viously[25] for other polyphosphines containing PCH_2CH_2P structural units. Terminal phenyl and vinyl groups exhibit the expected four and two resonances, respectively, with each resonance except for the p-phenyl carbon being a doublet from the carbon-phosphorus splitting. Methyl resonances from $P[N(CH_3)_2]_2$ groups appear as doublets at δ 40.8 ± 0.1 with 12-13 Hz splittings, methyl resonances from $P(OCH_3)_2$ groups appear as doublets at δ 53.6 ± 0.1 with 9-12 Hz splittings, and methyl resonances from $P(CH_3)_2$ groups appear as doublets at δ 13.9 ± 0.2 with 13-15 Hz. splittings. The assignments of the carbon resonances in the PCH_2CH_2P bridges and the corresponding $|^1J(C-P)|$ and $|^2J(C-P)|$ are difficult and somewhat uncertain. However, the assignments presented for the PCH_2CH_2P carbons in Table III appear to be self-consistent and are reasonable when compared with previous data.[25] Terminal dialkylamino and methoxy groups, like terminal hydrogen atoms but unlike terminal alkyl and aryl groups, lead to nonequivalence of the two couplings $|^1J(C-P)|$ and $|^2J(C-P)|$ for the PCH_2CH_2P carbons so that these resonances appear as double doublets rather than triplets. For $-CH_2CH_2P(OCH_3)_2$ units the two $J(C-P)$ couplings are 21 ± 1 and 11 ± 2 Hz, whereas for $-CH_2CH_2P[N(CH_3)_2]_2$ units the two $J(C-P)$ couplings are 21 ± 2 and 14 ± 3 Hz. The carbon-13 NMR spectra of the terminal groups of the 1,4-diphosphacyclohexane derivatives $(C_2H_5)_2NP(CH_2CH_2)_2PR$ ($R = C_6H_5$ and $C_6H_5CH_2$) like their phosphorus-31 NMR spectra exhibit two sets of resonances, further demonstrating the presence of the two stereoisomers Ia and Ib. The carbon-13 NMR resonances from the $P(CH_2CH_2)_2P$ ring carbons appear as a very complex group of lines in the region δ 30-20. The complexity and overlapping of these resonances make it impossible to identify reliably individual ring carbon resonances in these 1,4-diphosphacyclohexane stereoisomers.

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Tetracarbon Metallocarboranes. 1. Iron, Nickel, and Molybdenum Complexes Derived from $(CH_3)_4C_4B_8H_8$. Crystal Structure of $(\eta^5\text{-}C_5H_5)Fe(CH_3)_4C_4B_7H_8$

William M. Maxwell, Robert F. Bryan, and Russell N. Grimes*

Contribution from the Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901. *Received December 9, 1976*

Abstract: Reduction of the carborane $(CH_3)_4C_4B_8H_8$ with sodium in tetrahydrofuran produces the apparent $(CH_3)_4C_4B_8H_8{}^{2-}$ dianion, which in turn reacts with $FeCl_2$ and NaC_5H_5 to generate a series of iron tetracarbon metallocarboranes. These include four isomers of a 14-vertex system, $(\eta^5\text{-}C_5H_5)_2Fe_2(CH_3)_4C_4B_8H_8$, and one isomer of a nido 12-vertex species, $(\eta^5\text{-}C_5H_5)Fe(CH_3)_4C_4B_7H_8$. The latter complex was structurally characterized by x-ray diffraction and was shown to contain an open face with a bridging B-H-B hydrogen atom. The four skeletal carbon atoms occupy three-, four-, four-, and five-coordinate vertices, three of them on the open face. The reaction of dichloro-1,2-bis(diphenylphosphine)ethanenickel(II) with $(CH_3)_4C_4B_8H_8{}^{2-}$ ion produces two isomers of the 12-vertex system $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_7H_7$ and three isomers of a 13-vertex system, $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$. Direct reaction of $Mo(CO)_6$ and of $W(CO)_6$ with the neutral species $(CH_3)_4C_4B_8H_8$ produces the 13-vertex species $(CO)_3M(CH_3)_4C_4B_8H_8$ (M = Mo or W). Crystal data for $(C_5H_5)Fe(CH_3)_4C_4B_7H_8$: space group $P2_1/c$, $Z = 4$, $a = 9.492(2)$, $b = 13.476(2)$, $c = 15.176(2)$ Å, $\beta = 124.01(1)°$, $V = 1609.2$ Å^3, $R = 3.8\%$ for 2370 reflections.

Carboranes containing more than two carbon atoms in the same polyhedral cage are rare. The only known tricarbon systems, all prepared in this laboratory, are $C_3B_3H_7$ (as methyl derivatives),[1] $C_3B_5H_7$,[2] and $(CO)_3MnCH_3C_3B_3H_5$.[3] The single example of a tetracarbon species[4] prior to this work is the pentagonal pyramidal molecule $C_4B_2H_6$, which has been synthesized by several different methods in parent[6,7] or peralkylated[8] form and structurally confirmed by microwave[9] and

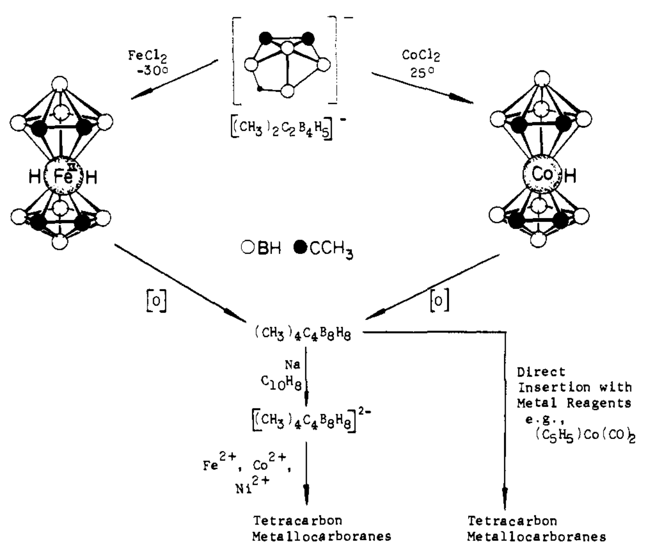

Figure 1. Schematic diagram showing routes for synthesis of tetracarbon metallocarboranes from the dicarbon species $Na^+[(CH_3)_2C_2B_4H_5]^-$.

electron diffraction[10] studies. All of these species are difficult to prepare, and the development of their potentially very interesting chemistry has been hampered accordingly.

Recently we reported[11] a new tetracarbon system, $(CH_3)_4C_4B_8H_8$, a compound obtainable in high yield by a straightforward preparative route involving the air oxidation of $[(CH_3)_2C_2B_4H_4]_2Co^{III}H$[12] or $[(CH_3)_2C_2B_4H_4]_2Fe^{II}H_2$[13] complexes. The ready accessibility of the tetracarbon carborane has permitted extensive studies of its chemistry, as a result of which a large family of tetracarbon metallocarboranes—the first examples of such species—has been generated. In this paper we describe the synthesis and characterization of several 12-, 13-, and 14-vertex systems containing iron, nickel, and molybdenum. Other aspects of tetracarbon metallocarborane chemistry, including an extensive series of cobalt species, will be presented in later reports.

