Registry No. [Mn(BuSal((−)pn))Cl], 58846-87-0; [Mn(BuSal((−)pn))H_2O]ClO_4, 58846-89-2; [Mn_2(BuSal((−)pn))$_2$(O)OH], 58933-75-8; [Mn(BuAcet((−)pn))Cl], 58846-90-5; [Mn(BuAcet((−)pn))H_2O]ClO_4, 58846-92-7; [Mn_2(BuAcet((−)pn))$_2$(O)OH], 58933-76-9.

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Solvation Effects in Intermediate-Spin Ferric Complexes

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The formation of a highly covalent six-coordinate complex when bis(*N,N*-dialkyldithiocarbamato)iron(III) halide is dissolved in tetrahydrofuran is proved by Mössbauer studies in the temperature range between 4.2 and 300 K. Both infrared and Mössbauer studies have shown that THF is only weakly bonded to the paramagnetic center of the five-coordinate original complex. Analysis of quadrupole splitting, isomer shift, and hyperfine interactions shows that in the solvated complex the Fe^{3+} ion has $S = {}^5/_2$. The crystal field parameter D is negative, the $|\pm{}^5/_2\rangle$ Kramers doublet is the lowest spin state of the six-coordinate complex, and $|D| \geq 1.4° \text{ cm}^{-1}$.

I. Introduction

Most common trivalent iron complexes are six-coordinate, with octahedral symmetry around the paramagnetic center. Strong fields of O_h symmetry stabilize the "low-spin" ${}^2T_2(t_{2g}{}^5)$ term which originates from the free-ion ${}^2I$ state. The "high-spin" ${}^6A_1(t_{2g}{}^3\,eg^2)$ term is found with weak ligand fields. In octahedral coordination no other term, except ${}^6A_1$ and ${}^2T_2$, can become the molecular ground state.[2a] By lowering the ligand field symmetry however, the ${}^4T_1(t_{2g}{}^4\,e_g)$ term (derived from ${}^4G$ in the free ion) can become the lowest lying state. The structural requirement for intermediate spin is met in the class of five-coordinate bis(*N,N*-dialkyldithiocarbamato)iron(III) halide complexes [hereafter denoted simply as Fe(dtc)$_2$X] which have nearly square-pyramidal symmetry around the ferric ion[2b] (Figure 1a). Considerable attention has been focused on these low-symmetry complexes with the unusual, for Fe^{3+}, coordination number 5 and total spin $S = {}^3/_2$.[3] Despite extensive studies in the solid state, there is only limited knowledge of solvation effects in Fe(dtc)$_2$X. de Vries et al.[4] have published some preliminary results which indicate that six-coordination occurs when Fe(dtc)$_2$X is dissolved in a solvent with good coordination properties. These authors observed, in the 77 K Mössbauer spectra, the appearence of a species with a small quadrupole splitting (QS = 0.7 mm/s) when Fe(dtc)$_2$Cl was dissolved in DMF, acetonitrile, etc. Since this value is characteristic of six-coordinate Fe^{3+}, they concluded that a solvent molecule was bound to the sixth vacant coordination site of the Fe^{3+}, giving rise to a complex with octahedral structure around the paramagnetic center. However it is not possible to make any safe predictions concerning the spin state of the six-coordinate complex from the QS magnitude alone. Magnetic susceptibility measurements, on the other hand, are very ambiguous, since these unstable complexes cannot be isolated from the solution where they exist in equilibrium with the five-coordinate parent compound of intermediate spin.

In this paper we report on studies of paramagnetic hyperfine structure and temperature dependence of IS and QS, measured by Mössbauer spectroscopy, which conclusively prove the formation of a highly covalent six-coordinate complex with $S = {}^5/_2$, when Fe(dtc)$_2$X is dissolved in tetrahydrofuran (THF).

