covalency in the metal–ligand bond.[8] H_{eff} is related to the expectation value $\langle S\rangle$ of the electronic spin by (3) where H_c

$$H_{\mathrm{eff}} = H_c\langle \mathrm{S}\rangle \qquad (3)$$

is the hyperfine field per unit spin, equal to 250 kG.[9] $\langle S\rangle$ satisfies the spin Hamiltonian (4) for a given Kramers state.

$$\mathcal{H}_s = D[S_z{}^2 - S(S+1)/3] + E[S_x{}^2 - S_y{}^2] \qquad (4)$$

D and E are the axial and rhombic zero-field splitting parameters. The values of $\langle S\rangle$ calculated from eq 3 for the bromo and chloro six-coordinate complexes are $\langle S\rangle = 1.72$ and 1.88, respectively. Since the spin–spin relaxation rate in these dilute solutions is very slow, $\langle S\rangle$ must arise from only the ground electronic state, namely, the $|\pm{}^5/_2\rangle$ $(D < 0)$. Hyperfine structure corresponding to the $|\pm{}^3/_2\rangle$ doublet of $(\mathrm{THF})\mathrm{Fe(dtc)_2X}$ is not observed at 4.2 K. Therefore this state is not populated at this temperature. Consequently, ignoring the rhombic term E, $4|D|/K \geq 4.2$ and $|D| \geq 1.4\ \mathrm{cm^{-1}}$ $(D < 0)$. The lower experimental value of $\langle S\rangle$, compared with $\langle S\rangle = 2.5$ expected for a $|\pm{}^5/_2\rangle$ state, results from covalency, which removes d electrons from the metal valence orbitals. Values of H_{eff} in high-spin ferric compounds range from 620 kG in ionic $\mathrm{FeF_3}$[10] to 460 kG in highly covalent $(\mathrm{pyrr(dtc)})_3\mathrm{Fe}$.[11]

Further evidence supporting the high-spin assignment for $(\mathrm{THF})\mathrm{Fe(dtc)_2X}$ is provided by the temperature dependence of the nuclear quadrupole splitting. Contrary to low-spin systems, in which the lifting of the ground-state orbital degeneracy $({}^2\mathrm{T}_2)$ causes substantial temperature variation of the QS,[12] in high-spin $({}^6\mathrm{A}_1)$ $\mathrm{Fe^{3+}}$ complexes, the magnitude of the QS is expected to be independent of the temperature. This is the case for the six-coordinate $(\mathrm{THF})\mathrm{Fe(dtc)_2X}$ where the value of QS was found constant between 4.2 and 300 K (Table I). The relatively large value of QS = 0.7 mm/s for an assumed high-spin $\mathrm{Fe^{3+}}$ nucleus is understood in terms of differences in the covalency of the various metal–ligand bonds. These differences cause inequivalence in the radial part of the $\mathrm{Fe^{3+}}$ d orbitals giving rise to the EFG.

Typical isomer shift values for low-spin $\mathrm{Fe^{3+}}$ are about zero, whereas for high-spin complexes they range between 0.3 and 0.5 mm/s.[13] The isomer shifts therefore measured in the six-coordinate molecules (Table I) also favor the high-spin assignment. The temperature dependence of the IS corresponds to the well-known second-order Doppler effect.[14]

In conclusion, some comments concerning the structure of $(\mathrm{THF})\mathrm{Fe(dtc)_2X}$ seem appropriate. It has been suggested[4] that the six-coordinate complex probably has the structure depicted in Figure 1b. However, this is not consistent with the considerably higher covalent character of the metal–ligand bonds, observed in $(\mathrm{THF})\mathrm{Fe(dtc)_2X}$ compared to $\mathrm{Fe(dtc)_2X}$. Since the two molecules are assumed to have closely related ligand arrangements around the paramagnetic ion (Figure 1a and b), with the only exception being the weakly bonded THF, the large difference in their covalencies is rather surprising. However, the structure of Figure 1d, which is similar to the approximate structure of the tris(dialkyldithiocarbamato)iron(III) complexes (Figure 1c), can probably account for both the readiness of the transformation of the five- to the six-coordinate complex and the covalency change following $\mathrm{Fe(dtc)_2X} \rightleftharpoons (\mathrm{THF})\mathrm{Fe(dtc)_2X}$.

Registry No. $\mathrm{Fe(dtc)_2Br}$, 54163-77-8; $(\mathrm{THF})\mathrm{Fe(dtc)_2Br}$, 58815-46-6; $(\mathrm{THF})\mathrm{Fe(dtc)_2Cl}$, 58815-47-7.

References and Notes

(1) Predoctoral fellow of the Greek AEC.
(2) (a) J. S. Griffith, *J. Inorg. Nucl. Chem.*, **2**, 1 (1956); (b) B. F. Hoskins and A. H. White, *J. Chem. Soc. A*, 1668 (1970).
(3) H. H. Wickman, *J. Chem. Phys.*, **56**, 976 (1971), and references cited therein.
(4) J. L. K. F de Vries, J. M. Trooster, and E. de Boer, *Inorg. Chem.*, **10**, 81 (1971).
(5) R. L. Martin and A. H. White, *Inorg. Chem.*, **6**, 712 (1967).
(6) G. Lang, *Phys. Lett. A*, **26**, 223 (1968).
(7) H. H. Wickman and A. M. Trozzolo, *Inorg. Chem.*, **7**, 63 (1968).
(8) R. Rickards, C. E. Johnson, and H. A. O. Hill, *J. Chem. Phys.*, **48**, 5231 (1968).
(9) A. Abragam, J. Horowitz, M. H. L. Pryce, and K. W. Morton, *Proc. R. Soc. London, Ser. A*, **230**, 169 (1955).
(10) D. N. E. Buchanan and G. K. Wertheim, *Bull. Am. Phys. Soc.*, **117**, 227 (1962).
(11) H. H. Wickman and C. F. Wagner, *J. Chem. Phys.*, **51**, 435 (1969).
(12) R. M. Golding, *Mol. Phys.*, **12**, 13 (1967).
(13) P. R. Brady, J. F. Duncan, and K. F. Mok, *Proc. R. Soc. London, Ser. A*, **287**, 343 (1965).
(14) G. Lang and W. Marshall, *Proc. Phys. Soc., London*, **87**, 3 (1966).

