^1H resonances arising from the open-ring portion of IV are comparable to those of other complexes of the formal $C_2B_3H_7^{2-}$ ligand.[1d,2a,b] The broad resonances of area 2 at τ 15.8 and of area 1 at τ 24.3 in the proton spectrum are readily assigned to the pair of B–H–B groups and the Co–H proton, respectively. In the ^{11}B-decoupled spectrum, the τ 15.8 peak is resolved into a doublet of doublets (as in the case of II above), with J = 4.0 Hz and J' = 7.2 Hz. In this case, unlike II, the B–H–B and Co–H resonances are widely separated, possibly reflecting association of the metal-bound proton with both cobalt atoms in IV.

The formation of IV from III extends a pattern we had noted in earlier work and observed several times in the present study: *direct* insertion of a second metal atom into a monometallocarborane frequently occurs at a position adjacent to the first metal, particularly in reactions conducted under mild conditions. Further discussion of this point appears later in the paper.

Insertion of Cobalt into $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2CoH$ (I). The reaction of the *commo*-cobaltacarborane I with $(\eta^5\text{-}C_5H_5)Co(CO)_2$ in THF under ultraviolet irradiation followed by air oxidation produces a complex mixture of materials, most in low yield. Two of the products have been isolated by thick-layer chromatography and characterized as a green *C,C′*-dimethyl derivative (V) of the previously reported[21] 1,2,4,5-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$, and a black tricobalt species $(\eta^5\text{-}C_5H_5)Co[(CH_3)_2C_2B_3H_3]CoH[(CH_3)_2C_2B_3H_3]Co(\eta^5\text{-}C_5H_5)$ (VI). The proposed structures of V and VI, shown in Figure 1, were inferred from ^{11}B and ^1H FTNMR spectra utilizing arguments similar to those invoked for compound IV above. The spectra of V are very close to those of the parent 1,2,4,5 isomer[21] (e.g., the ^{11}B resonances of the latter compound occur at δ −44.7 and −11.4, and its C_5H_5 peaks in the proton spectrum are found at τ 5.12 and 5.44). The structure proposed for VI is strongly supported by the ^{11}B FTNMR spectra which combine the features associated with the two types of 7-vertex cages present. Thus, the area 1 resonance at δ −61.6 is assigned to the unique boron in the planar C_2B_3 ring (as in the triple-decked sandwich[2b] 1,7,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_3$), and the area 2 band at δ −30.0 is attributed to the equivalent pair of boron atoms in the lower CoC_2B_2 ring, as in compounds IV, V, and 1,2,4,5-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$. The broad resonance at δ −9.3 is assumed to arise from overlapping signals of the remaining borons, and has a δ value consistent with their locations. It is interesting to note that migration of the equatorial $(C_5H_5)Co$ group in VI to the adjacent apex BH position would produce a quadruple-decked sandwich, of which no known examples currently exist. From related work on thermal isomerizations of cobaltacarboranes[21] it appears that such a migration might well occur at elevated temperatures. The minute quantity of VI obtained in the present work precluded our examining this possibility.

Compounds V and VI were also obtained when the identical reagents were refluxed in THF without ultraviolet irradiation. The same experiment produced a brown product (VII) which exhibited a mass spectrum corresponding to $(\eta^5\text{-}C_5H_5)Co[(CH_3)_2C_2B_3H_3]CoH[(CH_3)_2C_2B_4H_4]$. Attempts to purify this material by chromatography on silica gel led to its decomposition to IV, and NMR data for VII were not obtained. However, its mode of preparation and its decomposition products suggest that the structure of VII is probably that of VI with a BH group replacing the apex $(C_5H_5)Co$ unit.