Results and Discussion

Routes to Metallocarboranes from $(CH_3)_4C_4B_8H_8$. The synthesis of the carborane (described in detail elsewhere[11,13]) and the two main pathways by which transition metals have been incorporated into the cage framework are outlined in Figure 1. The methods depicted—alkali metal reduction of a carborane to a dianion followed by metal ion insertion[14] and direct reaction of a neutral carborane[15]—have both been employed in the past to synthesize metallocarboranes from dicarbon carboranes. In the work reported here the first of these techniques was the one primarily used, although examples of direct metal insertion will be given.

Reduction of $(CH_3)_4C_4B_8H_8$ to the Dianion. As reported previously,[11,13] the carborane is a colorless crystalline solid of measurable volatility at room temperature, mp 138 °C, which exists in solution as an equilibrium mixture of two isomers, A and B; the [A]/[B] ratio is ~2.0, essentially independent of solvent. On evaporation of solvent, the mixture reverts to a single isomer, A. An x-ray crystallographic study[16] of isomer A has established the structure as a distorted icosahedron (Figure 2), a geometry close to that which had been tentatively suggested for isomer B; the structure of B itself, which thus far has been observed only in solution, remains in doubt. Further discussion of the geometry of A and full details of the structure determination will be given in a separate publication.[16]

On treatment of the carborane with sodium naphthalide in tetrahydrofuran (THF) at −196 °C and subsequent warming to room temperature with stirring, the initially dark green solution changes to wine-red and finally to a clear yellow. The color changes suggest the stepwise reduction to a monoanion and a dianion. Although we have been unable to isolate a pure solid salt of the $(CH_3)_4C_4B_8H_8^{2-}$ ion due to a tendency to decompose on solvent removal, its formulation is supported by (1) the absence of H_2 evolution in its formation, (2) the normal ^{11}B NMR spectrum (vide infra) indicating a diamagnetic species, and (3) the facile formation of numerous metal complexes containing a formal $(CH_3)_4C_4B_8H_8^{2-}$ ligand. A proton-decoupled ^{11}B NMR spectrum of a CD_3CN solution of $Na_2(CH_3)_4C_4B_8H_8$ contained singlet peaks of equal area at δ −1.7, −13.3, −22.9, and −38.6 (parts per million relative to boron tetrafluoride etherate *with negative sign denoting upfield shift*[17]). These values compared with shifts[18] of δ 9.2, 8.4, −22.4, and −29.5 for neutral $(CH_3)_4C_4B_8H_8$ (isomer A); the fact that the dianion resonances are found at higher field, indicating increased shielding relative to the neutral molecule, is as expected. Also, the 2:2:2:2 pattern is consistent with the presence of a C_2 axis or a mirror plane in the dianion. In view of the known solid-state structure of the neutral carborane (Figure 2), the dianion is assumed to have a somewhat similar, but more open structure in which the pseudo-C_2 symmetry of the neutral molecule is retained. One possible means of achieving this would be to sever the C3–B4 and C7–B11 links (which are quite long even in the neutral species), thereby creating two five-sided open faces.

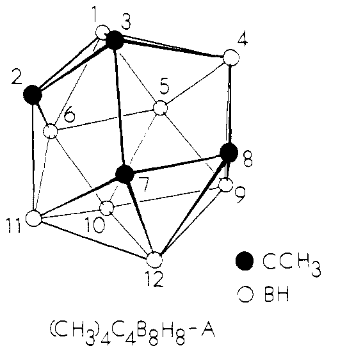

Figure 2. Structure[16] of $(CH_3)_4C_4B_8H_8$, isomer A. The distances C2–C7, C3–B11, C7–B4, and C3–C8 are nonbonding.

The $(CH_3)_4C_4B_8H_8^{2-}$ ion, a *C*-tetramethyl derivative of the unknown species $C_4B_8H_{12}^{2-}$, contains four more skeletal electrons than the closed-shell icosahedral systems $C_2B_{10}H_{12}$ and $B_{12}H_{12}^{2-}$, and is a $(2n + 6)$-electron (arachno) system, isoelectronic with the hypothetical $B_{12}H_{12}^{6-}$ species. The definition of an arachno cage as derived from a closo polyhedron by removal of two vertices[19] is in accord with the above suggestion for the structure of $(CH_3)_4C_4B_8H_8^{2-}$.

Iron Complexes. The ability of the $(CH_3)_4C_4B_8H_8^{2-}$ ion to readily accept transition metal ions is illustrated in the case of iron. When a THF solution of the ion, prepared from sodium naphthalide, was treated with sodium cyclopentadienide and ferrous chloride with subsequent exposure to the atmosphere, a series of mono- and diiron ferracarboranes was isolated in about 10% total yield.

$$(CH_3)_4C_4B_8H_8 \xrightarrow{NaC_{10}H_8} (CH_3)_4C_4B_8H_8^{2-}$$

$$\xrightarrow[FeCl_2]{NaC_5H_5} \underset{\text{V, red-brown}}{(C_5H_5)Fe(CH_3)_4C_4B_7H_8} + \underset{\substack{\text{four isomers:}\\ \text{I, brown}\\ \text{II, green}\\ \text{III, gray-brown}\\ \text{IV, gray}}}{(C_5H_5)_2Fe_2(CH_3)_4C_4B_8H_8}$$

The principal products were characterized from their ^{11}B and

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

Compd	δ,[b] ppm (*J*, Hz)	Rel areas
$(C_5H_5)_2Fe_2(CH_3)_4C_4B_8H_8$		
Isomer 1 (I)	38.5 (156), 26.6 (127),[c] 22.7 (137),[c] 19.0 (137),[c] 12.9 (180), −3.8 (157), −18.7 (136)	1,1,2,1,1,1,1
Isomer 2 (II)	9.3 (160), 2.3,[d] −1.6,[d] −12.5[d]	~2,2,3,1[c]
Isomer 3 (III)[d]	5.0, −3.5, −8.9, −23.9	~3,2,1,1,1[c]
$(C_5H_5)Fe(CH_3)_4C_4B_7H_8$ (V)	5.4 (166), −0.1 (168), −6.2 (175), −15.0 (160), −25.0 (146)	2,1,1,1,2
$[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4$-$C_4B_7H_7$		
Isomer 1 (VI)[d]	17.3, 4.2, −16.8, −26.9	2,1,3,1
Isomer 2 (VII)	1.8,[d] −13.8,[d] −36.0 (156)	~3,3,1[c]
$[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4$-$C_4B_8H_8$		
Isomer 1 (VIII)[d]	7.5, −15.0, −30.5	~2,2,4[c]
Isomer 2 (IX)	5.2,[d] −2.7 (165), −17.6 (157)	~2,4,2[c]
Isomer 3 (X)[d]	22.1, 12.4, −13.8, −21.7	~2,2,2,2
$(CO)_3Mo(CH_3)_4C_4B_8H_8$ (XI)	50.9 (156), 43.7 (176), 41.0 (172), 29.5 (168)	3,1,2,2[c]

[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 17. [c] Estimated from overlapped resonances. [d] Chemical shifts obtained from proton-decoupled spectra; ^{1}H−^{11}B coupling was unobservable in the heavily overlapped undecoupled spectra.

