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New Chemistry of the Iron Dihydrogen Metallocarborane $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2FeH_2$. Reaction with CO and Cage Insertion of Germanium, Tin, and Cobalt

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The reaction of the title compound with carbon monoxide gas at 200 °C and 1.6 atm produced in good yield a ten-vertex dicarbon ferracarborane, $2,1,4\text{-}(CO)_3Fe(CH_3)_2C_2B_7H_7$, an analogue of *closo*-$C_2B_8H_{10}$. The $[(CH_3)_2C_2B_4H_4]_2FeH^-$ anion reacted with GeI_2 and with $SnCl_2$ to give $M^{IV}Fe(CH_3)_4C_4B_8H_8$ (M^{IV} = Ge or Sn), each product containing a "bare" germanium or tin atom; treatment of the same anion with $PbBr_2$ gave the tetracarbon carborane $(CH_3)_4C_4B_8H_8$. From ^{11}B and ^1H data and electron-counting arguments, the structures of these electron-hyperdeficient $M^{IV}Fe(CH_3)_4C_4B_8H_8$ systems are proposed to consist of two seven-vertex pentagonal bipyramids fused at a common iron vertex with an additional atom wedged between the polyhedra, as in the analogous $(\eta^5\text{-}C_5H_5)CoFe(CH_3)_4C_4B_8H_8$ structure reported earlier by Maxwell, Sinn, and Grimes. However, in the germanium and tin complexes the metal atom is proposed to occupy the wedging position, in contrast to the established Fe–Co structure in which the metal is in the equator of one of the polyhedra. Treatment of the title compound with $CoCl_2$ and cyclopentadiene in ethanolic KOH produced a mixture of cobaltaferracarboranes, cobaltacarboranes, iron(III) ferracarboranes, and a *B*-diethoxy derivative of the tetracarbon system $(CH_3)_4C_4B_8H_8$. The major new products were $\sigma\text{-}C_2H_5O\text{-}(\eta^5\text{-}C_5H_5)Fe^{III}(CH_3)_2C_2B_4H_3$, $(\eta^5\text{-}C_5H_5)Fe^{III}(CH_3)_2C_2B_4H_4$, $\sigma\text{-}C_2H_5O\text{-}(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_6$, and $(\eta^5\text{-}C_5H_5)Co[(CH_3)_2C_2B_3H_3]FeH_2[(CH_3)_2C_2B_4H_4]$, with smaller amounts of $1,2,4,5\text{-}(\eta^5\text{-}C_5H_5)Co[(CH_3)_2C_2B_3H_3]FeH(\eta^5\text{-}C_5H_5)$ and $(\sigma\text{-}C_2H_5O)_2\text{-}(CH_3)_4C_4B_8H_6$. The known triple-decked complex $1,7,2,3\text{-}(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$ was also isolated. The new compounds were isolated by thin-layer and column chromatography and characterized from their ^{11}B and ^1H pulse Fourier transform NMR, IR, and mass spectra. An x-ray structure determination of $\sigma\text{-}C_2H_5O\text{-}(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_6$ revealed it to be a distorted icosahedron related to $(CH_3)_4C_4B_8H_8$ with $Co(\eta^5\text{-}C_5H_5)$ replacing an apex BH group.

Introduction

The red metallocarboranes $[(CH_3)_2C_2B_4H_4]_2FeH_2$ and $[(CH_3)_2C_2B_4H_4]_2CoH$ are remarkable chemical species which have been shown to undergo several types of reaction,[1,2] including reversible deprotonation, insertion of $(\eta^5\text{-}C_5H_5)Co$, and, most strikingly, high-yield formation of the tetracarbon carborane $(CH_3)_4C_4B_8H_8$ on exposure of either metallocarborane to the atmosphere.[1-3] The known structure[4] of $(CH_3)_4C_4B_8H_8$, a distorted icosahedron consisting of two $(CH_3)_2C_2B_4H_4$ pyramids joined face-to-face, suggests that it forms by elimination of the FeH_2 or CoH moiety accompanied by oxidative fusion of the two $(CH_3)_2C_2B_4H_4^{2-}$ ligand groups. The face-to-face ligand-fusion phenomenon is thus far unique in boron chemistry, and it has seemed to us increasingly likely that the unusual behavior of $[(CH_3)_2C_2B_4H_4]_2FeH_2$ and $[(CH_3)_2C_2B_4H_4]_2CoH$ is associated with the metal-bound hydrogen atoms, structural features that are absent in other bis-ligand transition-metal carborane complexes. A recent x-ray analysis[5] has confirmed the gross structure proposed earlier[1] for $[(CH_3)_2C_2B_4H_4]_2FeH_2$, except that the carborane ligands are rotated in the solid such that the CCH_3 units are inequivalent with only one cage carbon atom in each ligand "eclipsed" relative to its counterpart in the other ligand. Related crystallographic studies have been conducted on $(\eta^5\text{-}C_5H_5)CoFe(CH_3)_4C_4B_8H_8$[6] (a product generated by insertion of $(C_5H_5)Co$ into the iron complex), on $(CH_3)_4C_4B_8H_8$ itself,[4] and on several metallocarboranes[7] derived from the latter molecule. At present, our information on the behavior of the metal-bound protons in solution consists of ^1H and ^{11}B NMR data[1,2] which indicate tautomeric exchange through several face-bound locations on the polyhedral surface in the vicinity of the metal.

As part of a continuing investigation of the chemistry of these species, we have extended our earlier study[1] of $[(CH_3)_2C_2B_4H_4]_2FeH_2$ and now present the recent findings.