Conclusions

A principal finding of this work, taken together with our studies on iron metallocarboranes,[1d,6] is that the formal $[Co^{III}H]^{4+}$ and $[Fe^{II}H_2]^{4+}$ units[23] can function as isoelectronic surrogates for tetrapositive metals such as Ni^{4+}, and are versatile structural members in polyhedral carborane chemistry. A consequence of this fact is the existence of a family of neutral cobalt and iron *commo*-metallocarboranes incorporating pairs of dinegatively charged carborane ligands such as $C_2B_4H_6^{2-}$ and $C_2B_3H_7^{2-}$ and the planar difunctional cyclocarboranyl ligand $C_2B_3H_5^{4-}$. One of the more intriguing avenues for exploration that this suggests is the construction of neutral multidecked sandwich complexes from $C_2B_3H_5^{4-}$ and CoH^{4+} and/or FeH_2^{4+} groups, a possibility we are currently examining. Certainly the availability of $(C_2B_4H_6)Co^{III}H^{2+}$, $(C_2B_3H_7)Co^{III}H^{2+}$, and $(C_2B_4H_6)Fe^{II}H_2^{2+}$ groups (or their methyl derivatives) as substitutes for $(C_5H_5)Co^{2+}$ and $(CO)_3Fe^{2+}$ units in carborane frameworks enhances the already rich chemistry of this area; complexes which are end-capped with carboranyl ligands are amenable to further reactions such as metal insertion or boron removal, as seen in the behavior of species I and II. In contrast, $C_5H_5^-$ is a relatively inert capping group when η^5-coordinated to a metal ion, as shown by the fact that only one example is known of $C_5H_5^-$ pentahapto bonding to two metal ions simultaneously, as occurs in the $(\eta^5\text{-}C_5H_5)_3Ni_2^+$ cation.[24]

The apparent tendency toward metal-metal bond formation, in the metal insertion reactions described here, has been noted earlier. In addition to the three cases observed in this work, previous examples of direct insertion which produced species having metals in adjacent polyhedral vertices include the reactions of $(C_5H_5)CoC_2B_3H_5$ with $(C_5H_5)Co(CO)_2$ at 230°,[25] $(CO)_3FeC_2B_3H_5$ with $Fe(CO)_5$ at 230°,[25] $[(CH_3)_2C_2B_4H_4]_2FeH_2$ with $(\eta^5\text{-}C_5H_5)Co(CO)_2$ under ultraviolet irradiation,[6,26] $C_2B_5H_7$ with $(C_5H_5)Co(CO)_2$ at 260°,[25] and $C_2B_4H_7^-$ with $NiBr_2$ and $C_5H_5^-$ at 25°.[2b] The detailed nature of metal-metal interactions in polyhedral borane systems is largely unexplored, but a recent investigation of the thermal rearrangements[21] of small cobaltacarboranes indicated that complex and subtle factors are operative. Thus, the thermal isomerization of the 9-vertex $(\eta^5\text{-}C_5H_5)_2Co_2C_2B_5H_7$ system at 240–340° involves a reversible migration of the cobalt atoms between nonadjacent and adjacent vertices resulting in a measureable equilibrium of two isomers, both of which have now been crystallographically characterized.[27] These earlier results suggested that there are factors favoring metal-metal bonding in metallocarborane systems under moderate conditions, although other influences (such as steric repulsions between bulky ligands) may induce separation of the metal atoms at high temperatures. It may also be pointed out, as other workers have done recently,[28] that the few crystallographically established metal-metal bond lengths in metallocarboranes are at least comparable to those in metal cluster systems; thus, Co-Co distances in $(\eta^5\text{-}C_5H_5)_2Co_2C_2B_6H_8$, $(\eta^5\text{-}C_5H_5)_2Co_2C_2B_8H_{10}$, and $(\eta^5\text{-}C_5H_5)_2Co_2C_2B_5H_7$ are 2.489 (1),[28] 2.387 (2),[29] and 2.444 (2) Å[27] which compare with Co-Co lengths of 2.43–2.55 Å in cobalt clusters such as $(CO)_9Co_3OH$ and its derivatives.[30] Much further work remains in order to fully elucidate these early findings on metal-metal interactions in polyhedral metallocarboranes.

Experimental Section

Materials. 2,3-Dimethyl-2,3-dicarbahexaborane(8) [2,3-$(CH_3)_2C_2B_4H_6$] was prepared from 2-butyne and pentaborane(9) as described elsewhere,[31] and purified by GLC on 30% Apiezon L/Chromosorb W at 60°. All other reagents were reagent grade and used as received. Tetrahydrofuran (THF) was dried over $LiAlH_4$ before use.

Spectra. Boron-11 FTNMR spectra at 32.1 MHz and proton FTNMR spectra at 100 MHz were obtained on a JEOL PS-100P pulse Fourier transform spectrometer interfaced to a JEOL-Texas Instrument EC-100 computer system. Unit resolution mass spectra were obtained on a Hitachi-Perkin-Elmer RMU-6E mass spectrometer. High resolution mass spectra were recorded on an AEI MS-902 double-focusing instrument equipped with an SRI chemical ionization source and interfaced to a PDP-8I computer. All high resolution spectra were obtained under chemical ionizing conditions. Infrared spectra were obtained on a Beckman IR-8 instrument.