Contribution from the Department of Chemistry,
University of Virginia, Charlottesville, Virginia 22901

Iron–Hydrogen and Iron–Cobalt Metallocarboranes. Synthesis and Chemistry of $[(\mathrm{CH_3})_2\mathrm{C_2B_4H_4}]_2\mathrm{Fe^{II}H_2}$ and a Novel Tetracarbon Carborane System, $(\mathrm{CH_3})_4\mathrm{C_4B_8H_8}$

WILLIAM M. MAXWELL, VERNON R. MILLER, and RUSSELL N. GRIMES*

Received February 5, 1976 AIC600980

The reaction of $\mathrm{Na^+(CH_3)_2C_2B_4H_5^-}$ with $\mathrm{FeCl_2}$ below −30 °C produces red $[C,C'\text{-}(\mathrm{CH_3})_2\mathrm{C_2B_4H_4}]_2\mathrm{Fe^{II}H_2}$ in which two hydrogen atoms are bonded to the iron atom and probably occupy bridging locations centered over triangular faces on the polyhedra. Unlike its $\mathrm{Co^{III}H}$ counterpart, the compound was not observed to convert to a nido,closo species, but treatment with NaH in THF forms the $[(\mathrm{CH_3})_2\mathrm{C_2B_4H_4}]_2\mathrm{Fe^{II}H^-}$ ion, which on air oxidation produces the $[(\mathrm{CH_3})_2\mathrm{C_2B_4H_4}]_2\mathrm{Fe^{III-}}$ ion. Reaction of the latter species with HCl gas generates $[C,C'\text{-}(\mathrm{CH_3})_2\mathrm{C_2B_4H_4}]_2\mathrm{Fe^{II}H_2}$ and a novel air-stable carborane, $(\mathrm{CH_3})_4\mathrm{C_4B_8H_8}$; this latter product is also formed in high yield on air oxidation of the commo species $[(\mathrm{CH_3})_2\mathrm{C_2B_4H_4}]_2\mathrm{Fe^{II}H_2}$. The compound $(\mathrm{CH_3})_4\mathrm{C_4B_8H_8}$ exists in at least two isomeric forms which are in equilibrium in a variety of polar and nonpolar solvents; one form is proposed to have an open structure consisting of two edge-linked $(\mathrm{CH_3})_2\mathrm{C_2B_4H_4}$ units, while the other is postulated to be a distorted icosahedron. The latter isomer exhibits fluxional NMR behavior at 40 °C. Reaction of $[C,C'\text{-}(\mathrm{CH_3})_2\mathrm{C_2B_4H_4}]_2\mathrm{Fe^{II}H_2}$ with $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Co(CO)_2}$ yields $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Co}[(\mathrm{CH_3})_2\mathrm{C_2B_3H_3}]\mathrm{Fe(CO)_3}$, in which the metal atoms are proposed to occupy the apexes of a pentagonal-bipyramidal cage, and a structurally novel compound, $[(\mathrm{CH_3})_4\mathrm{C_4B_8H_8}]\mathrm{FeCo}(\eta^5\text{-}\mathrm{C_5H_5})$, which contains a BH group simultaneously capping the faces on two polyhedra.

A separate paper[1] describes the preparation of the *commo*-cobaltacarborane $[C,C'\text{-}(\mathrm{CH_3})_2\mathrm{C_2B_4H_4})_2\mathrm{Co^{III}H}$ and the use of this compound as a precursor to other new species, several of which were proposed to have cobalt–cobalt bonds in the cage framework. A subsequent study of the ferracarboranes containing the same formal $[C,C'\text{-}(\mathrm{CH_3})_2\mathrm{C_2B_4H_4}]^{2-}$ ligand[2] developed some interesting contrasts with the cobalt system and also led to the preparation of two

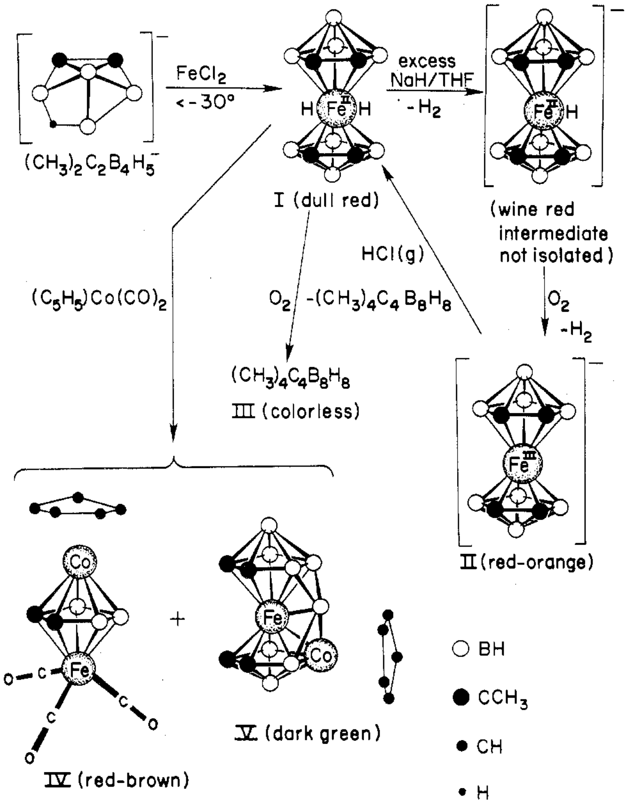

Figure 1. Reaction scheme showing proposed structures of new metallocarboranes I–IV and established structure of V. Metal-bonded hydrogens are indicated schematically.