Results and Discussion

Reaction with Carbon Monoxide. In an earlier report[1] we described the room-temperature interaction of $[(CH_3)_2C_2B_4H_4]_2FeH_2$ with $(\eta^5\text{-}C_5H_5)Co(CO)_2$ under UV light to generate two iron–cobalt metallocarboranes formulated as $(\eta^5\text{-}C_5H_5)CoFe(CH_3)_4C_4B_8H_8$ and $(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_3H_3Fe(CO)_3$, the latter species consisting of a seven-vertex CoC_2B_3Fe polyhedron. The remarkable aspect of the formation of the second compound is the transfer of carbonyl groups from cobalt to iron, with the carbonyls replacing one of the $(CH_3)_2C_2B_4H_4$ carborane ligands in the process. As a follow-up to that observation we have examined the direct thermal reaction of the iron complex with CO gas at low pressure (1.6 atm). The main product, isolated in 76% yield after 4 h at 200 °C, was a bright yellow solid which has been characterized as $(CO)_3Fe(CH_3)_2C_2B_7H_7$ (I) and assigned the structure shown in Figure 1.

The structural characterization of I follows from its ^{11}B and ^1H NMR spectra (Tables I and II) which reveal a 2:2:2:1 pattern of BH groups as well as nonequivalent methyl groups. The molecule is cage-isoelectronic with $B_{10}H_{10}^{2-}$, $C_2B_8H_{10}$, and

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

Compd	δ,[b] ppm (J, Hz)	Rel. areas
$2,1,4\text{-}(CO)_3Fe(CH_3)_2C_2B_7H_7$ (I)	+19.1 (156), +6.4 (156), −13.1 (136),[c] −15.9 (156)[c]	1, 2, 2, 2
$GeFe(CH_3)_4C_4B_8H_8$ (II)	+13.8 (166), +3.7 (156), −9.9 (126)	2, 4, 2
$SnFe(CH_3)_4C_4B_8H_8$ (III)	+11.4 (175), +2.3 (170), −10.9 (160)	2, 4, 2
$(C_5H_5)Co[(CH_3)_2C_2B_3H_3]FeH_2[(CH_3)_2C_2B_4H_4]$ (IV)	+10.9,[d] +7.3[d]	
$(C_5H_5)_2CoFeH(CH_3)_2C_2B_3H_3$ (V)	+28.7 (156), +4.3 (166)	2, 1
$(C_5H_5)Fe^{III}(CH_3)_2C_2B_4H_4$ (VI)	−355,[e,f] −564[e,g]	
$\sigma\text{-}C_2H_5O\text{-}(C_5H_5)Fe^{III}(CH_3)_2C_2B_4H_3$ (VIa)	+6,[e,h] −303[e,i]	
$\sigma\text{-}C_2H_5O\text{-}(C_5H_5)Co(CH_3)_4C_4B_7H_6$ (VII)	+11.1 (136), +9.1,[j] +1.2 (137), −7.9 (127), −16.8 (136)	1, 1, 2, 2, 1
$(\sigma\text{-}C_2H_5O)_2\text{-}(CH_3)_4C_4B_8H_6$ (VIII)	+1.0,[k] −10.0 (127),[c] −12.7 (112)[c]	2, 1, 1

[a] All spectra obtained in $CDCl_3$ solution. [b] Chemical shifts relative to $BF_3 \cdot O(C_2H_5)_2$ with *positive values indicating downfield shift* (*deshielding*); see ref 11. [c] Coupling constant estimated from overlapped resonances. [d] Chemical shifts obtained from proton-decoupled spectrum; $^1H-^{11}B$ coupling was unmeasurable in the heavily overlapped undecoupled spectrum. [e] Extremely broad singlet. [f] $W^{1/2} \approx$ 1500 Hz. [g] $W^{1/2} \approx$ 3000 Hz. [h] $W^{1/2} \approx$ 1000 Hz. [i] $W^{1/2} \approx$ 1300 Hz. [j] $C_2H_5O-^{11}B$ resonance. [k] $C_2H_5O-^{11}B$ resonance superposed on $H-^{11}B$ peak.

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

Compd	δ,[b] ppm (rel area)	Assignment
I ($CDCl_3$, undecoupled)	3.10 (1), 2.64 (1)	CH_3
(C_6D_6, ^{11}B decoupled)	3.69 (1)	H-B(10)
	3.09 (2)[c]	H-B(6,9)
	1.36 (2)[d]	H-B(3,5)
	1.19 (2)	H-B(7,8)
	3.10 (3), 2.64 (3)	CH_3
II	3.93	CH_3
III	1.99	CH_3
IV	5.14 (5)	C_5H_5
	2.17 (6), 2.02 (6)	CH_3
	−12.7 (2)[e]	Fe-H
V	4.87 (5), 3.98 (5)	C_5H_5
	2.06 (6)	CH_3
	−16.5 (1)[f,g]	Fe-H
	5.57 (2),[f] 1.16 (1)[f]	H-B
VI	11.3[h]	
VIa	14 (~1), 8.2 (~3), 7.0 (~3), −80[i]	
VII	4.96 (5)	C_5H_5
	3.88 (2)[j]	$-O-CH_2-$
	2.22 (3), 1.81 (3), 1.77 (3), 1.64 (3)	Cage CH_3
	1.11 (3)[k]	Ethoxy CH_3
VIII	3.75 (2)[j]	$-O-CH_2-$
	2.01 (3), 1.74 (3)	Cage CH_3
	1.12 (3)[l]	Ethoxy CH_3

[a] All spectra run in $CDCl_3$ solution at room temperature except where otherwise indicated. [b] Chemical shifts relative to $(CH_3)_4Si$; positive values indicate downfield shift. [c] BH resonance at δ 3.09 was observed unobscured by the CH_3 peak by partial relaxation employing a 180°–τ–90° pulse sequence to null out the CH_3 resonance ($\tau = 1.6$ s). The area of this peak was obtained by measuring its integrated intensity before and after ^{11}B decoupling. [d] Resonance appeared as a triplet on ^{11}B decoupling, indicating BH linked to only two other BH groups. [e] $W^{1/2} = 80$ Hz in undecoupled spectrum, 12 Hz in ^{11}B-decoupled spectrum. [f] Resonance observed only in ^{11}B-decoupled spectrum. [g] $W^{1/2} = 18$ Hz. [h] $W^{1/2} \approx 140$ Hz. [i] Too broad for area measurement; $W^{1/2} \approx$ 2000 Hz. [j] Multiplet (1:3:3:1) pattern further split by H_A-H_B coupling. [k] Triplet, $J = 7.1$ Hz. [l] Triplet, $J = 7.2$ Hz.