General Procedure. Except where otherwise indicated, all reactions were run in high vacuum systems or in an inert atmosphere. Thin layer and preparative layer chromatography were conducted in air on precoated plates of silica gel F-254 purchased from Brinckmann Instruments, Inc.

$[(CH_3)_2C_2B_4H_4]_2CoH$ (I). A tetrahydrofuran (THF) solution of $Na^+[(CH_3)_2C_2B_4H_5]^-$ was prepared[16] by distillation of $(CH_3)_2C_2B_4H_6$ (0.57 g, 5.53 mmol) onto NaH (0.20 g, 8.34 mmol) in 30 ml of THF in vacuo. The solution was filtered in the vacuum line onto anhydrous $CoCl_2$ (0.394 g, 3.02 mmol) at −196° in a 100-ml round-bottom flask. The reaction vessel was allowed to come to room temperature. After stirring for ~10 min, the color of the solution was dark green. No evolution of gas was detected. The reaction mixture was stirred magnetically for 2 h. After removal of THF via vacuum distillation, dry nitrogen was introduced into the reaction vessel, and the vessel was quickly attached to a sublimator. On heating at 60° and 10^{-5} Torr the tomato red product began to collect on the dry ice-cooled (−78°) cold finger. After 6 h of subliming, nitrogen was introduced into the flask, and the flask removed to a nitrogen-filled glove bag. The red-brown solid I was washed from the cold finger with degassed hexane to produce 216 mg of solid product (34% based on $(CH_3)_2C_2B_4H_6$ used). The yield of I has varied considerably.

The black material remaining in the reaction flask after sublimation was stirred for 1 h in air, in THF which had been acidified with ethyl acetate saturated with concentrated aqueous HCl. This solution was filtered and solvent was removed. The brown residue was placed on a column of silica (which had previously been acidified with acetic acid by stirring in a 10% acetic acid-hexane solution and then washed with hexane until all excess acetic acid had been removed) and eluted with hexane. The first band was bright yellow $[(CH_3)_2C_2B_4H_4]CoH[(CH_3)_2C_2B_3H_5]$ (II), 50 mg, and the second band obtained was colorless $(CH_3)_4C_4B_8H_8$, 60 mg.

Conversion of I to $(CH_3)_4C_4B_8H_8$. $[(CH_3)_2C_2B_4H_4]_2CoH$ on standing in the solid state in air decomposed rapidly (hours) to yield $(CH_3)_4C_4B_8H_8$. When stored in vacuo at room temperature, solid I darkened consderably over a period of several months, forming the tetracarbon species in low (<10%) yield.

$[C,C'\text{-}(CH_3)_2C_2B_4H_4]Co^{III}H[C,C'\text{-}(CH_3)_2C_2B_3H_5]$ (II). A 31.5-mg quantity of $[C,C'\text{-}(CH_3)_2C_2B_4H_4]_2CoH$ (I) was dissolved in 5 ml of acidified ethyl acetate (prepared by shaking 25 ml of ethyl acetate with 5 ml of concentrated aqueous HCl and pipetting off the ethyl acetate layer), to give the red-brown solution. After ~10 min, no color change was observed. THF (5 ml) was added to the solution, which slowly turned greenish yellow. After about 5 min, the solvent was removed on a rotary evaporator, leaving a yellow solid which was then taken up in CH_2Cl_2 and passed through a silica gel column. The yield of bright yellow solid II was 24.0 mg (79%). A 5.2-mg quantity of $(CH_3)_4C_4B_8H_8$ was also recovered. This preparation was conducted entirely in air using undegassed solvents.

Compound II sublimes at 10^{-5} Torr at 25° and is thermally stable in the gas phase below 150°; furthermore, no change was observed on refluxing in THF/acidified ethyl acetate solution under N_2 gas for 2 h. Following treatment with 0.17 M KOH in 50% THF/H_2O solution for 15 min followed by acidification with excess HCl, 60% of the original II was recovered unchanged.