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

Compd	δ,[b] ppm (rel area)[c]	Assignment
I ($CDCl_3$)	4.58 (5) 4.54 (5)	C_5H_5
	2.80 (3), 2.67 (3), 2.64 (3), 1.11 (3)	CH_3
I (toluene-*d*$_8$)[d]	4.27 (5), 4.00 (5)	C_5H_5
	2.51 (3), 1.46 (3), 1.24 (6)	CH_3
II ($CDCl_3$)	4.31 (10)	C_5H_5
	2.68 (3), 2.30 (6), 2.01 (3)	CH_3
II (toluene-*d*$_8$)	3.97 (10)	C_5H_5
	2.82 (3), 2.28 (3), 1.94 (6)	CH_3
II (toluene-*d*$_8$, −32 °C)	4.02 (5), 3.84 (5)	C_5H_5
	2.82 (3), 2.28 (3), 1.99 (3), 1.78 (3)	CH_3
III[e]	4.53 (5), 4.29 (5)	C_5H_5
V	4.43 (5)	C_5H_5
	2.26 (3), 1.79 (3), 1.60 (6)	CH_3
	−4.54[f]	B-H-B
VI	7.35 (20)[g]	C_6H_5
	1.42 (3), 1.35 (3),[h] 1.22 (3), 0.77 (3)[i] ~2.4[j]	CH_3
VII	7.38 (20)[g]	C_6H_5
	2.22 (3), 1.54 (3), 1.32 (3), 0.71 (3) ~2.3[j]	CH_3
VIII	7.48 (20)[g]	C_6H_5
	1.64 (3), 1.47 (3), 1.42 (3),[k] 1.27 (3)[m] 2.32[j]	CH_3
IX	7.54 (20)[g]	C_6H_5
	1.72 (3),[n] 1.66 (3),[n] 1.40 (3), 0.47 (3), 2.78[j]	CH_3
X	7.97, 7.38 (20)[g]	C_6H_5
	1.87 (3), 1.83 (3), 1.51 (3), 1.06 (3) 2.53[j]	CH_3
XI	2.18 (3), 1.99 (3), 1.84 (3), 1.45 (3)	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 (deshielding). [c] Singlet resonance except where otherwise indicated. [d] Spectrum obtained at 70 °C was identical with that found at room temperature. [e] Methyl group resonances were not clearly identifiable due to impurities in the sample. [f] Observed on ^{11}B decoupling; seen as a triplet with J_{BH} = 6.5 Hz, $w_{1/2}$ = 17 Hz. [g] Most intense peak of multiplet. [h] Triplet, *J* = 2.8 Hz, possibly arising from ^{31}P−^{1}H coupling. [i] Triplet, *J* = 2.4 Hz. [j] Broad signal, probably due to -CH_2CH_2-. [k] Triplet, *J* = 3.8 Hz, partially overlapped with neighboring singlet. [m] Poorly resolved triplet. [n] Doublet, *J* = 2.44 Hz.

^{1}H Fourier transform NMR (Tables I and II), infrared (Table III), and mass spectra, and consist of several isomers of a 14-vertex $(\eta^5\text{-}C_5H_5)_2Fe_2(CH_3)_4C_4B_8H_8$ polyhedral system (I–IV) plus a 12-vertex species, $(\eta^5\text{-}C_5H_5)Fe(CH_3)_4C_4B_7H_8$ (V). The NMR data on these compounds reveal low symmetry and do not allow unambiguous structural assignments. Consequently, x-ray diffraction studies were undertaken on the 12-vertex system V and on isomers I and II of the diiron series. The structures[20] of the latter compounds (Figure 3) consist of $Fe_2C_4B_8$ polyhedra containing a five-sided open face in the case of I, and a four-sided open face in isomer II. Both structures violate the skeletal electron-count theory,[19b,c] which predicts closo geometry for these 14-vertex, 30-electron cages. However, at elevated temperatures both I and II undergo rearrangement to a single new isomer, which in turn converts ultimately to a highly symmetrical closo structure. The thermal rearrangement and detailed crystal structures of several of these isomers are discussed in the accompanying article.[20b]

The 12-vertex species V contains 28 skeletal electrons and hence was predicted to have a nido structure. This expectation was confirmed in an x-ray diffraction investigation, which disclosed the geometry shown in Figure 4 (crystallographic

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

I	2955 sh, 2930 s, 2860 m, 2500 vs, 1730 br, w, 1437 br, m, 1380 w, 1365 w, 1175 w, 1117 w, 1048 w, 1000 br, m, 915 w, 865 sh, 835 s, 815 sh
II	2930 m, 2865 w, 2505 s, 1440 br, w, 1375 w, 1112 w, 1005 w, 988 w, 830 s
V	2970 m, 2940 m, 2878 m, 2860 w, 2525 vs, 1840 br, w, 1775 br, w, 1690 br, w, 1445 s, 1390 w, 1380 m, 1367 sh, 1182 m, 1145 w, 1120 w, 1070 m, 1020 s, 997 w, 955 s, 915 w, 875 m, 840 s, 822 w
VI	2955 sh, 2925 m, 2863 w, 2520 s, 1600 br, w, 1482 w, 1430 m, 1380 w, 1100 m, 1005 w, 885 w, 815 w
VII	2925 m, 2875 w, 2500 m, 1710 br, w, 1600 w
VIII	3050 br, w, 2957 sh, 2925 m, 2870 w, 2520 vs, 1587 w, 1575 w, 1485 m, 1430 m, 1382 w, 1370 w, 1328 w, 1310 w, 1230 w, 1190 m, 1100 s, 1025 m, 1000 w, 960 m, 908 w, 875 m, 810 m, 670 sh, 645 m
IX	2950 sh, 2925 m, 2865 m, 2530 s, 1720 br, w, 1588 w, 1482 br, m, 1430 br, m, 1380 sh, 1180 m, 1120 w, 1100 m, 1070 w, 1033 w, 1000 m, 875 w, 810 m, 680 w, 645 w
X	2925 s, 2855 m, 2595 s, 2450 sh, 1735 br, w, 1480 w, 1430 br, w, 1188 w, 1098 m, 1005 w, 920 w, 875 w, 810 w
XI	2970 w, 2930 m, 2870 w, 2570 s, 2010 vs, 1955 vs, 1915 vs, 1435 br, m, 1385 s, 1375 w, 1200 sh, 1175 m, 1133 w, 1075 w, 1055 m, 1020 s, 985 m, 945 w, 917 w, 883 w, 855 m

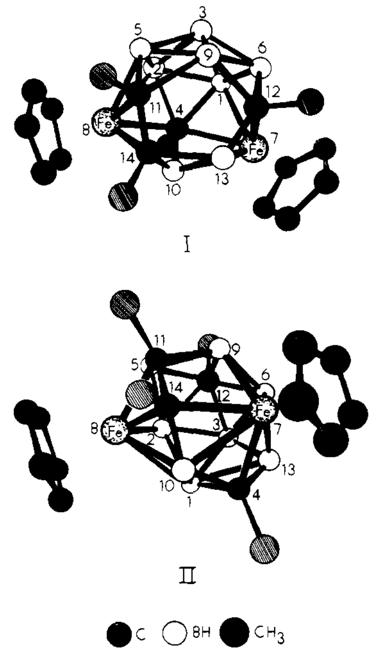

Figure 3. Structures[20] of (η^5-$C_5H_5)_2Fe_2(CH_3)_4C_4B_8H_8$ isomers I and II. The open face on I is defined by C11, B9, C12, B13, and C14, and the open face on II by C11, B9, Fe7, and C14.