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

Compd	δ,[b] ppm (J, Hz)	Rel areas
$[(CH_3)_2C_2B_4H_4]_2FeH_2$ (I)	−1.8 (180),[c] +5.2 (171),[c] +18.3 (169)	1, 2, 1
$(CH_3)_4N^+[(CH_3)_2C_2B_4H_4]_2(Fe^{III})^-$ (II)[g]	−14,[d] +527[e]	*f*
$(CH_3)_4C_4B_8H_8$ (III)[h]		
Isomer A	−9.2 (152),[c] −8.4 (152),[c] +22.4 (161), +29.5 (140)	1, 1, 1, 1
Isomer B	+2.4 (150), +11.0 (148)	3, 1
$(C_5H_5)Co[(CH_3)_2C_2B_3H_3]Fe(CO)_3$ (IV)	−43.1 (156), −26.1 (156)	2, 1
$(CH_3)_4C_4B_8H_8FeCo(C_5H_5)$ (V)	−92.7 (180), −57.4 (166), −12.4 (160),[c] −8.4 (150),[c] +2.2 (186),[c] +8.9 (176)[c]	1, 1, 3, 1, 1, 1

[a] 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] $w_{1/2} \simeq$ 2500 Hz. [e] $w_{1/2} \simeq$ 5000 Hz. [f] Ratio could not be measured due to extreme peak widths; peak at +527 ppm was largest in area. [g] CD_3CN solution. [h] CCl_4 solution.

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

Compd	Resonance, τ[b] (rel area)[c]	Assignment
I	7.71 (6)	CH_3
	20.44 (1)[d]	Fe–H
II[e]	7.71 (6)[f]	CH_3(carborane)
	2.18 (6)	$(CH_3)_4N^+$
III		
Isomer A	8.30 (1), 8.38 (1)	CH_3
Isomer B (25 °C)	7.93 (1), 7.99 (1)	CH_3
Isomer B (40 °C)	7.96	CH_3
IV	5.12 (5)	C_5H_5
	7.76 (6)	CH_3
V	5.05 (5)	C_5H_5
	7.97 (3)	CH_3
	8.08 (9)[g]	CH_3

[a] All spectra run in $CDCl_3$ solution except where otherwise indicated. [b] Chemical shifts relative to $(CH_3)_4Si$, τ 10.00. [c] Singlet resonance except where otherwise indicated. [d] $w_{1/2}$ = 55 Hz. [e] CD_3CN solution. [f] $w_{1/2}$ = 32 Hz. [g] Asymmetric peak with shoulder on high-field side.

Table III. High-Resolution Mass Measurements[a]

Compd	Formula	Mass	
		Calcd	Obsd
I	$^{56}Fe^{12}C_8{}^{11}B_8{}^1H_{22}{}^+$	262.1815	262.1818
III	$^{12}C_8{}^{11}B_8{}^1H_{20}{}^+$	204.2310	204.2310
IV	$^{56}Fe^{59}Co^{16}O_3{}^{12}C_{12}{}^{11}B_3{}^1H_{15}{}^+$ [b]	354.9981	354.9975
V	$^{56}Fe^{59}Co^{12}C_{13}{}^{11}B_8{}^1H_{26}{}^+$ [b]	385.1460	385.1459

[a] Mass of parent ion obtained in methane under chemical ionizing conditions. [b] P + 1 (protonated parent ion). Peaks corresponding to both parent (P) and P + 1 ions were observed in all spectra; the choice of peaks selected for exact mass determination by peak matching against a known standard was dependent on peak shape and freedom from overlap with neighboring peaks.

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

I[a]	2980 w, 2960 w, 2920 m, 2860 w, 2570 vs, 1440 m, 1380 m, 1048 w, 905 w, 875 w, 845 w, 822 w, 732 w, 700 m
II[a]	3040 m, 2980 m, 2965 m, 2935 m, 2865 w, 2498 vs, 1490 s, 1455 s, 1285 w, 1118 m, 1040 w, 998 w, 948 s, 928 w, 870 s, 802 sh, 792 m, 750 s, 695 s, 620 m
III[a]	2985 w, 2965 w, 2930 m, 2865 w, 2555 vs, 1450 s, 1380 m, 1213 w, 1180 w, 1050 m, 1008 m, 950 m, 875 w, 845 m, 738 s, 691 w, 675 w, 610 m
IV[b]	2950 sh, 2925 s, 2855 m, 2530 s, 2042 vs, 1985 vs, 1738 w, 1437 m, 1378 w, 1108 w, 1045 w, 1005 w, 905 m, 845 sh, 825 m, 615 m
V[b]	2940 m, 2920 s, 2860 m, 2540 vs, 1430 m, br, 1360 w, br, 1250 w, br, 1105 m, 1048 m, 1015 w, 1004 w, 920 vs, 900 sh, 828 vs, 690 m, br

[a] KBr pellet. [b] CH_2Cl_2 solution vs. CH_2Cl_2.

mixed-metal metallocarboranes. In the present article we report this chemistry and also present a detailed account of the synthesis and properties of a novel four-carbon carborane which was discovered in the course of this work.

Results and Discussion

Reaction of the *C,C′*-$(CH_3)_2C_2B_4H_5^-$ Ion with $FeCl_2$. Solutions of $Na^+[(CH_3)_2C_2B_4H_5]^-$ in tetrahydrofuran (THF) react with anhydrous $FeCl_2$ at low temperatures (below −30 °C) to produce brownish red crystalline solid [*C,C′*-$(CH_3)_2C_2B_4H_4]_2Fe^{II}H_2$ (I) in 90% yield (Figure 1). Evolution of gas is not observed, and in contrast to the corresponding reaction with $CoCl_2$,[1] no free metal is obtained and the iron retains a formal oxidation state of +2.

The structural characterization of I (Figure 1) is based on ^{11}B and ^1H pulse Fourier transform nuclear magnetic resonance (FTNMR) spectra, high-resolution mass spectra, and infrared spectra (Tables I–IV). As in the case of the corresponding cobalt(III) species, [*C,C′*-$(CH_3)_2C_2B_4H_4]_2Co^{III}H$,[1] the FTNMR spectra of I indicate high symmetry with all methyl groups equivalent. The ^1H resonance of area 2 at τ 20.4 is assigned to two equivalent "extra" hydrogens which are associated with the metal atom and are assumed to undergo rapid tautomerism through bridging positions on the equivalent FeB_2 triangular faces. The argument for this face-bonded proton tautomerism is similar to that advanced previously in the very similar cases of 1,2,3- and 1,2,4-(η^5-C_5H_5)-$Fe^{II}HC_2B_4H_6$,[3,4] [*C,C′*-$(CH_3)_2C_2B_4H_4]_2Co^{III}H$ and related cobalt–hydrogen species,[1] and the octahedral CB_5H_7 system[5] and recently given strong support in an electron diffraction study of CB_5H_7 which located the extra hydrogen in a face-bridging position over the center of a B_3 triangle.[6]