$[(CH_3)_4N]^+[C,C'\text{-}(CH_3)_2C_2B_4H_4]Co^{III}[C,C'\text{-}(CH_3)_2C_2B_3H_5]^-$ (III). This salt was prepared by two different methods.

(a) Aqueous KOH in Air. $[(CH_3)_2C_2B_4H_4]CoH[(CH_3)_2C_2B_3H_5]$ (II) (8.2 mg, 0.032 mmol) was dissolved in 0.5 ml of CH_3OH; 1.0 ml of 40% aqueous KOH solution was added and the solution stirred for a few minutes. Excess aqueous $(CH_3)_4N^+Cl^-$ solution was then added, and a yellow precipitate immediately formed. The precipitate was collected, washed with water, dissolved in CH_2Cl_2, and passed through a silica column, giving a 6.3 mg (63%) yield of yellow crystalline III, mp 259–262°.

(b) NaH/THF in vacuo. A 38.2-mg (0.152 mmol) quantity of $[(CH_3)_2C_2B_4H_4]CoH[(CH_3)_2C_2B_3H_5]$ (II) was added to excess NaH (0.082 g, 3.4 mmol) in 2.5 ml of THF on the vacuum line. Vigorous bubbling ensued and a total of 0.17 mmol of H_2 was collected and measured in a Toepler pump. The reaction vessel was opened to a nitrogen atmosphere and the THF was removed on a rotary evaporator, leaving a dark amber oil in the flask. This oil was dissolved in water and an excess of aqueous $(CH_3)_4N^+Cl^-$ was added, forming a yellow precipitate. The solid was collected on a fritted glass filter, washed with water, dissolved in CH_2Cl_2, and column-chromatographed on silica using 20% CH_3CN/CH_2Cl_2 solution. The yield of yellow crystalline III was 28.5 mg (57%).

The solid salt III is stable in air but decomposes in solutions when exposed to air, and is soluble in CH_2Cl_2 and CH_3CN.

Protonolysis of III. Approximately 5 mg of the salt (III) was dissolved in 2 ml of THF. A small amount of ethyl acetate, acidified with concentrated aqueous HCl, was added. After stirring for a few minutes, the solvent was removed by distillation and the yellow-white residue extracted with pentane. The yellow pentane solution was evaporated leaving a bright yellow solid which was identified from its TLC behavior and mass spectrum as the neutral species $[(CH_2)_2C_2B_4H_4]CoH[(CH_3)_2C_2B_3H_5]$ (II).

Insertion of Cobalt into III. Formation of $[(\eta^5\text{-}C_5H_5)Co$-

$[(CH_3)_2C_2B_3H_3]CoH[(CH_3)_2C_2B_3H_5]$ (IV). A diglyme solution of $Na^+[(CH_3)_2C_2B_4H_4]Co[(CH_3)_2C_2B_3H_5]^-$ was prepared by reaction of II (26.3 mg, 0.104 mmol) with excess NaH in THF. The resulting solution was combined with a THF solution of $C_5H_5^-$ prepared by reaction of cyclopentadiene (C_5H_6, 0.4 mmol) with excess NaH. The mixture was filtered into a 10-ml round-bottom flask containing $CoCl_2$ (42.8 mg, 0.332 mmol). After stirring for ~1 h, 3 ml of 0.1 M HCl (aq) was added to the solution which was stirred for 20 min. Following filtration of the reaction mixture and removal of solvent, the black residue was thick-layer chromatographed on silica gel in hexane. One mobile band (red-brown, $R_f \sim 0.7$) was collected, giving a yield of 1.5 mg of $(\eta^5\text{-}C_5H_5)Co[(CH_3)_2C_2B_3H_3]CoH[(CH_3)_2C_2B_3H_5]$ (IV). This compound was also obtained in the following experiment.