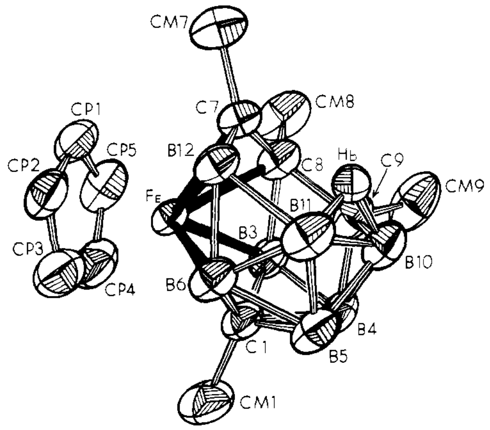

Figure 4. Structure of (η^5-$C_5H_5)Fe(CH_3)_4C_4B_7H_8$ (V).

data are given in Tables IV–VII). This molecule is the first example of a 12-vertex open-cage metallocarborane, and the structure raises some novel problems in carborane stereochemistry. First, it is noteworthy that while three of the skeletal carbon atoms occupy adjacent positions on the open face, the fourth carbon (C1) is as far removed from the open face as possible; this is surprising, since the $(CH_3)_4C_4B_8H_8$ precursor has four contiguous carbon atoms (Figure 2), and the synthesis of V was conducted under mild conditions not ordinarily conducive to carbon migration.[21]

Second, the four C–CH_3 units occupy respectively three-, four-, four-, and five-coordinate vertices in the framework, frustrating any simple rationalization of the carbon locations in terms of a preference for low-coordinate sites as Williams[22] has given for carboranes in general. Third, there is a marked difference between the structure of V and that of its analogue $(C_6H_5)_2C_2B_{10}H_{11}^-$, a *C,C'*-diphenyl derivative of $C_2B_{10}H_{13}^-$, which is obtained by protonation of the $C_2B_{10}H_{12}^{2-}$ ion. Each of these dicarbon carborane anions, like V, contains 28 skeletal electrons, but a crystallographic study[23] of $(C_6H_5)_2$-$C_2B_{10}H_{11}^-$ disclosed that only one of the cage carbon atoms is fully integrated into the cage framework. The other carbon is methylenic and exists as a C_6H_5CH unit connected to just two boron atoms on the open face of an 11-vertex CB_{10} skeleton; no bridging hydrogen atoms are present, the "extra" hydrogen being part of the C_6H_5CH moiety. In compound V, there is no methylenic carbon atom[24] and the "extra" hydrogen adopts a B–H–B location on the open face. Unfortunately, direct comparisons between V and the parent species $C_2B_{10}H_{12}^{2-}$ and $C_2B_{10}H_{13}^-$ are not possible, since these ions have not been structurally characterized.

Several other points relevant to the structure are worth noting. The molecule can be viewed as a metallocene-type sandwich, since the ring C7–B12–B6–C1–B3–C8 coordinated to iron is planar, as is the C_5H_5 ligand, and the two rings are nearly parallel (Table VII). The two framework C–C distances are considerably different [1.454 (3) Å for C7–C8 and 1.616(3) Å for C8–C9], but this can be ascribed to constraints of the cage structure rather than to electronic factors. The relatively long distances from C1 to its neighbors in the cage are comparable to those of other carbon atoms occupying five-coordinate vertices in polyhedral carboranes.[25] Finally, there is no obvious pattern to the arrangement of framework carbon atoms relative to the metal, in that three of the four carbons are adjacent to iron. The distribution of carbons indicates rather strongly that kinetic rather than thermodynamic factors are predominant in dictating the locations of heteroatoms in this cage.

Nickel Complexes. The addition of dichloro-1,2-bis-(diphenylphosphino)ethanenickel(II) to a solution of $(CH_3)_4C_4B_8H_8^{2-}$ in THF with subsequent workup in air produced five isolable metallocarboranes, of which two (VI and VII) were identified as isomers of $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4$-$C_4B_7H_7$, and the other three (VIII, IX, and X) as isomers of $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$. The total yield was 24% based on carborane consumed. The characterization of these compounds from spectroscopic data (Tables I–III) and high resolution mass measurements did not permit rigorous assignment of structure, but some inferences can be drawn. Since