Reaction of $[C,C'-(CH_3)_2C_2B_4H_4]_2Fe^{II}H_2$ (I). Metal Deprotonation and Oxidation. The chemistry of the bis(dimethyldicarbahexaboranyl)iron(II) dihydrogen species (I) differs from its cobalt(III) counterpart, $[C,C'-(CH_3)_2C_2B_4H_4]_2Co^{III}H$,[1] in several respects. The red crystalline iron compound is more stable in air than is the cobalt species (although decomposition does occur over periods of a few hours) and is not converted to an Fe^{3+} system; also, unlike the cobalt compound, I exhibits no noticeable tendency to lose an apex BH and form a nido,closo species analogous to $[(CH_3)_2C_2B_3H_5]CoH[(CH_3)_2C_2B_4H_4]$ (compound II in the earlier paper[1]). Indeed, we have been unable to synthesize any such nido,closo iron compound despite the fact that a related species, $(CO)_3FeC_2B_3H_7$, is easily prepared from $Fe(CO)_5$ and 2,3-$C_2B_4H_8$.[4,7] Thus, I is inert toward ethanolic KOH, and acidified THF converts I to the tetracarbon carborane $(CH_3)_4C_4B_8H_8$, described below.

Compound I is readily deprotonated by hydride ion in THF, and as in the cobalt system, a metal-bonded proton is selectively removed (Figure 1). Although two such protons are present in I, only 1 mol of H_2 is generated even on treatment with excess NaH at elevated temperature. The resulting wine red solution contains an intermediate species, $[(CH_3)_2C_2B_4H_4]_2Fe^{II}H^-$, which was not characterized but whose nature is evident from its chemistry (Figure 1). Solutions of this ion in THF on exposure to air undergo rapid oxidative deprotonation to yield the paramagnetic $[2,3-(CH_3)_2C_2B_4H_4]_2(Fe^{III})^-$ ion which has been isolated as an orange-red tetramethylammonium salt (II). This species can be reprotonated by HCl in ethylene chloride solution to regenerate I, but the process is not quantitative and is accompanied by formation of the tetracarbon carborane $(CH_3)_4C_4B_8H_8$ (III). Although II is evidently air stable as a solid salt, decomposing at its melting point of 243 °C, solutions of II exposed to air are oxidized to give III in 70–80% yield.

Properties of $(CH_3)_4C_4B_8H_8$ (III). The new carborane[8] is a colorless, sublimable crystalline solid, mp 138 °C, which appears stable in air both in solution and in the solid state. This compound displays extraordinary behavior on FTNMR spectroscopic analysis, most notably a reversible change of structure which occurs when the solid compound is dissolved in any of the solvents examined. A freshly prepared solution exhibits the ^{11}B FTNMR spectrum shown in Figure 2a. Within a few minutes of the preparation of the solution, the spectrum of the original compound (A) changes dramatically with the addition of new peaks (Figure 2b) which we ascribe to a second isomer (B). The area of the B peaks increases until an equilibrium [B]/[A] ratio of ~0.5 is established, usually within 15–20 min of the addition of solvent. This isomerization is remarkable in two respects: (1) the [B]/[A] ratio appears to be solvent-independent insofar as can be detected in CCl_4, CH_2Cl_2, THF, C_2H_5OH, CH_3CN, $CDCl_3$, and benzene; (2) it is completely reversible, since removal of the solvent followed by addition of new solvent produces the original spectrum of the A isomer (Figure 2a). On standing, the solution reestablishes the A–B equilibrium as before.

The 100-MHz ^1H FTNMR spectra undergo similar changes (Figure 3). Variable-temperature studies of both the ^{11}B and ^1H spectra revealed no notable changes between −80 and +20 °C, the main effect being peak broadening at low temperature which is ascribed to increased viscosity. Above 30 °C the two methyl peaks in the ^1H NMR spectrum of B coalesce, collapsing at ~40 °C to a sharp singlet indicating equivalence of all four methyl groups. However, the ^1H spectrum of A is essentially unchanged at 40 °C as are the ^{11}B spectra of both isomers.

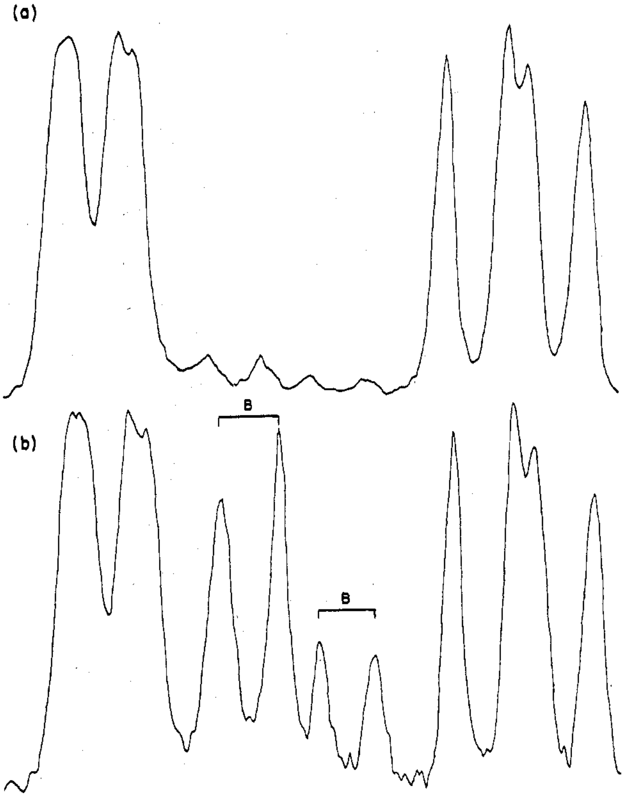

Figure 2. The 32.1-MHz ^{11}B FTNMR spectra of $(CH_3)_4C_4B_8H_8$ (III) in CCl_4 at 23 °C: (a) 3 min after preparation of solution; large peaks are BH doublets of isomer A; (b) same sample 12 min later, showing peaks (labeled B) due to isomer B; further change in the spectrum was limited to slight increase in the areas of the B resonances.