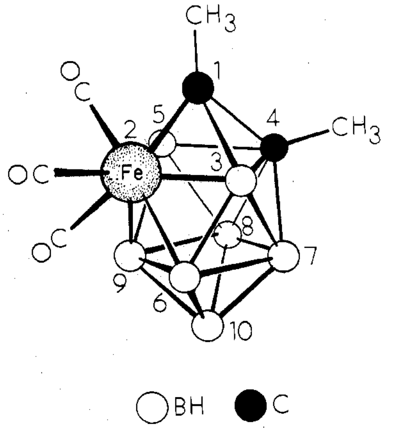

Figure 1. Proposed structure of $2,1,4\text{-}(CO)_3Fe(CH_3)_2C_2B_7H_7$.

Table III. Infrared Absorptions (CH_2Cl_2 Solution, cm^{-1})

I	2975 m, 2940 m–s, 2880 m, 2560 vs, 2092 vs, 2030 vs, 1998 s, 1940 s, 1455 m, br, 1390 m, 1085 w, 990 s, 960 m, 933 w, 905 w, 865 w, 850 w
II ($CHCl_3$ solution)	2990 m, 2970 m, sh, 2930 m, sh, 2870 m, 2570 vs, sh, 1445 s, 1380 m, 1265 m, sh, 1215 w, 1115 m, 1046 m, 1000 m, 950 w, 835 w, 815 w, 805 w, 780 w, 760 w
III	3020 s, sh, 2970 w, 2920 m, sh, 2860 w, 2570 vs, sh, 2000 m, 1935 w, 1520 w, 1445 m, 1215 vs, sh, 1115 w, 1045 w, 1000 w, 845 w, 765 w
IV	2950 sh, 2920 m, 2860 m, 2540 vs, 1430 w, br, 1375 w, 1350 w, 1120 w, 1045 w, 1000 m, br, 950 w, br, 970 m, 930 s
V	2940 sh, 2925 m, 2855 m, 2508 vs, 1740 m, br, 1350 w, br, 1145 m, br, 1110 m, 1045 w, 1000 m, 815 s
VI	2950 sh, 2925 m, 2860 m, 2545 vs, 1740 w, br, 1430 m, br, 1380 m, 1115 m, 1010 s, 970 w, 910 w, 860 w, 830 vs
VIa	2970 s, 2920 s, 2895 sh, 2870 sh, 2518 vs, 1910 w, 1820 w, br, 1750 w, br, 1670 w, br, 1480 w, 1430 w, br, 1393 w, 1372 s, 1305 vs, 1280 w, 1235 vs, 1155 m, 1115 m, 1095 m. 1042 s, 1008 m–s, 905 w, 880 m, 830 s, 790 m, br
VII	2966 w, sh, 2920 m, 2845 sh, m, 2500 vs, 1471 w, 1431 m, 1372 m, 1272 vs, 1154 w, 1098 m, 1038 m, 1001 s, 964 w, 936 m, 821 s

several known ten-vertex metallocarboranes [e.g., $(C_5H_5)CoC_2B_7H_9$,[8] $(C_5H_5)_2Co_2C_2B_6H_8$,[9] and $(C_5H_5)_3Co_3C_2B_5H_7$[10]] and hence should have bicapped square-antiprism geometry. A mirror plane is indicated, but there can be no higher symmetry; furthermore, the absence of a ^{11}B NMR signal at very low field tends to rule out the presence of a low-coordinate BH adjacent to the metal.[9] However, the area-1 BH resonance at δ +19.1 (applying the new boron sign convention[11]) can be assigned to *one* BH group in a low-coordinate (apex) location (B10). The CCH_3 groups are on the mirror plane and hence must occupy positions 1 and 4, as shown; they cannot be in 2 and 4 (with iron in 1) since this would generate equivalency. The only remaining location for the $Fe(CO)_3$ group (which must also be on the mirror) is position 2, which in fact is nonadjacent to the apex boron. The proposed structure for I is further supported by the ^{11}B-decoupled proton NMR spectrum (Table II), which reveals a 2:2:2:1 pattern of BH groups, one of the equivalent pairs having triplet fine structure indicative of spin coupling to just two adjacent BH units; this resonance can thus be assigned to H–B(3,5).

Compound I readily sublimes at 25 °C and 10^{-5} Torr and is evidently stable in air but somewhat sensitive to light. Its formation in relatively high yield suggests that displacement of the $(CH_3)_2C_2B_4H_4$ ligand occurs via a concerted process, possibly initiated by insertion of CO into an Fe–H bond in $[(CH_3)_2C_2B_4H_4]_2FeH_2$; indeed, we suspect that the oxidative ligand-fusion process[1,2] which generates $(CH_3)_4C_4B_8H_8$ is similarly instigated by the attack of O_2 on a metal–hydrogen link. Displacement of hydrogen in metal hydrides by carbon monoxide is a fairly common phenomenon in organometallic chemistry,[12a] as in the conversion of $HRe(\eta^5\text{-}C_5H_5)_2$ to $(CO)Re(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_6)$[12b] or the reaction of CO with $HRhCl(SiCl_3)[P(C_6H_5)_3]_2$[12c,d] to produce $(CO)RhCl[P(C_6H_5)_3]_2$ and Cl_3SiH. A pathway for the formation of I might well involve conversion of $[(CH_3)_2C_2B_4H_4]_2FeH_2$ to $[(CH_3)_2C_2B_4H_4]Fe(CO)_3$ [the C,C′-dimethyl derivative of the known species[13] 1,2,3-$(CO)_3FeC_2B_4H_6$], which in turn interacts with a reactive borane fragment produced by thermal decomposition of the original iron complex, to yield I.