Reaction of $[(CH_3)_2C_2B_4H_4]_2CoH$ (I) with $(\eta^5\text{-}C_5H_5)Co(CO)_2$. (a). In Refluxing THF. A 45-mg (0.17 mmol) quantity of I and $(\eta^5\text{-}C_5H_5)Co(CO)_2$ (101 mg, 0.57 mmol) were placed in a 10-ml round-bottom flask under dry nitrogen. After evacuation, 5 ml of THF was distilled into the flask and the solution was refluxed under dry nitrogen for 26 h. The reaction solution was then opened to air, stirred for 1 h, and filtered through silica gel. After removal of solvent, the black residue was chromatographed on silica in hexane. Two major bands were observed: a brown band (5.3 mg) and a red-brown band, R_f 0.71 (1 mg). The red-brown band was subsequently identified as IV. The brown solid exhibited a mass spectroscopic cutoff at *m/e* 376 with a less intense grouping at 338, in an intensity ratio of ~5:1. This material was developed several times on a thin-layer silica gel plate in hexane, yielding two products, one of which was bright green 1,2,4,5-$(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$ (V) (1 mg, R_f 0.13), with a mass spectroscopic cutoff at *m/e* 338. The remaining compound was identical with the previously characterized IV, and was assumed to have formed from the brown *m/e* 376 species (VII) on the silica plate (no IV was present prior to TLC treatment as shown by mass spectroscopic analysis). Compound VII was not isolated but was postulated to be $(\eta^5\text{-}C_5H_5)Co[(CH_3)_2C_2B_3H_3]CoH[(CH_3)_2C_2B_4H_4]$ (see text). (It is possible that IV could have formed via initial conversion of I to II followed by $(C_5H_5)Co$ insertion, but this is unlikely since no II was detected.)

(b). Under Ultraviolet Light. A 45-mg (0.17 mmol) quantity of I and 130 mg (1.0 mmol) of $(\eta^5\text{-}C_5H_5)Co(CO)_2$ were placed in 1-2 ml of THF in a quartz reactor and evacuated. The mixture was irradiated with a Sears 275-W sun lamp for 28 h with stirring. The reaction mixture was opened to the atmosphere, 5 ml of CH_2Cl_2 was added, and the solution was stirred for several hours. The remaining black residue was placed on silica plates and developed in hexane. A large number of bands of various colors were obtained, most of them weak. Two major bands were collected and purified by further thick-layer chromatography on SiO_2 with hexane and were identified as red-brown IV (1 mg) and green V (~0.1 mg). The remaining material on the TLC plate was collected and separated by TLC in 20% benzene-hexane, yielding one major band, dark brown with R_f 0.2. This material was collected as black solid $(\eta^5\text{-}C_5H_5)Co[(CH_3)_2C_2B_3H_3]CoH[(CH_3)_2C_2B_3H_3]Co(\eta^5\text{-}C_5H_5)$ (VI).

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References and Notes

(1) (a) C. P. Magee, L. G. Sneddon, D. C. Beer, and R. N. Grimes, *J. Organomet. Chem.*, **86**, 159 (1975); (b) A. Tabereaux and R. N. Grimes, *Inorg. Chem.*, **12**, 792 (1973); (c) M. L. Thompson and R. N. Grimes, *ibid.*, **11**, 1925 (1972); (d) L. G. Sneddon, D. C. Beer, and R. N. Grimes, *J. Am. Chem. Soc.*, **95**, 6623 (1973); (e) C. G. Savory and M. G. H. Wallbridge, *Chem. Commun.*, 622 (1971); (f) C. G. Savory and M. G. H. Wallbridge, *J. Chem. Soc., Dalton Trans.*, 918 (1972).

(2) (a) R. N. Grimes, *J. Am. Chem. Soc.*, **93**, 261 (1971); (b) R. N. Grimes, D. C. Beer, L. G. Sneddon, V. R. Miller, and R. Weiss, *Inorg. Chem.*, **13**, 1138 (1974); (c) N. N. Greenwood, C. G. Savory, R. N. Grimes, L. G. Sneddon, A. Davison, and S. S. Wreford, *J. Chem. Soc., Chem. Commun.*, 718 (1974).

(3) (a) R. N. Grimes, W. J. Rademaker, M. L. Denniston, R. F. Bryan, and P. T. Greene, *J. Am. Chem. Soc.*, **94**, 1865 (1972); (b) D. C. Beer, V. R. Miller, L. G. Sneddon, R. N. Grimes, M. Mathew, and G. J. Palenik, *ibid.*, **95**, 3046 (1973).

(4) R. N. Grimes, *Pure Appl. Chem.*, **39**, 455 (1974).

(5) M. F. Hawthorne and G. B. Dunks, *Science*, **178**, 462 (1972), and references therein.

(6) W. M. Maxwell, V. R. Miller, and R. N. Grimes, *Inorg. Chem.*, **15**, 1343 (1976).