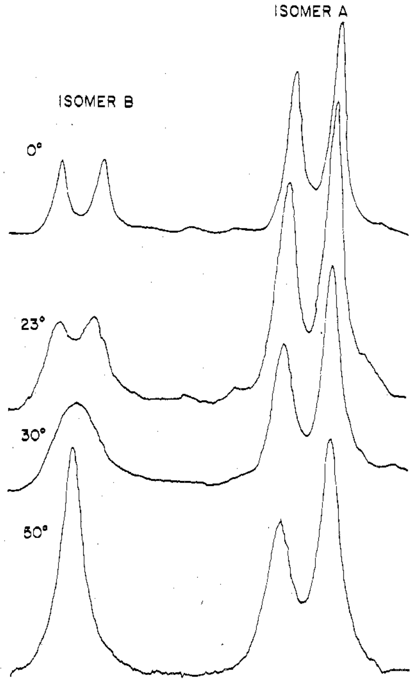

Figure 3. 100-MHz ^1H FTNMR spectra of $(CH_3)_4C_4B_8H_8$ (III) in $CDCl_3$ as a function of temperature. The four main peaks are CH_3 resonances; H–B quartets are weak and broad.

We assume that the solid-state structure is essentially that of isomer A in solution and that it is an open-cage (nido)

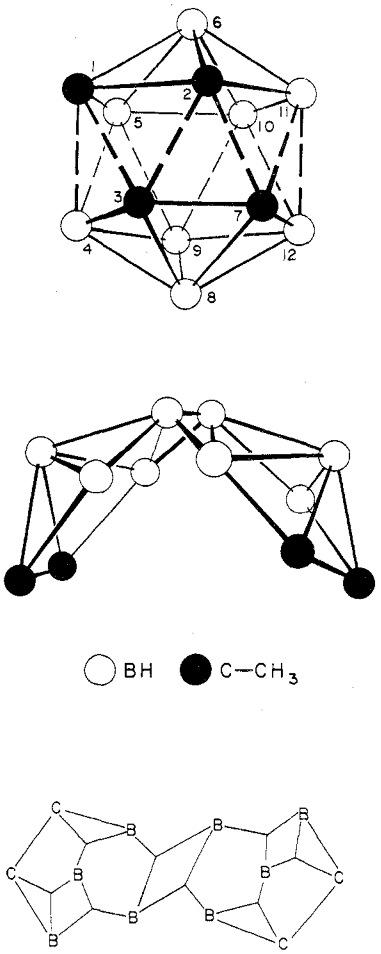

Figure 4. Possible structures for $(CH_3)_4C_4B_8H_8$ isomers B (top) and A (middle), with one of several possible valence-bond diagrams for A shown at the bottom (terminal H atoms and CH_3 groups omitted).

geometry rather than a closed polyhedron. The basis for this conjecture is primarily the large range of ^{11}B chemical shifts (nearly 40 ppm) in the spectrum of A, which is unlikely in a closed polyhedral carborane. In contrast, the relatively small range of the ^{11}B spectrum of isomer B (8.6 ppm) and considerably simpler appearance are suggestive of a *closo*-carborane. However, a framework of four carbon and eight boron atoms contains 28 skeletal valence electrons exclusive of B–H and C–CH_3 bonds, two more than are present in the icosahedral $C_2B_{10}H_{12}$ system; thus, whereas $C_2B_{10}H_{12}$ fulfills the "$2n + 2$ rule" for closed triangulated polyhedra,[9] $C_4B_8H_{12}$ (and its *C*-tetramethyl derivative, III) is predicted to have a structure significantly distorted from that of a regular icosahedron. A successful x-ray analysis of $(CH_3)_4C_4B_8H_8$ has not yet been achieved, but even in the absence of definitive structural information several limiting observations can be made. The structures of isomers A and B (1) must be sufficiently related to permit facile, reversible conversion at ambient temperature, (2) must be compatible with the observed fluxional behavior of B above 30 °C, (3) must contain no B–H–B bridges or BH_2 groups, which are eliminated by the NMR and ir data, and (4) must be consistent with the direct insertion of transition metal atoms to generate four-carbon metallocarborane systems, of which over a dozen have been prepared[10] thus far from reagents of molybdenum,[8] tungsten, cobalt, iron, and nickel. Possible structures for A and B are shown in Figure 4. That indicated for B is a schematic representation of a distorted icosahedron which deviates from regular icosahedral symmetry by cooperative stretching of several bonds,[11] rather than the usual opening of one side of the polyhedron to form a nido structure. Several kinds of fluxional rearrangements which would make the four C–CH_3 groups in B NMR equivalent are conceivable; one possibility is a relative twisting of the two $(CH_3)_2C_2B_4H_4$ pentagonal pyramids. Such a process has been proposed[12] for icosahedral $C_2B_{10}H_{12}$ rearrangements at high temperature, and a recent study[13] of the isomerization of the $PCB_{10}H_{10}Cl$ icosahedral cage has given evidence supporting this mechanism. Since the $(CH_3)_4C_4B_8H_8$ fluxional behavior occurs at a much lower temperature, it is not unreasonable to suppose that the distorted-icosahedral geometry suggested for isomer B serves to lower drastically the activation energy required for a twist rearrangement, as compared with the "normal" icosahedral $C_2B_{10}H_{12}$ carboranes. Clearly, there are other possibilities for the structures of isomers A and B, as well as for the fluxional rearrangement of B, and we are in no position to exclude these at this time.

In addition to the preparation from $[(CH_3)_2C_2B_4H_4]_2Fe^{II}H_2$ and from $[(CH_3)_2C_2B_4H_4]_2Co^{III}H$,[1] $(CH_3)_4C_4B_8H_8$ has also been obtained in reactions of the $[(CH_3)_2C_2B_4H_4]_2(Fe^{III})^-$ ion, as described below. The fact that the tetracarbon carborane has been isolated thus far only from reactions of *commo*-bis(dicarbahexaboranyl)metallocarboranes implies that its formation depends upon a linkage of the two C_2B_4 units facilitated by the metal. If the details of this process could be established, it might be developed into a general technique for linking carboranyl units in concerted fashion.[14] At present, we have no direct evidence bearing on the mechanism of $(CH_3)_4C_4B_8H_8$ formation from the metal complexes.