Table IV. Atomic Parameters and their Standard Deviations for $(\eta^5\text{-}C_5H_5)Fe(CH_3)_4C_4B_7H_8$[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	38691 (5)	19112 (3)	17486 (3)	85.6 (6)	37.9 (2)	41.6 (2)	1.2 (3)	42.1 (3)	−0.8 (2)
C1	1650 (4)	2738 (2)	693 (2)	102 (5)	57 (2)	45 (2)	13 (3)	47 (3)	7 (2)
C7	3750 (3)	1643 (2)	3036 (2)	120 (5)	41 (2)	41 (2)	9 (2)	52 (3)	2 (1)
C8	2286 (4)	1147 (2)	2139 (2)	124 (5)	34 (2)	60 (2)	−3 (2)	64 (3)	−1 (2)
C9	401 (4)	1620 (2)	1532 (3)	101 (5)	45 (2)	74 (2)	−18 (2)	65 (3)	−7 (2)
CM1	1358 (5)	3091 (3)	−360 (3)	179 (7)	104 (3)	54 (2)	40 (4)	60 (4)	30 (2)
CM7	4976 (4)	1031 (3)	4010 (3)	200 (7)	57 (2)	60 (2)	32 (3)	73 (4)	16 (2)
CM8	2243 (4)	15 (2)	2175 (3)	209 (7)	34 (2)	110 (3)	−4 (3)	102 (4)	1 (2)
CM9	−1008 (4)	903 (3)	1308 (4)	151 (7)	67 (3)	151 (4)	−33 (3)	111 (5)	−18 (3)
CP1	6200 (4)	1180 (3)	2452 (3)	112 (5)	70 (2)	67 (3)	31 (3)	60 (3)	16 (2)
CP2	6374 (4)	2171 (3)	2273 (3)	101 (5)	66 (2)	78 (3)	−3 (3)	63 (3)	1 (2)
CP3	5312 (4)	2353 (3)	1190 (3)	185 (7)	75 (3)	97 (3)	35 (4)	115 (4)	31 (2)
CP4	4469 (4)	1453 (3)	691 (3)	148 (6)	117 (3)	60 (3)	25 (4)	70 (4)	−12 (2)
CP5	5025 (4)	738 (3)	1480 (3)	156 (6)	62 (2)	108 (3)	10 (3)	100 (4)	−15 (2)
B3	1336 (4)	1544 (3)	824 (3)	96 (6)	55 (2)	48 (2)	−10 (3)	41 (3)	−17 (2)
B4	−159 (4)	2439 (3)	585 (3)	78 (5)	70 (3)	53 (3)	7 (3)	35 (3)	−3 (2)
B5	808 (4)	3554 (3)	1178 (3)	129 (6)	44 (2)	74 (3)	24 (3)	67 (4)	13 (2)
B6	3052 (4)	3356 (2)	1809 (3)	125 (6)	29 (2)	64 (3)	−3 (3)	63 (3)	5 (2)
B10	239 (4)	2738 (3)	1860 (3)	111 (6)	54 (2)	71 (3)	6 (3)	69 (4)	0 (2)
B11	2144 (5)	3520 (3)	2536 (3)	144 (6)	34 (2)	66 (3)	1 (3)	67 (4)	−5 (2)
B12	4068 (4)	2739 (3)	3039 (3)	101 (5)	42 (2)	42 (2)	−2 (3)	38 (3)	−7 (2)
H3	85 (3)	102 (2)	18 (2)	3.1 (8)[b]					
H4	−145 (4)	237 (2)	−20 (2)	3.3 (8)					
H5	24 (4)	424 (2)	76 (2)	4.2 (9)					
H6	365 (3)	403 (2)	176 (2)	2.0 (8)					
H10	−85 (3)	288 (2)	193 (2)	0.7 (7)					
H11	220 (4)	418 (2)	298 (2)	4.1 (9)					
H12	523 (4)	304 (2)	370 (2)	1.9 (8)					
Hb	169 (4)	284 (2)	281 (2)	2.2 (8)					
HM1a	28 (5)	351 (3)	−77 (3)	5.6 (10)					
HM1b	232 (5)	355 (3)	−21 (3)	8.2 (12)					
HM1c	100 (5)	255 (3)	−84 (3)	7.6 (11)					
HM7a	444 (5)	84 (3)	436 (3)	7.4 (11)					
HM7b	526 (4)	39 (2)	383 (2)	5.1 (10)					
HM7c	598 (4)	143 (3)	459 (3)	6.0 (10)					
HM8a	334 (4)	−25 (2)	243 (3)	2.9 (8)					
HM8b	213 (4)	−19 (3)	272 (3)	6.2 (10)					
HM8c	134 (4)	−26 (3)	150 (3)	7.1 (11)					
HM9a	−62 (5)	59 (3)	198 (3)	12.6 (17)					
HM9B	−122 (4)	36 (2)	86 (2)	5.0 (9)					
HM9c	−199 (4)	125 (2)	97 (2)	4.1 (9)					
HCP1	685 (4)	85 (2)	313 (2)	3.0 (8)					
HCP2	706 (4)	264 (2)	277 (2)	4.9 (9)					
HCP3	513 (5)	303 (2)	86 (3)	5.1 (10)					
HCP4	367 (4)	134 (3)	−1 (3)	6.2 (10)					
HCP5	463 (4)	9 (3)	139 (3)	6.9 (11)					

[a] Positional parameters are given as fractions of the unit cell edges (Fe × 10^5, C and B × 10^4, H × 10^3), anisotropic thermal parameters (×10^4) are given for the exponent in the form $-[h_i{}^2\beta_{ii} + \ldots 2h_ih_j\beta_{ij} + \ldots]$, and isotropic thermal parameters as B (Å^2). Standard deviations, in parentheses, are applicable to the least significant digits given. [b] All hydrogen atoms were refined isotropically.

the $[(C_6H_5)_2PCH_2]_2Ni$ group is expected to supply two electrons to the polyhedral framework,[19] VI and VII are 28-electron, 12-vertex systems and are electronically analogous to the monoiron nido complex, V. However, unlike V, VI and VII contain no extra hydrogen atoms and hence no B-H-B bridges, as confirmed by ^1H NMR, IR, and CI mass spectra. Thus we expect VI and VII to have a gross geometry similar to the known structure of V, but with differing locations of C-CH_3 units in the cage. The absence of bridging hydrogens in the nickel compounds may induce some structural differences from V, but these are likely to be minor given the steric constraints of 12-vertex nido cages; i.e., a large open face as in V seems unavoidable. The arrangements of C-CH_3 groups in VI and VII cannot be assigned at present, but it is clear from the NMR data that no symmetry exists in either molecule.

The 13-vertex isomers VIII, IX, and X present a more challenging structural problem. With 30 framework electrons, these are $2n + 4$ systems and therefore a nido geometry derived from a 14-member closed polyhedron with one missing vertex is to be expected.[19] However, this prediction is complicated by the fact that the only structurally established 14-atom polyhedra are the diiron species I and II together with two other isomers which are described in the following paper.[20b] These systems represent three different gross geometries, from any of which a 13-vertex nido cage might be derived by removal of one framework atom. Again, the NMR spectra afford little help in elucidating the geometries of VIII, IX, and X, except that the proton spectra rule out symmetry in any of these species. The broad, diffuse ^{11}B NMR resonances are typical of nickel metallocarboranes and yield little useful information. Structural characterization of the NiC_4B_8 systems VIII-X consequently appears attainable only with x-ray diffraction studies.

Molybdenum and Tungsten Complexes. In contrast to the iron and nickel compounds described above, the species $(CO)_3Mo(CH_3)_4C_4B_8H_8$ (XI) and $(CO)_3W(CH_3)_4C_4B_8H_8$ (XII) were generated by direct reaction of the neutral carborane I with $Mo(CO)_6$ or $W(CO)_6$ in heptane as described in

Table V. Bond Distances (Å) for $(\eta^5\text{-}C_5H_5)Fe(CH_3)_4C_4B_7H_8$[a]