Insertion of Germanium and Tin. Displacement of Hydrogen from $[(CH_3)_2C_2B_4H_4]_2FeH^-$ below Room Temperature. The biscarboranyl iron dihydrogen complex can be deprotonated by sodium hydride in tetrahydrofuran (THF) as described elsewhere.[1] The resulting anion reacted with germanium(II) iodide or tin(II) chloride, producing species characterized as

$$\begin{tikzcd}
{[(CH_3)_2C_2B_4H_4]_2FeH_2} \arrow[r, "NaH", "-H_2"'] & {} \\
{Na^+[(CH_3)_2C_2B_4H_4]_2FeH^-} \arrow[r, "GeI_2", "0\ ^\circ C"'] \arrow[d, "PbBr_2"', "-Pb^0"] \arrow[dr, "SnCl_2", "25\ ^\circ C"'] & {\underset{II,\ 10\%}{GeFe(CH_3)_4C_4B_8H_8}} \\
{\underset{50\%}{(CH_3)_4C_4B_8H_8}} & {\underset{III,\ 10\%}{SnFe(CH_3)_4C_4B_8H_8}}
\end{tikzcd}$$

$M^{IV}Fe(CH_3)_4C_4B_8H_8$ (M^{IV} = Ge, Sn) in ~10% yield. In contrast, the reaction of the same ferracarborane anion with lead(II) bromide gave only the tetracarbon carborane $(CH_3)_4C_4B_8H_8$, identical with the material produced by air oxidation of the iron–dihydrogen complex; thus, Pb^{2+} acts as an oxidant and does not effect metal insertion. These observations can be compared with the behavior of GeI_2, $SnCl_2$, and $PbBr_2$ toward $C_2B_5H_7^{2-}$ ion,[14] all of which gave only $C_2B_5H_7$ and free metal; the same metal reagents combine with the $C_2B_4H_7^-$ ion to give *closo*-$MC_2B_4H_6$ metallocarboranes,[14] whose stability decreases in the order Sn > Pb ≫ Ge.

The structural characterization of compounds II and III poses an intriguing problem. If it is assumed that the "bare" tin or germanium atom contributes two electrons to the polyhedral framework bonding (as in the group 4 metallocarboranes such as $MC_2B_9H_{11}$[15] and $MC_2B_4H_6$,[14] where M = Ge, Sn, or Pb), then II and III are electronic analogues of the previously reported[1] molecule $(\eta^5\text{-}C_5H_5)CoFe(CH_3)_4C_4B_8H_8$, in which the $(\eta^5\text{-}C_5H_5)Co$ group is a formal two-electron donor. The latter compound was revealed by an x-ray study[6] to have a unique structure (Figure 2a) in which the iron atom is sandwiched between $(CH_3)_2C_2B_4H_4$ and $(CH_3)_2C_2B_3H_3Co(C_5H_5)$ ligands, with an additional BH unit bound to iron and wedged between the two polyhedra. This geometry has been rationalized[6] in terms of the skeletal electron-counting theory[16] by observing that the molecular framework falls two electrons short of the number which would be required in order to have a "normal" geometry consisting of C_2B_4Fe and C_2B_4CoFe closo cages sharing a common iron atom. As in other cluster systems having fewer than $2n + 2$ framework valence electrons in an n-vertex polyhedron (a situation we have labeled[6] "electron hyperdeficiency"), the geometry adopted is that of a capped polyhedron; in the Fe–Co molecule, the unique feature is that a single BH unit caps two polyhedra simultaneously.

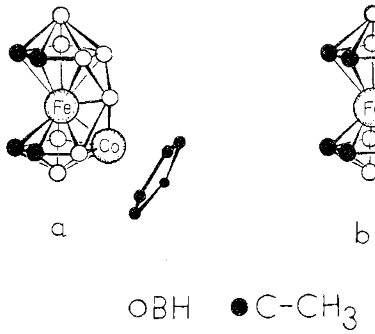

Figure 2. (a) Established[6] structure of $(\eta^5\text{-}C_5H_5)CoFe(CH_3)_4C_4B_8H_8$. (b) Proposed structure of $SnFe(CH_3)_4C_4B_8H_8$ and $GeFe(CH_3)_4C_4B_8H_8$. In each molecule, fluxional motion of the wedging metal atom is implied by the NMR spectra (see text).

The Fe–Ge and Fe–Sn systems (II and III) clearly have a different structure from the Fe–Co species, since the ^{11}B NMR 2:4:2 pattern and the single methyl resonance in the ^1H NMR spectra of II and III both point to a highly symmetrical geometry. The structure shown in Figure 2b is analogous to that of the Fe–Co compound except that the metal atom is placed in the wedging position instead of in a regular polyhedral vertex. Fluxional motion of the metal atom, alternating between two equivalent wedging locations involving the four FeB_2 triangular faces, would produce a time-averaged symmetry having a single methyl environment and a 2:4:2 BH pattern, thus satisfying the proton and boron NMR data. Such fluxionality, if it exists, must persist at low temperature in the tin species at least, since the proton NMR spectrum of III in toluene-d_8 at −66 °C exhibited a single methyl resonance.

The difference in the structures of II and III compared to the Fe–Co compound can perhaps be rationalized in terms of steric crowding of the $(\eta^5\text{-}C_5H_5)Co$ moiety with neighboring BH hydrogen atoms, which would occur if the Co occupied the wedging position as in Figure 2b; such interaction might induce the cobalt to move to the known equatorial location (Figure 2a). The "bare" tin or germanium atom, lacking an external ligand, would presumably be subject to no such steric constraints. All of these speculations are consistent with the idea that the original attack of the metal-inserting group (Co, Sn, Ge) occurs at the iron atom, so that the newly inserted metal would initially occupy a wedging position, moving elsewhere only when dictated by steric requirements.