Preparation of Iron–Cobalt Metallocarboranes. The reaction of $[(CH_3)_2C_2B_4H_4]_2Fe^{II}H_2$ (I) with $(\eta^5\text{-}C_5H_5)Co(CO)_2$ under ultraviolet light produces a red-brown solid formulated as $1,7,2,3\text{-}(\eta^5\text{-}C_5H_5)Co[(CH_3)_2C_2B_3H_3]Fe(CO)_3$ (IV) and a structurally unique metallocarborane, $(CH_3)_4C_4B_8H_8FeCo(\eta^5\text{-}C_5H_5)$ (V), obtained as dark green crystals. A likely structure for IV, depicted in Figure 1, is based on the mass spectrum, which exhibits a $(C_5H_5)Co^+$ peak and indicates successive loss of three CO units, and on the ^{11}B and ^1H FTNMR spectra which reveal equivalent CH_3 groups and a pair of equivalent BH units. The placement of both metals in apex positions in the seven-vertex polyhedron is based on the similarity of chemical shifts of the ^{11}B resonances, but alternative isomers containing one metal in an equatorial location cannot be ruled out (structures containing carbon atoms in the five-coordinate apexes, which would also place both metals in the equator, are unprecedented and can be rejected as exceedingly improbable).

The formation of IV from I is mechanistically curious in that a $(CH_3)_2C_2B_4H_4^{2-}$ ligand and the two metal-bound protons in I are replaced by three carbonyl groups (these are, of course, net effects; the actual mechanism is unknown). Compound IV is the first mixed-metal complex of the planar $C_2B_3H_5^{4-}$ ligand (an analogue of $C_5H_5^-$) and is isoelectronic with the triple-decked sandwich species 1,7,2,3- and 1,7,2,4-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$.[15-17]

The structure of V could not be elucidated from the NMR and other spectroscopic evidence, but an x-ray diffraction study[18] disclosed the geometry shown in Figure 5. Aside from providing another example of adjacent-metal insertion,[1] the chief significance of this structure lies in the unique boron atom B8 which simultaneously caps triangular faces on two seven-vertex polyhedra. The important bond distances (Fe–Co, 2.480 (1) Å; B8–Fe, 1.912 (7) Å; B8–Co, 2.057 (7) Å; B8–B6, 1.861 (10) Å; B8–B2', 2.100 (10) Å; B8–B6', 2.186 (10) Å) indicate that B8 is clearly bonded to five other cage atoms despite the somewhat long B–B interactions with respect to

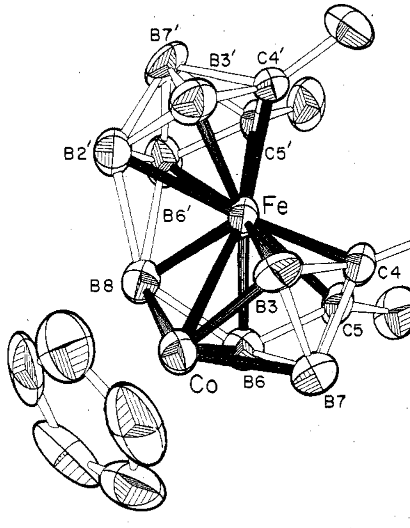

Figure 5. Molecular structure[18] of $(CH_3)_4C_4B_8H_8FeCo(\eta^5\text{-}C_5H_5)$.

B2' and B6'.[19] The "double capping" effect has not to our knowledge been previously observed. We have presented elsewhere[18] a rationalization for this structure based on the skeletal electron-counting approach;[9,22] in essence, our argument is that the adoption of a face-capping location by B8–H is a consequence of a hyperdeficiency[18] of electrons in the molecular framework, relative to the "normal" requirement of $2n + 2$ electrons for each polyhedron. Capping of triangular faces has been observed previously in the ferracarborane $1,6,2,3\text{-}(\eta^5\text{-}C_5H_5)_2Fe_2C_2B_6H_8$[23] and in the osmium clusters[24] $Os_6(CO)_{18}$ and $Os_7(CO)_{21}$, each of which is electron hyperdeficient with only $2n$ valence electrons available for skeletal bonding. In the case of V, the novel aspect is that the capping atom interacts with faces on two different polyhedra, thus avoiding the presumably unfavorable three-coordinate BH vertex which would exist if B8–H capped only one polyhedron. The geometry of V can also be viewed as two closed cages (capped pentagonal bipyramids) fused on a common edge, an apparently unprecedented geometric feature.

Conclusions

The iron–hydrogen *commo*-ferracarboranes prepared in this study are related to the family of cobalt complexes described in a separate publication,[1] although a major difference was noted in the resistance of the iron species to degradation to a nido,closo system. Both the iron compound I and its cobalt analogue, however, undergo oxidative conversion to the tetracarbon carborane $(CH_3)_4C_4B_8H_8$.

The new metallocarboranes reported here further extend the already considerable range of synthetic possibilities inherent in metalloboron cage chemistry. It is significant, moreover, that these compounds are derived from readily accessible reagents and can be prepared via standard organometallic vacuum-line techniques. The reaction of pentaborane(9) and 2-butyne[25] generates $C,C'\text{-}(CH_3)_2C_2B_4H_6$ in high yield and is cleaner and considerably safer (avoiding the hazards associated with acetylene) than the corresponding pentaborane–acetylene reaction[25] which produces parent $2,3\text{-}C_2B_4H_8$.

The $(CH_3)_4C_4B_8H_8$ system discovered in the course of this work is the only example, other than $C_4B_2H_6$,[26] of a carborane containing four carbon atoms in the same cage framework (mention should be made, however, of the $C_4B_{18}H_{22}$ species[27] which consists of a pair of $C_2B_9H_{11}$ icosahedral fragments linked at the edges). In addition, $(CH_3)_4C_4B_8H_8$ is the first neutral carborane shown to be capable of direct η coordination to transition metal atoms.[8] Like its isoelectronic counterpart, the $C_2B_{10}H_{12}{}^{2-}$ ion,[28] the tetracarbon species accepts metal atoms, generating in this case the first four-carbon metallocarboranes. The synthesis and structural characterization of a number of compounds in this class will be reported elsewhere.[10]

Experimental Section

Materials. 2,3-Dimethyl-2,3-dicarbahexaborane(8) $[C,C'\text{-}(CH_3)_2C_2B_4H_6]$ was prepared from 2-butyne and pentaborane(9) by the method of Onak et al.[25] and purified by GLC on 30% Apiezon L/Chromosorb W at 60 °C. NaH (50% in mineral oil) was rinsed in hexane before use. All other reagents were reagent grade.