Fe-CP1	2.089 (3)	C8-CM8	1.528 (4)
Fe-CP2	2.072 (2)	C8-C9	1.616 (3)
Fe-CP3	2.061 (3)	C9-CM9	1.526 (4)
Fe-CP4	2.074 (3)	C9-B10	1.621 (4)
Fe-CP5	2.090 (3)	B10-H10	1.110 (23)
Fe-C1	2.114 (2)	B10-Hb	1.332 (28)
Fe-B3	2.054 (3)	B10-B11	1.832 (4)
Fe-B6	2.116 (3)	B11-H11	1.102 (29)
Fe-C7	2.051 (2)	B11-Hb	1.177 (27)
Fe-C8	2.160 (2)	B11-B12	1.861 (4)
Fe-B12	2.168 (3)	B12-H12	1.074 (28)
C1-CM1	1.537 (4)	CP1-CP5	1.391 (4)
C1-B3	1.668 (4)	CP1-CP2	1.390 (4)
C1-B4	1.688 (4)	CP2-CP3	1.387 (4)
C1-B5	1.747 (4)	CP3-CP4	1.417 (5)
C1-B6	1.676 (4)	CP4-CP5	1.390 (5)
B3-H3	1.074 (28)	CP1-HCP1	0.963 (27)
B3-B4	1.739 (4)	CP2-HCP2	0.917 (32)
B3-C8	1.751 (4)	CP3-HCP3	1.009 (32)
B3-C9	1.737 (4)	CP4-HCP4	0.903 (32)
B4-H4	1.136 (30)	CP5-HCP5	0.928 (35)
B4-B5	1.729 (5)	CM1-HM1a	1.019 (37)
B4-C9	1.646 (4)	CM1-HM1b	1.017 (60)
B4-B10	1.798 (5)	CM1-HM1c	0.944 (36)
B5-H5	1.083 (29)	CM7-HM7a	0.953 (34)
B5-B6	1.801 (4)	CM7-HM7b	0.980 (33)
B5-B10	1.789 (5)	CM7-HM7c	1.014 (34)
B5-B11	1.713 (5)	CM8-HM8a	0.954 (29)
B6-H6	1.096 (27)	CM8-HM8b	0.933 (32)
B6-B11	1.753 (4)	CM8-HM8c	0.963 (34)
B6-B12	1.759 (4)	CM9-HM9a	0.967 (38)
C7-CM7	1.514 (4)	CM9-HM9b	0.933 (31)
C7-C8	1.454 (3)	CM9-HM9c	0.909 (31)
C7-B12	1.507 (4)		

[a] All distances given are intramolecular. All *inter*molecular distances under 3.0 Å are H-H contacts, the nearest being 2.44 Å between H11 and HM9a and 2.45 Å between H3 and HM8c.

Table VI. Selected Bond Angles (deg) for $(\eta^5\text{-}C_5H_5)Fe(CH_3)_4C_4B_7H_8$

C7-Fe-C8	40.3 (1)	C7-C8-B3	122.7 (2)
C7-Fe-B3	86.6 (1)	C7-C8-C9	121.7 (2)
C7-Fe-C1	104.6 (1)	C7-C8-CM8	117.1 (3)
C7-Fe-B6	84.5 (1)	B3-C8-C9	62.0 (2)
C7-Fe-B12	41.7 (1)	B3-C8-CM8	109.8 (2)
C8-Fe-B3	49.0 (1)	C9-C8-CM8	111.8 (2)
C8-Fe-C1	84.7 (1)	C8-C9-B3	62.8 (2)
C8-Fe-B6	95.7 (1)	C8-C9-B4	118.4 (2)
C8-Fe-B12	73.7 (1)	C8-C9-B10	117.2 (2)
B3-Fe-C1	47.2 (1)	C8-C9-CM9	115.4 (2)
B3-Fe-B6	86.2 (1)	B3-C9-B4	61.8 (2)
B3-Fe-B12	102.6 (1)	B3-C9-B10	114.5 (2)
C1-Fe-B6	46.7 (1)	B3-C9-CM9	120.8 (3)
C1-Fe-B12	87.7 (1)	B4-C9-B10	66.8 (2)
B6-Fe-B12	48.5 (1)	B4-C9-CM9	114.5 (3)
Fe-C1-CM1	118.4 (2)	B10-C9-CM9	115.8 (3)
Fe-C1-B3	64.5 (1)	B10-Hb-B11	94 (2)
Fe-C1-B6	66.7 (2)	B6-B11-Hb	122 (1)
Fe-C1-B4	118.6 (2)	B5-B11-Hb	106 (1)
Fe-C1-B5	120.6 (2)	B12-B11-Hb	84 (1)
CM1-C1-B3	118.9 (3)	B10-B11-Hb	47 (1)
CM1-C1-B6	118.4 (3)	H11-B11-Hb	108 (2)
CM1-C1-B4	113.1 (2)	C9-B10-Hb	102 (1)
CM1-C1-B5	112.6 (3)	B11-B10-Hb	40 (1)
B3-C1-B6	116.9 (2)	B4-B10-Hb	131 (1)
B3-C1-B4	62.6 (2)	B5-B10-Hb	95 (1)
B3-C1-B5	113.8 (2)	H10-B10-Hb	110 (2)
B6-C1-B4	114.1 (2)	C9-B10-B11	118.2 (2)
B6-C1-B5	63.5 (2)	B10-B11-B12	109.8 (2)
B4-C1-B5	68.6 (2)	B11-B12-C7	113.8 (2)
Fe-C7-C8	73.9 (2)	Fe-B3-B4	118.8 (2)
Fe-C7-B12	73.3 (2)	B3-B4-B5	111.1 (2)
Fe-C7-CM7	127.2 (2)	B4-B5-B6	105.8 (2)
C8-C7-B12	122.6 (2)	Fe-B6-B5	117.8 (2)
C8-C7-CM7	118.3 (3)	CP1-CP2-CP3	108.4 (3)
B12-C7-CM7	119.2 (3)	CP2-CP3-CP4	107.5 (3)
Fe-C8-C7	65.8 (2)	CP3-CP4-CP5	107.7 (3)
Fe-C8-B3	62.3 (1)	CP4-CP5-CP1	108.1 (3)
Fe-C8-C9	112.0 (2)	CP5-CP1-CP2	108.4 (3)
Fe-C8-CM8	121.5 (2)		

a preliminary communication.[11] The tungsten complex was isolated in extremely low yield as a blue-green solid and was identified from its mass spectrum, which exhibited a cutoff at *m/e* 474 corresponding to the $^{186}W^{16}O_3{}^{12}C_{11}{}^{11}B_8{}^{1}H_{20}{}^+$ parent ion, a profile in the parent region consistent with the indicated formula, and intense peaks corresponding to the successive loss of three carbonyl groups. The formula was confirmed by a high resolution mass measurement. Efforts to produce XII in higher yield under a variety of experimental conditions were unsuccessful.

The bright green molybdenum compound XI was obtained in 17% yield and was fully characterized spectroscopically (Tables I-III). A closo-13-vertex geometry with the metal in a six-coordinate vertex is suggested for this $2n + 2$, 28-electron cage, which is isoelectronic with the previously reported $[(CO)_3MoC_2B_{10}H_{12}]^{2-}$ dianion.[26] The ^{11}B NMR spectrum exhibits only four resonances in a 3:1:2:2 area ratio, but low symmetry is indicated by the proton spectrum, in which four distinct methyl peaks are observed. The arrangement of $C\text{-}CH_3$ units on the 13-vertex polyhedron can of course be established only by x-ray diffraction.