Insertion of Cobalt in Ethanolic KOH Solution. As a sequel to the previously described[1] photolytic reaction of $[(CH_3)_2C_2B_4H_4]_2FeH_2$ with $(\eta^5\text{-}C_5H_5)Co(CO)_2$, an attempt was made to insert one or more $(C_5H_5)Co$ moieties into the iron complex under drastically different conditions. A mixture of $[(CH_3)_2C_2B_4H_4]_2FeH_2$ with excess $CoCl_2$, KOH, and cyclopentadiene in anhydrous ethanol was heated at 70 °C under nitrogen, after which the mixture was separated in air on TLC plates. Seven characterizable products were isolated in a total yield of 32%, including two cobaltaferracarboranes, an iron(III) ferracarborane and its σ-ethoxy derivative, two cobaltacarboranes, and a diethoxy derivative of a tetracarbon carborane (Scheme I). The cobaltaferracarboranes included brown–violet $(\eta^5\text{-}C_5H_5)Co[(CH_3)_2C_2B_3H_3]FeH_2[(CH_3)_2C_2B_4H_4]$ (IV) and brown $(\eta^5\text{-}C_5H_5)_2CoFeH(CH_3)_2C_2B_3H_3$ (V) for which we propose the structures shown in Figure 3. Electron-counting considerations,[16] the presence of only one C_5H_5 ligand in IV, and the method of synthesis all suggest that both IV and V contain a central seven-vertex $CoFeC_2B_3$ cage with adjacent equivalent carbon atoms, as shown in Figure 3. The ^{11}B NMR spectrum of V exhibits a

Scheme I. Products of Cobalt Insertion in Ethanolic KOH

$$[(CH_3)_2C_2B_4H_4]_2FeH_2 \xrightarrow[KOH,\ C_2H_5OH]{CoCl_2,\ C_5H_6} \xrightarrow[N_2]{70\ °C}$$

	mol % of isolated products
Ferracarboranes	
$(\eta^5\text{-}C_5H_5)Fe^{III}(CH_3)_2C_2B_4H_4$ (VI)	20.6
$B\text{-}\sigma\text{-}C_2H_5O\text{-}(\eta^5\text{-}C_5H_5)Fe^{III}(CH_3)_2C_2B_4H_3$ (VIa)	40.1
Cobaltaferracarboranes	
$(\eta^5\text{-}C_5H_5)_2CoFeH(CH_3)_2C_2B_3H_3$ (V)	4.5
$(\eta^5\text{-}C_5H_5)Co[(CH_3)_2C_2B_3H_3]FeH_2[(CH_3)_2C_2B_4H_4]$ (IV)	8.2
Cobaltacarboranes	
$B\text{-}\sigma\text{-}C_2H_5O\text{-}(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_6$ (VII)	14.2
$1,7,2,3\text{-}(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$	9.0
Carborane	
$B\text{-}\sigma\text{-}(C_2H_5O)_2\text{-}(CH_3)_4C_4B_8H_6$ (VIII)	3.5

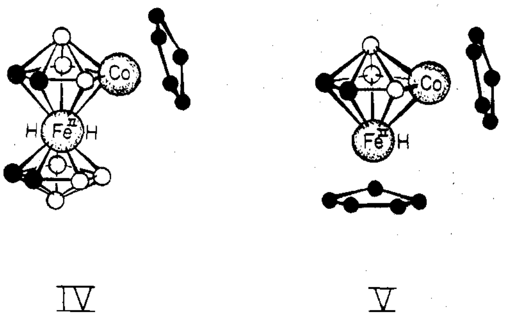

Figure 3. Proposed structures of $(\eta^5\text{-}C_5H_5)Co[(CH_3)_2C_2B_3H_3]\text{-}FeH_2[(CH_3)_2C_2B_4H_4]$ (IV) and $(\eta^5\text{-}C_5H_5)_2CoFeH(CH_3)_2C_2B_3H_3$ (V).

low-field resonance of area 2 which is indicative of a 1,2,4,5-type system as found in $1,2,4,5\text{-}(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$,[17] its C,C′-dimethyl derivative,[2] and several related compounds;[1,2,6,10] the dicobalt system has been the subject of detailed NMR studies via both proton spin decoupling (triple resonance)[18] and T_1 relaxation time measurements,[19] and thus provides a sound basis for comparison.

The ^{11}B NMR spectrum of IV exhibits a very short range of chemical shifts with heavily overlapped peaks even under proton decoupling, and the lowest field resonance is only 10.9 ppm below BF_3 etherate. Given the choice of placing the $(C_5H_5)Co$ group in an equatorial or an apical vertex, the former is preferred (Figure 3a) because of the similarity to V and also in view of the clear tendency[1,2,10] for the insertion of a second metal atom into a small monometallocarborane to occur at a vertex adjacent to the first metal.[20]

The major product isolated from this reaction was dark green $\sigma\text{-}C_2H_5O\text{-}(\eta^5\text{-}C_5H_5)Fe^{III}(CH_3)_2C_2B_4H_3$ (VIa), a B-substituted ethoxy derivative of the greenish brown parent species $1,2,3\text{-}(\eta^5\text{-}C_5H_5)Fe^{III}(CH_3)_2C_2B_4H_4$ (VI). Both compounds are evidently derivatives of the known[13] molecule $1,2,3\text{-}(\eta^5\text{-}C_5H_5)Fe^{III}C_2B_4H_6$ which has been assigned[13] a pentagonal bipyramidal structure with iron in the apex and adjacent carbon atoms in the equator; since the NMR spectra of all three species are typical of paramagnetic systems and exhibit extremely broad signals with very large chemical shifts, the exact location of the $B\text{-}OC_2H_5$ group in VIa cannot be given.