Spectra and Chromatography. Boron-11 and proton FTNMR, mass spectra, and infrared spectra were obtained on instruments described elsewhere.[1] Thin-layer and preparative-layer chromatography were conducted in air on precoated plates of silica gel F-254 purchased from Brinckmann Instruments, Inc.

$[(CH_3)_2C_2B_4H_4]_2FeH_2$ (I). A THF solution of $Na^+[(CH_3)_2C_2B_4H_5]^-$ was prepared by distillation of $(CH_3)_2C_2B_4H_6$ (0.427 g, 4.12 mmol) onto NaH (0.317 g, 13.2 mmol) in 15 ml of THF. This solution, in vacuo, was filtered onto anhydrous $FeCl_2$ (0.340 g, 2.68 mmol) in a 100-ml round-bottom flask cooled in liquid nitrogen. The solution was allowed to warm from −196 °C until melting occurred, but the temperature was held below ∼−30 °C (above this temperature decomposition occurs and product yields are lower). After stirring for 10 min with no gas evolution, the solution was bright red-brown. At this point the THF was quickly removed, leaving a dark red-brown residue. Dry nitrogen was then introduced into the flask and a vacuum sublimator was attached to the vessel. At 40 °C and 10^{-5} Torr the red-brown product, II, rapidly collected (∼1.5 h) on the −78 °C cold finger, giving a yield of 0.485 g (90%).

Deprotonation of $[C,C'\text{-}(CH_3)C_2B_4H_4]_2Fe^{II}H_2$ (I) and Preparation of the $[(CH_3)_2C_2B_4H_4]_2(Fe^{III})^-$ Ion (II). A 131-mg (0.504-mmol) sample of I and 140 mg (5.8 mmol) of NaH were placed in a 25-ml round-bottom flask. Approximately 5 ml of THF was distilled in vacuo into the flask, which was cooled in liquid nitrogen. The reactor was allowed to warm, and at ∼0 °C vigorous bubbling began, continuing for 1 min. The solution was warmed to room temperature with stirring, and the evolved H_2 was Toepler-pumped and measured as 0.50 mmol. The solution at this point was dark wine red. The solution was then stirred in air for 15 min. Initially some gas evolution was observed, and the color changed to orange-red. The THF was removed on a rotatory evaporator and the resultant residue, an orange-red oil, was dissolved in 30 ml of water. An aqueous solution of excess $(CH_3)_4N^+Cl^-$ was then added with stirring, producing a bright orange-red precipitate. This material was filtered, washed with water and dissolved in a 50% CH_3CN/CH_2Cl_2 solution. The material was placed on a silica column and eluted with CH_2Cl_2/CH_3CN solution, which yielded one bright red-brown band containing 98 mg (59%) of $(CH_3)_4N^+[(CH_3)_2C_2B_4H_4]_2(Fe^{III})^-$ (II) as orange-red crystals, mp 243–246 °C dec.

The salt II is apparently air stable in the solid state but decomposes in solutions exposed to air, producing $(CH_3)_4C_4B_8H_8$ (III), obtained in 70–80% yield as colorless crystals which are readily purified by sublimation at 25 °C and 10^{-5} Torr or by TLC in hexane (R_f 0.43).

Attempted Protonation of II. Approximately 40 mg of the tetramethylammonium salt II was placed in a Pyrex reactor on the vacuum line and ∼3 ml of $C_2H_4Cl_2$ was distilled into the evacuated reaction flask. A twofold excess of anhydrous HCl was condensed into the reaction vessel at −196 °C and the mixture was allowed to come to room temperature. After 15 min of stirring, the HCl and THF were removed and the system was opened to a dry nitrogen atmosphere. The material in the flask was extracted with degassed hexane and chromatographed on a silica plate in hexane. Two compounds were isolated: red-brown solid I (15.1 mg) and the tetracarbon carborane III (5.6 mg), identified from their ir, NMR, and mass spectra.

Cobalt Insertion into $[C,C'\text{-}(CH_3)_2C_2B_4H_4]_2FeH_2$ (I). A 50-mg sample of II and 200 mg of $(\eta^5\text{-}C_5H_5)Co(CO)_2$ were placed into a 5-ml round-bottom flask, the reactor was evaculated, and 2 ml of dry hexane was added. The reaction mixture was irradiated with stirring for 23 h. The reactor was opened to the atmosphere, stirred, and filtered through silica, washing with methylene chloride. The solution was placed on a TLC plate and developed in cyclohexane. Two bands were collected, the first yielding 8.2 mg (11%) of dark green $(CH_3)_4C_4B_8H_8FeCo(\eta^5\text{-}C_5H_5)$ (V), R_f 0.33. This compound appears stable for indefinite periods in the solid state and in solutions of CH_2Cl_2, hexane, and THF.

The second band collected gave 1.5 mg of red-brown $(\eta^5\text{-}C_5H_5)Co[(CH_3)_2C_2B_3H_3]Fe(CO)_3$ (IV), R_f 0.76.

Acknowledgment. The pulse Fourier transform NMR spectrometer and associated computer utilized in this research were acquired by the Department of Chemistry via a matching grant from the National Science Foundation. This work was supported in part by the Office of Naval Research.

Registry No. I, 58846-86-9; II($(CH_3)_4N$), 58815-25-1; III (isomer A), 58815-26-2; III (isomer B), 54387-54-1; IV, 58814-73-6; V, 58814-74-7; $(CH_3)_2C_2B_4H_6$, 20741-68-8; $(\eta^5\text{-}C_5H_5)Co(CO)_2$, 12078-25-0.

References and Notes

(1) W. M. Maxwell, V. R. Miller, and R. N. Grimes, *J. Am. Chem. Soc.*, in press.

(2) The anion was first reported by T. Onak and G. B. Dunks, *Inorg. Chem.*, **5**, 439 (1966).

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

(4) L. G. Sneddon, D. C. Beer, and R. N. Grimes, *J. Am. Chem. Soc.*, **95**, 6623 (1973).

(5) (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).

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

(7) R. N. Grimes, *J. Am. Chem. Soc.*, **93**, 261 (1971).