The ^{11}B NMR resonances in XI occur entirely within the low-field[18] range of δ 30-51, indicating substantial deshielding throughout the cage in comparison to other metallocarboranes. For example, the ^{11}B signals[26] of the isoelectronic analogue $[(CO)_3MoC_2B_{10}H_{12}]^{2-}$ in acetone fall between[18] δ −20.5 and 2.4. Except for the presence of methyl groups in XI and possible variation in the arrangement of heteroatoms in the 13-vertex polyhedra, neither of which is likely to produce a dramatic difference in the *range* of ^{11}B shifts, the principal distinction between these systems is the formal replacement of two B^- units in the dicarbon system with two neutral carbon atoms in XI. The effect of such a replacement, given the higher electronegativity of the carbon nucleus relative to boron, is probably to concentrate electron density in the vicinity of the carbon atoms in XI, but it is not clear how this would affect the ^{11}B chemical shifts, since these are normally considered to be dominated by the paramagnetic term.

Conclusion

It is evident that the chemistry of $(CH_3)_4C_4B_8H_8$ and its metallocarborane derivatives is not merely a routine extension of the intensively studied dicarbon carborane area, but instead presents significant new structural and stereochemical problems and synthetic opportunities. From the present vantage point, problems, of particular interest include (1) the mechanism of formation of $(CH_3)_4C_4B_8H_8$ by oxidative elimination of the metal from $[(CH_3)_2C_2B_4H_4]_2Co^{III}H$ or its $Fe^{II}H_2$ analogue; (2) the structure of isomer B of the tetracarbon species, and the nature of the A $\rightleftharpoons$ B interconversion in solution; (3) the structure of the $(CH_3)_4C_4B_8H_8{}^{2-}$ dianion; (4) the stereochemical details of metal ion insertion into the dianion; (5) the factors which dictate carbon atom location in the tetracarbon systems, particularly with respect to migration of cage carbon atoms at low temperature; (6) the applicability of the skeletal electron-counting theory to supraicosahedral cages (in light of the apparent violations in the case of the 14-vertex diiron systems described above); and others. The present work

Table VII. Least-Squares Planes for $(\eta^5\text{-}C_5H_5)Fe(CH_3)_4C_4B_7H_8$

Atom	Deviation, Å	Atom[a]	Deviation, Å
Plane 1: Cyclopentadienyl Ring			
$-0.96308x + 0.24730y + 0.10640z = -2.94190$			
CP1	0.0006	CP	0.0018
CP2	0.0005	CP5	−0.0015
CP3	−0.0014	*Fe	1.7045
Plane 2: Cage Atoms Bonded to Iron			
$-0.94892x + 0.29635y + 0.10827z = 0.26342$			
C7	0.1276	*Fe	−1.3394
B12	−0.0270	*CM7	−0.5593
B6	−0.0301	*CM8	−0.2307
C1	0.0042	*CM1	−0.5911
B3	0.0745	*B11	1.5977
C8	−0.1492	*C9	1.4646
Plane 3: Ring on Open Face			
$-0.50333x - 0.23631y + 0.83116z = 1.64733$			
B12	−0.0109	C8	−0.0438
B11	0.0596	*C7	0.5066
B10	−0.1047	*CM8	0.4777
C9	0.0998	*CM9	0.4722
		*Fe	−1.5306
Plane 4: Ring Bonded to C1			
$-0.48782x - 0.26658y + 0.83124z = 0.04814$			
Fe	−0.0248	B6	0.02812
B3	0.0188	*C1	−0.7848
B4	−0.0028		
B5	−0.0194		
Plane 5: C7, B12, C8, CM7			
$-0.90399x + 0.18844y + 0.38378z = 1.00001$			
C7	0.0074	*Fe	−1.6499
B12	−0.0025	*CM8	−0.2035
C8	−0.0026		
CM7	−0.0024		

Planes	Dihedral angle, deg	Planes	Dihedral angle, deg
1,2	2.93	2,5	60.16
3,4	1.95	2,4	61.71
3,5	43.16	2,5	17.21

[a] Atoms marked with an asterisk are not included in the calculated plane.

is part of an ongoing effort to resolve these questions by closely coordinated synthetic and x-ray crystallographic studies.

Experimental Section

Materials. Tetramethyltetracarbadodecaborane (12) $[(CH_3)_4C_4B_8H_8]$ was prepared as described in an earlier publication.[13] All other reagents were commercially obtained (reagent grade) and used as received.

Spectra. Boron-11 FT NMR spectra at 32.1 MHz and proton FT NMR 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.

Reduction of $(CH_3)_4C_4B_8H_8$ to $(CH_3)_4C_4B_8H_8{}^{2-}$. A THF solution of sodium naphthalide (prepared by the treatment of 0.87 mmol of naphthalene with excess sodium metal) was added via filtration in vacuo to $(CH_3)_4C_4B_8H_8$ (87 mg, 0.43 mmol), which was cooled in liquid nitrogen. The solution was warmed to room temperature with stirring, during which the color changed from dark green to wine-red, becoming yellow at room temperature. No gas evolution was detected at any stage. The reduction was also conducted in the absence of naphthalene by stirring 19 mg of the neutral carborane with excess sodium metal in 2 mL of THF at room temperature for 3 h. A white microcrystalline solid was observed in suspension; the solid proved insoluble in hexane, but was moderately soluble in THF (5 mg/mL) giving a clear, pale yellow solution. A filtered solution of the salt in dry CD_3CN was prepared for recording the ^{11}B NMR spectrum, described above.

Preparation of $(C_5H_5)Fe(CH_3)_4C_4B_7H_8$ and Isomers of $(C_5H_5)_2Fe_2(CH_3)_4C_4B_8H_8$. A solution of sodium naphthalide, prepared by the addition of 0.90 mmol of naphthalene to excess sodium metal in 3 mL of THF, was filtered in vacuo into a flask at −196 °C containing 97 mg (0.48 mmol) of $(CH_3)_4C_4B_8H_8$. To this was added a THF solution of sodium cyclopentadienide (2.45 mmol), prepared from cyclopentadiene and excess sodium hydride. The reaction flask was allowed to warm to room temperature and stirred for 45 min, after which it was again frozen in liquid nitrogen. Ferrous chloride (0.412 g, 3.25 mmol) was added via a side-arm addition flask, and the reactor was warmed to room temperature and stirred for 12 h. The mixture was opened to the air and stirred for 20 min, the THF was removed, and the residue was extracted with CH_2Cl_2 and chromatographed on preparative-layer silica gel plates using hexane and a mixture of 10% hexane in benzene as developers. Numerous bands of various colors were obtained, most of which were weak and were found on mass spectroscopic analysis to consist of several components. Four crystalline solid products of significant quantity and satisfactory purity were collected and characterized: red-brown $(C_5H_5)Fe(CH_3)_4C_4B_7H_8$ (V), 7 mg (5% yield based on starting material employed); $(C_5H_5)_2Fe_2(CH_3)_4C_4B_8H_8$, isomer I, brown, 3 mg; isomer II, green-gray, 1 mg; and isomer III, gray-brown, ~0.5 mg. In addition, a trace of an additional isomer (IV, gray) was collected and its mass spectrum obtained.

The mass spectra of compounds I–V all contained strong peaks corresponding to the parent ions, and intensity profiles in the parent region which corresponded closely to the calculated intensities based on natural isotope distributions. An exact mass measurement of V in methane–water gave 314.1953, corresponding to the $^{56}Fe^{12}C_{13}{}^{11}B_7H_{25}{}^+$ ion (protonated parent ion); calcd 314.1957.