Of the cobaltaboranes obtained, one was red–brown $1,7,2,3\text{-}(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$, a known triple-decker complex.[21] A red–orange product was characterized as $\sigma\text{-}C_2H_5O\text{-}(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_6$ (VII), a species related to the well-characterized carborane $(CH_3)_4C_4B_8H_8$[1,4] with $Co(C_5H_5)$ replacing a BH unit. An x-ray diffraction study[22] of VII has shown it to be a distorted icosahedron similar to $(CH_3)_4C_4B_8H_8$, with cobalt occupying the 1-vertex and an ethoxy group at B12, the boron furthest from cobalt (Figure 4). The cage carbon atoms in VII are grouped in bonded pairs, as in $(CH_3)_4C_4B_8H_8$,[4] reflecting in both cases the synthesis from $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2FeH_2$; however, the distortion from regular icosahedral symmetry is greater in VII, with at least three of the icosahedral "edges" stretched to nonbonding lengths. The distortion in VII is, however, not as great as in the cage-isoelectronic species[7a] $(\eta^5\text{-}C_5H_5)Fe\text{-}(CH_3)_4C_4B_7H_8$ which has a well-defined six-membered open face; in the latter case, there is a B–H–B bridge on the edge of the open face. All three molecules VII, $(CH_3)_4C_4B_8H_8$, and $(\eta^5\text{-}C_5H_5)Fe(CH_3)_4C_4B_7H_8$ are 28-electron, 12-vertex systems for which significant deviation from regular closo geometry is predicted by electron-counting arguments.[16] The fact that the details of such distortions vary from compound to compound underlines the importance of subtle electronic and stereochemical factors which are not yet well understood. Further discussion of this point, and a full report on the structures of VII and other tetracarbon cobaltacarboranes, will be given elsewhere.[22]

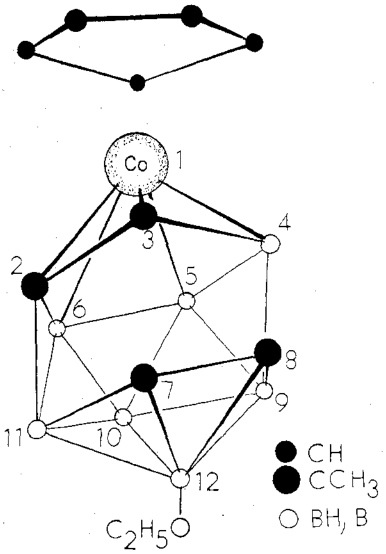

Figure 4. Schematic diagram of the structure of $\sigma\text{-}C_2H_5O\text{-}(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_6$ (VII) as determined crystallographically.[22] The molecule is a grossly distorted icosahedron with the distances C2–C7, C3–C7, and C3–C8 [2.694 (6), 2.854 (6), and 2.705 (6) Å, respectively] corresponding to nonbonding interactions; the distance B4–C8 [2.326 (7) Å] is at best marginally bonding. In comparison, the cage-isoelectronic molecule $(CH_3)_4C_4B_8H_8$[4] has a normal bond [1.53 (1) Å] between C3 and C7, with nonbonding distances for C2–C7 and C3–C8.

Also produced in this reaction, in low yield, was colorless $(\sigma\text{-}C_2H_5O)_2\text{-}(CH_3)_4C_4B_8H_6$ (VIII), a diethoxy derivative of the tetracarbon carborane itself. Significantly, neither $(CH_3)_4C_4B_8H_8$ nor $(C_5H_5)Co(CH_3)_4C_4B_7H_7$ (the unsubstituted counterparts of VII and VIII) were found among the products, suggesting that VII formed by replacement of a $B\text{-}OC_2H_5$ unit in VIII with a $(C_5H_5)Co$ group.

Summary. The variety of reactions and products based on $[(CH_3)_2C_2B_4H_4]_2FeH_2$ which have been described here and in earlier papers[1,6,7] is unusual even by the standards of metallocarborane chemistry. At least five kinds of processes can be identified, including (1) oxidative metal elimination and fusion of the C_2B_4 ligand groups to form a C_4B_8 cage; (2) reversible metal deprotonation by NaH; (3) loss of a $(CH_3)_2C_2B_4H_4$ ligand and replacement by CO groups; (4) oxidation to iron(III) metallocarboranes; and (5) insertion of transition- and main-group metals into the framework. The first two of these are exhibited as well by the cobalt analogue[2] $[(CH_3)_2C_2B_4H_4]_2CoH$, and it appears that the third may also (the reaction of the cobalt complex with CO gas yields an apparent cobaltacarborane carbonyl which has thus far defied structural characterization[23]). In all likelihood, process 5 is also characteristic of the cobalt compound, as shown by the insertion of second and third cobalt atoms on reaction with $(\eta^5\text{-}C_5H_5)Co(CO)_2$.[2]

Several of these reactions have previously been observed in certain larger metallocarborane systems,[24] notably metal oxidation and direct insertion of transition metals, but it is certainly uncommon to find a single species exhibiting so many different functions; obviously the metal–hydrogen iron and cobalt complexes are atypical, highly reactive metallocarboranes. We are currently attempting to extend this class to include analogues containing other transition metals and also to uncover the mechanistic details of these processes.

Experimental Section

Materials. The iron dihydrogen complex $[(CH_3)_2C_2B_4H_4]_2FeH_2$ was prepared as described elsewhere.[1] All other reagents were commercially obtained and were used as received except where otherwise stated.

Spectra. Boron-11 NMR spectra at 32.1 MHz and proton NMR spectra at 100 MHz were obtained on a JEOL PS-100P pulse Fourier transform spectrometer interfaced to a JEOL-Texas Instruments EC-100 computer system. Unit resolution mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E mass spectrometer; all compounds reported herein exhibited intense parent groupings and profiles consistent with their indicated formulas. High-resolution mass measurements were conducted on an AEI MS-902 double-focusing instrument equipped with an SRI chemical ionization source and 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.

Synthesis of 2,1,4-$(CO)_3Fe(CH_3)_2C_2B_7H_7$. A 70-mg (0.27 mmol) sample of $[(CH_3)_2C_2B_4H_4]_2FeH_2$ was placed in a dry-nitrogen filled Pyrex 1-L bulb fitted with a side arm containing a break-seal. The bulb was attached to the vacuum line, evacuated, and filled to 1 atm of pressure with CO gas (Matheson) which had been slowly passed through two −196 °C traps to remove impurities. The reactor was sealed and heated at 200 °C for 4 h, after which it was reattached to the vacuum line and the volatiles were pumped out through a −196 °C trap. A water bath at 80 °C was placed around the bulb while the neck was frozen with glass wool cooled by repeated application of liquid nitrogen; this caused the yellow solid product I to collect in the neck. The bulb was filled with dry nitrogen at 1 atm, the neck containing the product was cut off, and the yellow I was washed with degassed *n*-hexane into a storage flask. The yield of recrystallized product (hexane) was 57 mg (76% based on carborane starting material). The material appears stable in air but darkens on prolonged exposure to light. The unit-resolution mass spectrum of I contains a parent grouping with a cutoff at *m/e* 278 and fragment cutoffs indicating the successive loss of three carbonyl groups.