(8) A preliminary report on this compound has appeared: W. M. Maxwell, V. R. Miller, and R. N. Grimes, *J. Am. Chem. Soc.*, **96**, 7116 (1974).

(9) (a) R. W. Rudolph and W. R. Pretzer, *Inorg. Chem.*, **11**, 1974 (1972); (b) K. Wade, *Chem. Br.*, **11**, 177 (1975); (c) K. Wade, *Chem. Commun.*, 792 (1971).

(10) W. M. Maxwell and R. N. Grimes, to be submitted for publication.

(11) R. N. Grimes, *Ann. N.Y. Acad. Sci.*, **239**, 180 (1974).

(12) D. Grafstein and J. Dvorak, *Inorg. Chem.*, **2**, 1128 (1963).

(13) H. S. Wong and W. N. Lipscomb, *Inorg. Chem.*, **14**, 1350 (1975).

(14) A process which is related in at least a schematic sense is the fusion of CB_5H_9 units at 250 °C: R. R. Rietz and M. F. Hawthorne, *Inorg. Chem.*, **13**, 755 (1974).

(15) R. N. Grimes, D. C. Beer, L. G. Sneddon, V. R. Miller, and R. Weiss, *Inorg. Chem.*, **13**, 1138 (1974).

(16) D. C. Beer, V. R. Miller, L. G. Sneddon, R. N. Grimes, M. Mathew, and G. J. Palenik, *J. Am. Chem. Soc.*, **95**, 3046 (1973).

(17) W. T. Robinson and R. N. Grimes, *Inorg. Chem.*, **14**, 3056 (1975).

(18) W. M. Maxwell, E. Sinn, and R. N. Grimes, *J. Am. Chem. Soc.*, in press.

(19) Boron–boron bond lengths of 2.0 Å or greater have been observed in other cobaltacarborane polyhedra, e.g., the $(\eta^5\text{-}C_5H_5)CoCB_7H_8^-$ ion[20] and 1,7,5,6-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_5H_7$.[21]

(20) K. P. Callahan, C. E. Strouse, A. L. Sims, and M. F. Hawthorne, *Inorg. Chem.*, **13**, 1393 (1974).

(21) R. N. Grimes, A. Zalkin, and W. T. Robinson, submitted for publication.

(22) D. M. P. Mingos, *Nature* (*London*), *Phys. Sci.*, **236**, 99 (1972).

(23) K. P. Callahan, W. J. Evans, F. Y. Lo, C. E. Strouse, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **97**, 296 (1975).

(24) R. Mason, K. M. Thomas, and D. M. P. Mingos, *J. Am. Chem. Soc.*, **95**, 3802 (1973).

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

(26) (a) P. Binger, *Tetrahedron Lett.*, 2675 (1966); (b) T. P. Onak and G. T. F. Wong, *J. Am. Chem. Soc.*, **92**, 5226 (1970); (c) V. R. Miller and R. N. Grimes, *Inorg. Chem.*, **11**, 862 (1972).

(27) J. Plesek and S. Hermanek, *Chem. Ind.* (*London*), 890 (1972); Z. Janousek, S. Hermanek, J. Plesek, and B. Stibr, *Collect. Czech. Chem. Commun.*, **39**, 2363 (1974).

(28) D. F. Dustin, G. B. Dunks, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **95**, 1109 (1973).

Contribution No. 2252 from the Central Research Department,
Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Synthesis and Properties of Cobalt(I) Compounds. 3. Hydridoacetonitriletris(triaryl phosphite)cobalt Complexes

L. W. GOSSER

Received November 12, 1975 AIC50820E

The preparation and properties of the triaryl phosphite complexes $CoH[(ArO)_3P]_3(CH_3CN)$ are described. Surprisingly rapid selective hydrogenation of terminal olefins was observed with $CoH[(PhO)_3P]_3(CH_3CN)$. Qualitative data on ligand exchange are given.

Introduction

In contrast to the tertiary phosphine stabilized cobalt hydrides such as $CoH[Ph_3P]_3(N_2)$ the triaryl phosphite stabilized cobalt hydrides have been comparatively inert.[1] The triaryl phosphite Ni(0) complexes such as $[(PhO)_3P]_4Ni$ are also comparatively inert,[1a] but it was possible to increase greatly the reactivity of these complexes by increasing the bulk of the ligands.[2] The increased bulk led to greater reactivity because ligand dissociation made coordination sites available. In principle this same approach should lead to triaryl phosphite–cobalt hydride complexes of greatly enhanced activity. Unfortunately, the borohydride reduction which produced $CoH[P(OPh)_3]_4$ from cobalt(II) and the phosphite was not successful with more bulky phosphites.[1a]

A series of new triaryl phosphite cobalt hydrides, $CoH[(ArO)_3P]_3(CH_3CN)$, has now been prepared. These complexes are greatly more reactive than $CoH[(PhO)_3P]_4$ probably because dissociation of the nitrile ligand opens a coordination site. They are formally analogous to the complex $CoH(Ph_3P)_3(CH_3CN)$ prepared from $CoH(Ph_3P)_3(N_2)$ by Misono and co-workers[3] and characterized by elemental analyses and ir spectra.

Synthesis

The new hydridoorganonitrile complexes were prepared either by ligand exchange or by reaction of $Co(C_8H_{12})(C_8H_{13})$[4] with mixtures of acetonitrile and phosphorus ligands in a hydrogen atmosphere. A brief report of the use of this complex in cobalt hydride syntheses was made by Rossi and Sacco.[5] After some initial experiments in which a nonhydridic species was obtained when a nitrogen atmosphere was used[6] subsequent reactions were carried out in hydrogen atmospheres. This was true even when the goal was a complex of the type L_4CoH. Since the complex $Co(C_8H_{12})(C_8H_{13})$ reacts readily with hydrogen at room temperature to give cobalt metal and cyclooctane, care must be taken to add the hydrogen after the phosphorus and nitrile ligands have been added to the solutions. In some cases details of the procedures such as solvent composition appeared to be important. The hydridoacetonitriletris(triaryl phosphite)cobalt complexes were isolated and characterized. The analogous tertiary phosphine complexes were obtained by ligand exchange and were characterized only by their NMR spectra.

The ^1H and ^{31}P NMR measurements are summarized in Table I.