(7) The chemical shifts of "pure" B–H–B bridging protons (i.e., where no metal atom is involved) are usually found below $\tau \sim 15$, while M–H or M–H–B proton resonances (M = transition metal) normally appear at somewhat higher field.[1d,8-10] However, the rule is useful only as an approximation, and some overlap in the chemical shift ranges in these two categories is to be expected.

(8) L. G. Sneddon and R. N. Grimes, *J. Am. Chem. Soc.*, **94**, 7161 (1972).

(9) C. J. Jones, J. N. Francis, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **95**, 7633 (1973).

(10) (a) V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **95**, 5078 (1973), and **98**, 1600 (1976). (b) The proposed structure of 2-$(\eta^5\text{-}C_5H_5)CoB_4H_8$ containing two Co–H–B bridges[10a] has been crystallographically confirmed: L. G. Sneddon and D. Voet, *J. Chem. Soc., Chem. Commun.*, 18 (1976).

(11) E. A. McNeill and F. R. Scholer, *Inorg. Chem.*, **14**, 1081 (1975).

(12) G. L. McKown, B. P. Don, R. A. Beaudet, P. J. Vergamini, and L. H. Jones, *J. Chem. Soc., Chem. Commun.*, 765 (1974).

(13) (a) T. Onak and J. B. Leach, *Chem. Commun.*, 76 (1971); (b) E. Groszek, J. B. Leach, G. T. F. Wong, C. Ungermann, and T. Onak, *Inorg. Chem.*, **10**, 2770 (1971).

(14) W. M. Maxwell, V. R. Miller, and R. N. Grimes, *J. Am. Chem. Soc.*, **96**, 7116 (1974).

(15) J. P. Brennan, R. N. Grimes, R. Schaeffer, and L. G. Sneddon, *Inorg. Chem.*, **12**, 2266 (1973).

(16) T. Onak and G. B. Dunks, *Inorg. Chem.*, **5**, 439 (1966).

(17) T. E. Paxson and M. F. Hawthorne, *J. Am. Chem. Soc.*, **96**, 4676 (1974).

(18) The differentiation between these two classes rests on the conventional assignments of a +3 oxidation state to the cobalt and rhodium atoms, and of a −2 charge to each carborane ligand ($C_2B_3H_7^{2-}$, $C_2B_4H_6^{2-}$, and $C_2B_9H_{11}^{2-}$). However, the chemical consequences, if any, of the formal distinction between "metal–proton" and "metal–hydride" metallocarboranes have yet to be established.

(19) M. F. Hawthorne, L. F. Warren, Jr., K. P. Callahan, and N. F. Travers, *J. Am. Chem. Soc.*, **93**, 2407 (1971).

(20) D. F. Dustin, W. J. Evans, C. J. Jones, R. J. Wiersema, H. Gong, S. Chan, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **96**, 3085 (1974).

(21) V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **97**, 4213 (1975).

(22) R. Weiss and R. N. Grimes, *J. Organometal. Chem.*, in press.

(23) The designation of $[Co^{III}H]^{4+}$ and $[Fe^{II}H_2]^{4+}$ as formal groups is intended only as a convenience in discussion, and is irrespective of the precise locations of the "extra protons" as discussed above.

(24) A. Salzer and H. Werner, *Angew. Chem., Int. Ed. Engl.*, **11**, 930 (1972).

(25) V. R. Miller, L. G. Sneddon, D. C. Beer, and R. N. Grimes, *J. Am. Chem. Soc.*, **96**, 3090 (1974).

(26) W. M. Maxwell, E. Sinn, and R. N. Grimes, *J. Am. Chem. Soc.*, **98**, 3490 (1976).

(27) R. N. Grimes, A. Zalkin and W. T. Robinson, *Inorg. Chem.*, in press.

(28) E. L. Hoel, C. E. Strouse, and M. F. Hawthorne, *Inorg. Chem.*, **13**, 1388 (1974).

(29) K. P. Callahan, C. E. Strouse, A. L. Sims, and M. F. Hawthorne, *Inorg. Chem.*, **13**, 1397 (1974).

(30) (a) J. Lewis, *Pure. Appl. Chem.*, **10**, 11 (1965); (b) B. R. Penfold, *Perspect. Struct. Chem.*, **2**, 71 (1968).

(31) T. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, **3**, 1686 (1964).