Synthesis of $GeFe(CH_3)_4C_4B_8H_8$. A 0.42-mmol sample of $[(CH_3)_2C_2B_4H_4]_2FeH_2$ was added to excess NaH (2.0 mmol) in 5 mL of THF on the vacuum line. Vigorous bubbling ensued and a total of about 0.4 mmol of H_2 was collected. The resulting solution of $Na^+[(CH_3)_2C_2B_4H_4]_2FeH^-$ was filtered in vacuo and added to a solution of 0.4 mmol of GeI_2 in 5 mL of THF at −196 °C. The mixture was allowed to warm slowly and was stirred for 30 min at −30 °C followed by 30 min at 0 °C. After the removal of THF via vacuum distillation, the reaction vessel was opened in a dry nitrogen-filled glove bag, and the reaction vessel was quickly attached to a vacuum sublimator containing a dry ice cooled finger. Red-brown solid $GeFe(CH_3)_4C_4B_8H_8$ (II) sublimed from the blood-red reaction mixture at room temperature and 10^{-5} Torr and collected slowly on the cold finger. The yield was 17 mg (12%). Calcd for $^{76}Ge^{56}Fe^{12}C_8{}^{11}B_7{}^{10}B^1H_{20}{}^+$, 335.0909; obsd, 335.0900.

Synthesis of $SnFe(CH_3)_4C_4B_8H_8$. The procedure described above for the preparation of the germanium compound was employed, using 0.21 mmol of $Na^+[(CH_3)_2C_2B_4H_4]_2FeH^-$ and 0.32 mmol of $SnCl_2$ in THF. The reaction mixture was stirred for 1 h at room temperature and was worked up as described in the preceding synthesis. The isolated product III was a dull red solid (8 mg, 10% yield). Calcd for $^{120}Sn^{56}Fe^{12}C_8{}^{11}B_8{}^1H_{21}{}^+$, 381.0758; obsd, 381.0751.

Reaction of $Na^+[(CH_3)_2C_2B_4H_4]_2FeH^-$ with $PbBr_2$. A solution of the metallocarborane salt (0.21 mmol) with $PbBr_2$ (0.22 mmol) in THF, stirred below −30 °C for 30 min, gave a dark brown solution and a black precipitate. After removal of solvent in vacuo, white crystalline $(CH_3)_4C_4B_8H_8$ was sublimed out of the gray–brown reaction residue and condensed on a −78 °C cold finger. The carborane was identified as the previously reported species[1,3] from its mass spectrum and characteristic R_f value on a TLC plate and was obtained in a yield of 0.11 mmol (~50%). No other characterizable product could be obtained from the reaction mixture.

Reaction of $[(CH_3)_2C_2B_4H_4]_2FeH_2$ with $CoCl_2$ and C_5H_6 in Ethanolic KOH. The iron metallocarborane (160 mg, 0.61 mmol), $CoCl_2$ (1.61 g, 12.4 mmol), and KOH (85% pellets, 2.67 g, 40.5 mmol) were placed in a 25-mL round-bottom flask which was attached to the vacuum line. Anhydrous ethanol (~15 mL) and cyclopentadiene (9.1 mmol) were distilled into the reactor which was heated at 70 °C with stirring under a dry-nitrogen atmosphere for 17 h. The reaction mixture was opened to the atmosphere and the gray–brown slurry was poured onto a fritted glass filter containing about 30 mL of silica gel. The filter was washed with methylene chloride until the solvent passing through was colorless. Solvent was removed by distillation in vacuo from the red–brown filtrate, leaving a thick black liquid residue which was placed onto several large TLC plates (20 × 20, 0.5 mm thickness) and developed in 50% benzene–hexane. Six colored, intense bands were obtained. The first band was a dark green-gray, which on subsequent development in *n*-hexane yielded three compounds: brown $(\eta^5\text{-}C_5H_5)_2CoFeH(CH_3)_2C_2B_3H_3$ (V), 3 mg; an unidentified green compound, 3 mg; and brown–green $(\eta^5\text{-}C_5H_5)Fe^{III}(CH_3)_2C_2B_4H_4$ (VI), 3 mg. The second band was brown–violet $(\eta^5\text{-}C_5H_5)Co[(CH_3)_2C_2B_3H_3]FeH_2[(CH_3)_2B_4H_4]$ (IV), 6 mg. The third band was additional brown–green $(\eta^5\text{-}C_5H_5)Fe^{III}(CH_3)_2C_2B_4H_4$ (VI), 6 mg, identical to the compound obtained on further development of the first band (see above); that portion of VI which was obtained from the first band was probably formed by reaction of another species on the TLC plate. The fourth band was a red–orange material which on subsequent development in 30% benzene–hexane yielded two bands; the first of these was a mixture of red–orange $\sigma\text{-}C_2H_5O\text{-}(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_6$ (VII), 10 mg, and $(\sigma\text{-}C_2H_5O)_2\text{-}(CH_3)_4C_4B_8H_6$ (VIII), 2 mg, which were separated by TLC development in 85% benzene–hexane. The fifth band (in the original TLC separation) was red–brown 1,7,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$, 6 mg, identified from its mass spectrum, ^{11}B NMR spectrum, and characteristic R_f value.[21] The sixth and last band was dark green $\sigma\text{-}C_2H_5O\text{-}(\eta^5\text{-}C_5H_5)Fe^{III}(CH_3)_2C_2B_4H_3$ (VIa), 21 mg.