X-Ray Crystallographic Study of $(C_5H_5)Fe(CH_3)_4C_4B_7H_8$ (V). For the x-ray analysis a crystal 0.18 × 0.20 × 0.20 mm was mounted with the ϕ axis parallel to the $\bar{h}04h$ reciprocal axis. Precession photographs showed the crystal symmetry to be monoclinic, and systematic absences $h0l$ with l odd and $0k0$ with k odd uniquely established the space group as $P2_1/c$. Unit cell dimensions were established by a least-squares fit of the observed and calculated values of $\pm 2\theta$ for 24 strong general reflections measured on the diffractometer as: $a = 9.492(2)$, $b = 13.476(2)$, $c = 15.176(2)$ Å, and $\beta = 124.01(1)°$. With four molecules in the unit cell, the molecular volume is 402.3 Å^3 and the calculated density 1.29 g cm^{-3}. Since the molecular weight and formula were known from mass spectroscopic data, the density was not measured.

Intensity measurements were made with the same crystal mounted on a Picker four-circle diffractometer controlled by an XDS Sigma 2 computer. Graphite monochromatized Mo Kα radiation was used with scintillation counting and pulse-height analysis. A scan rate of 2° min^{-1} was used with a fixed scan width of 3° for the θ-2θ scans. Within a single quadrant of reciprocal space ($2\theta \leq 50°$) intensity significantly above background [$I > 3\sigma(I), p = 0.024$][27] was measured at 2370 of the 2996 independent lattice points surveyed. Two reference reflections, monitored after every 50 measurements, showed a root mean square deviation about their mean intensities of 1.5%, but with no systematic trends evident. No absorption corrections were applied ($\mu = 9.4$ cm^{-1}) and structure amplitudes were derived in the usual way.

The position of the iron atom in the cell was found from a sharpened three-dimensional Patterson function[28] and the structure solved by the heavy atom method. Structural parameters were refined by block-diagonal least-squares methods with anisotropic thermal parameters adopted for Fe, C, and B. Hydrogen atoms were located from a three-dimensional difference electron-density map and their parameters also refined. At convergence $[\Delta(p) < 0.06\sigma(p)]$ R was 0.038, R_w was 0.045, and the standard deviation of an observation of unit weight 1.1. Weights were assigned as $1/\sigma^2(F)$ where $\sigma^2(F) = \sigma^2(I)/4LpI$, I being the net intensity and Lp the Lorentz-polarization factor.

Atomic form factors were taken for the neutral atoms from the compilation of Hanson et al.[29] for Fe, C, and B, and from Stewart et al.[30] for H. Allowance was made for the real part of the anomalous dispersion correction for Fe.[31] All calculations were carried out on an XDS Sigma 2 computer using programs written in this laboratory.

A table of the observed structure factors is available (see paragraph at end of paper regarding supplementary material).

Preparation of $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_7H_7$ Isomers and $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$ Isomers. A sample of $(CH_3)_4C_4B_8H_8$ (87 mg, 0.43 mmol) was treated with excess sodium naphthalide in THF as described for the preparation of the iron complexes above. The resulting solution was stirred for 30 min at room temperature, cooled to −196 °C, and 300 mg (0.57 mmol) of dichloro-1,2-bis(diphenylphosphino)ethanenickel(II) (prepared as described elsewhere[32]) was added in vacuo from a side-arm addition flask. The mixture was warmed to room temperature, stirred for 14 h, opened to the atmosphere, stirred for 15 min, and filtered through silica gel. After removal of the THF solvent on a rotary evaporator, the red-brown residue was dissolved in CH_2Cl_2 and chromatographed on preparative-layer silica gel plates using a mixture of 40% benzene in hexene. Four intense, well-separated bands were obtained. The first band was colorless (but visible under ultraviolet light), and on development in hexane was resolved into naphthalene and $(CH_3)_4C_4B_8H_8$, 31 mg. The second band was further developed in 150 ml of benzene–hexane to give yellow $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_7H_7$, isomer 2 (VII), 2 mg, and yellow $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$, isomer 3 (X), 4 mg. The third band was orange-brown $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$, isomer 2 (IX), 16 mg, 9% yield based on $(CH_3)_4C_4B_8H_8$ consumed. The fourth band on repeated development in 45% benzene–hexane gave red-brown $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_7H_7$, isomer 1 (VI), 15 mg, 8% yield, and red $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$, isomer 1 (VIII), 6 mg. Unit resolution mass spectra were in all cases consistent with the formulas given. High resolution mass measurements in methane–water were as follows (parent ions in all cases): VI, calcd for $^{60}Ni^{31}P_2{}^{12}C_{34}{}^{11}B_7{}^{1}H_{43}{}^+$, 650.2824, found 650.2846; VII (isomeric with VI), found 650.2807; VIII, calcd for $^{60}Ni^{31}P_2{}^{12}C_{34}{}^{11}B_8{}^{1}H_{44}{}^+$, 662.2995, found 662.3002; IX (isomeric with VIII), found 662.2989.

Preparation of $(CO)_3Mo(CH_3)_4C_4B_8H_8$. An 18-mg (0.09 mmol) sample of $(CH_3)_4C_4B_8H_8$ and 55 mg (0.21 mmol) of $Mo(CO)_6$ (Pfaltz and Bauer, Inc.) were refluxed in 2 mL of dry, degassed heptane for 16 h, during which the solution changed from colorless to dark green. After removal of the hexane by vacuum distillation, the dark green residue was dissolved in methylene chloride, filtered, and chromatographed on preparative-layer silica gel plates in hexane. Aside from unreacted colorless $Mo(CO)_6$, the only band obtained was dark green $(CO)_3Mo(CH_3)_4C_4B_8H_8$, XI, 6 mg (17% yield). The mass spectrum exhibited a strong parent peak and showed successive loss of three CO groups. An exact mass measurement gave 389.1321, corresponding to the protonated parent ion (calcd for $^{100}Mo^{16}O_3{}^{12}C_{11}{}^{11}B_8{}^{1}H_{21}{}^+$, 389.1311).

Preparation of $(CO)_3W(CH_3)_4C_4B_8H_8$. A 20-mg sample of $(CH_3)_4C_4B_8H_8$ was treated with excess $W(CO)_6$ in refluxing heptane in a manner identical with the synthesis of the molybdenum analogue. Only a trace of the tungsten species was isolated as a greenish-blue solid, which was characterized from its mass spectrum as described above. An exact mass determination gave a value of 475.1796 for the protonated parent ion (calcd for $^{186}W^{16}O_3{}^{12}C_{11}{}^{11}B_8{}^{1}H_{21}{}^+$, 475.1778). Further characterization was precluded by the minute quantity available, and subsequent attempts to generate this complex by using higher boiling solvents, ultraviolet light, or the reagent $(CO)_3W(NCCH_3)_3$ were unsuccessful.

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Supplementary Material Available: A listing of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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