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Registry No. I, 64103-53-3; II, 64091-69-6; III, 64091-70-9; IV, 64091-67-4; V, 64091-68-5; VI, 64091-71-0; VIa, 64081-90-9; VII, 64091-72-1; VIII, 64045-12-1; 1,7,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$, 51108-06-6; $[(CH_3)_2C_2B_4H_4]_2FeH_2$, 58846-86-9; $Na^+[(CH_3)_2C_2B_4H_4]_2FeH^-$, 64091-73-2; GeI_2, 13573-08-5; $SnCl_2$, 7772-99-8; $PbBr_2$, 10031-22-8; $CoCl_2$, 7646-79-9.

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Mechanism and Equilibrium Constants of the Reaction between η^4-Heterodieneiron Tricarbonyl Complexes and Group 5 Ligands

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The complexes $Fe(CO)_3(\eta^2\text{-}C_6H_4XCH{=}CHCHO)L$ (where L = CO, X = 4-NMe$_2$, 4-OMe, 3-OMe, 4-Me, 4-Cl; L = SbPh$_3$, X = 3-OMe, 4-Cl) and $Fe(CO)_2(\eta^4\text{-}C_6H_4XCH{=}CHCHO)L$ (where L = CO, X = 4-NMe$_2$, 4-OMe, 3-OMe, 4-Me, 4-Cl; L = PPh$_3$, X = H, 4-Cl, 4-Me, 4-OMe, 3-OMe) have been prepared and characterized. The reaction between $Fe(CO)_3(\eta^4\text{-}C_6H_4XCH{=}CHCHO)$ (where X = H, 3-OMe, 4-Cl) and SbPh$_3$ has been studied and the equilibrium constants and forward and reverse rate constants for this reaction have been measured. From the results obtained, it is concluded that the mechanism of this reaction proceeds via a dissociative equilibrium of the η^4 complexes to η^2 unsaturated complexes. The reaction between $Fe(CO)_3(\eta^4\text{-}C_6H_4XCH{=}CHCHO)$ (where X = H, 4-NMe, 3-OMe, 4-OMe, 4-Me, 4-Cl) and PPh$_3$ has also been studied. The kinetic law, the activation parameters, and the substituent effect indicate a reaction mode proceeding in two parallel directions. One of these is the same as that found for SbPh$_3$ and the other corresponds to an associative process with the phosphine ligand. These results may be generalized to other diene complexes of iron tricarbonyl.

Introduction

There are several literature reports of mechanistic studies on the reactivity of metal carbonyl complexes containing bidentate ligands, in most of which the bidentate ligands involved form bonds to the metal which are almost independent of one another.[1-4] By way of contrast, the complexes $M(CO)_n(\eta^4\text{-diene})$ (M = Mo, Fe, etc.) are sandwich systems with a delocalized iron–ligand bond. They are very important intermediates in the reactions of organic compounds with metal carbonyls.[5]

Unfortunately, the complexes with iron are very inert in nonpolar solvents and only at temperatures higher than 120 °C do they react with group 5 ligands (such as phosphines). There is only a single study on the reaction mechanism of such complexes,[6] but the results were not conclusive. $[Fe(CO)_3(\eta^4\text{-heterodiene})]$ complexes are much more reactive than their diene analogues[7,8] and kinetic studies may be carried out in relatively mild conditions.

We previously reported results on the products of the reaction between $Fe(CO)_3(\eta^4\text{-PhCH{=}CHCOR})$ complexes and group 5 ligands.[9] The present article describes the results of a detailed study of the mechanism of this reaction; this forms the basis for an investigation of the reactivity of $Fe(CO)_3(\eta^4\text{-diene})$ complexes, which will thus allow us to arrive at a complete picture of the reactivity of these iron carbonyls.

Experimental Section

General Data. All reactions involving organometallic complexes were carried out under a dry nitrogen atmosphere. The acetone was a commercial product (Carlo Erba, Milan) and was used without further purification. The benzene was purified by distillation over metallic sodium and the ethyl ether by distillation over LiAlH$_4$. Dichloromethane was heated at reflux over P$_2$O$_5$, and acetonitrile (AN) was purified as described in the literature.[10]

NMR spectra were obtained on CS$_2$ solutions using a Jeol C-60HL spectrometer with TMS as reference. IR spectra were registered on Perkin-Elmer IR 521 and 257 spectrophotometers using 0.5-mm NaCl cells.

Preparations. $C_6H_4XCH{=}CHCHO$. The compounds with X = H, 4-NMe, and 2-NO$_2$ were commercial products (Fluka, CH-9470 Buchs). Those with X = 4-Cl, 3-Cl, 3-OMe, 4-OMe, 4-Me, and 3-NO$_2$ were prepared from the corresponding acids, $C_6H_4XCH{=}CHCO_2H$, available commercially (Fluka). The acids were reduced to alcohols as follows. LiAlH$_4$ (in 0.6:1 mole ratio with respect to the acid) was added with stirring to 50 mL of diethyl ether in a three-necked flask and the mixture cooled to 0 °C. A diethyl ether solution was then added, dropwise with stirring (for acids only slightly soluble in diethyl ether, the reaction was carried out on the acid suspended in 500 mL of ether). The reaction was allowed to continue for ca. 1 h and the alcohol obtained separated using the usual workup procedures.[11] Yields were 70–80%, except for the derivative having X = 3-NO$_2$, the low solubility of which in diethyl ether greatly lowered the yield.

The alcohols were oxidized to aldehydes using CrO$_3$(py)$_2$, prepared as described in the literature.[12] The oxidations were carried out using the procedures of ref 12. The products obtained by crystallization from *n*-hexane were all low-melting solids; yields ca. 70%.

$Fe(CO)_4(\eta^2\text{-}C_6H_4XCH{=}CHCHO)$. Equimolar quantities of $C_6H_4XCH{=}CHCHO$ and Fe$_2$(CO)$_9$[13] were allowed to react in deaerated benzene at 12–15 °C until the Fe$_2$(CO)$_9$ crystals were consumed. The reaction times varied from 10 h to 2 days, depending