II. Experimental Section

Fe(dtc)$_2$Br and Fe(dtc)$_2$Cl were prepared according to the method described by Martin and White,[5] which involves the reaction of Fe(dtc)$_3$ with a concentrated aqueous solution of the corresponding hydrohalide. The purity of the product, after recrystallization from $CHCl_3$–CCl_4, was confirmed by C, N, and H elemental analysis, as well as infrared and Mössbauer spectroscopy. The compounds used for preparation of solutions for the Mössbauer studies were synthesized with iron isotopically enriched in ${}^{57}Fe$. All solutions were prepared shortly before each measurement and immediately frozen to 77 K to prevent hydrolysis. The solid mixtures of five- and six-coordinate complexes (Figure 2) were obtained by recrystallizing solutions of Fe(dtc)$_2$X in THF under a continuous flux of nitrogen. The material used to record the spectra of Figure 2b was obtained by heating the product of the previous recrystallization for 48 h at 50 °C, to remove

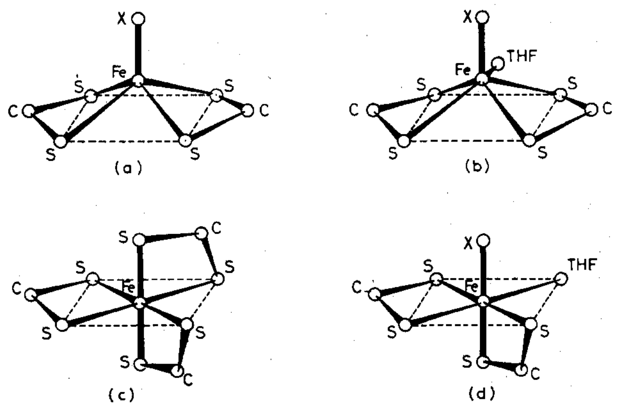

Figure 1. Molecular structures: (a) $Fe(dtc)_2X$; (b) six-coordinate complex according to ref 4; (c) octahedral $Fe(dtc(pyrr))_3$; (d) $(THF)Fe(dtc)_2X$.

all coordinated THF molecules. Mössbauer spectra were recorded using a 25-mCi ^{57}Co in Cu source in conjunction with a linear velocity drive. All isomer shift values are referred to the metallic iron standard. Infrared spectra were taken with the Perkin-Elmer 257 spectrophotometer.

III. Results and Discussion

A. Formation of the Six-Coordinate Complex. The Mössbauer spectra in Figure 2a and Figure 3 demonstrate the presence of two inequivalent iron sites in the absorber—the one labeled α, with QS = 2.88 mm/s (it corresponds to $Fe(dtc)_2X$), and the other, labeled β, with QS = 0.73 mm/s. The large difference in QS between α and β is understood in terms of a more symmetrical charge distribution (from both valence electrons and neighboring atoms) around the Fe^{3+} nucleus in β compared to α. This can conceivably result from the binding of one THF molecule to the sixth available coordination site of Fe^{3+} in $Fe(dtc)_2X$. When the solid used to obtain the spectra of Figure 2a is heated at 50 °C for 48 h, species β disappears from the Mössbauer absorption (Figure 2b). This is evidence that β is not a product of decomposition of $Fe(dtc)_2Br$ by THF, as well as that the solvent molecule is not strongly bound to Fe^{3+}. The ir spectra of Figure 2 confirm the assumption that THF is bound to $Fe(dtc)_2X$. The extra peaks shown in Figure 2a correspond to THF molecular vibrations, shifted from their position in pure THF due to coordination to $Fe(dtc)_2X$. These peaks disappear in Figure 2c and the characteristic ir spectrum of $Fe(dtc)_2X$ is obtained.

B. Spin State of the Six-Coordinate Complex. In Table I we list the temperature variation of IS, QS, and H_{eff} (the effective field) for the six-coordinate complex $(THF)Fe(dtc)_2X$. Some Mössbauer spectra from which these values were deduced are shown in Figures 2 and 3.

The decisive Mössbauer measurement, which determines the spin and the order of the Kramers doublets within the ground electronic state manifold, is the magnetic hyperfine interaction between the nuclear and electronic spins. Dilute solutions of paramagnetic ions, at low temperature, usually have total electronic spin relaxation rates slower than the nuclear precession frequency. In this case hyperfine structure

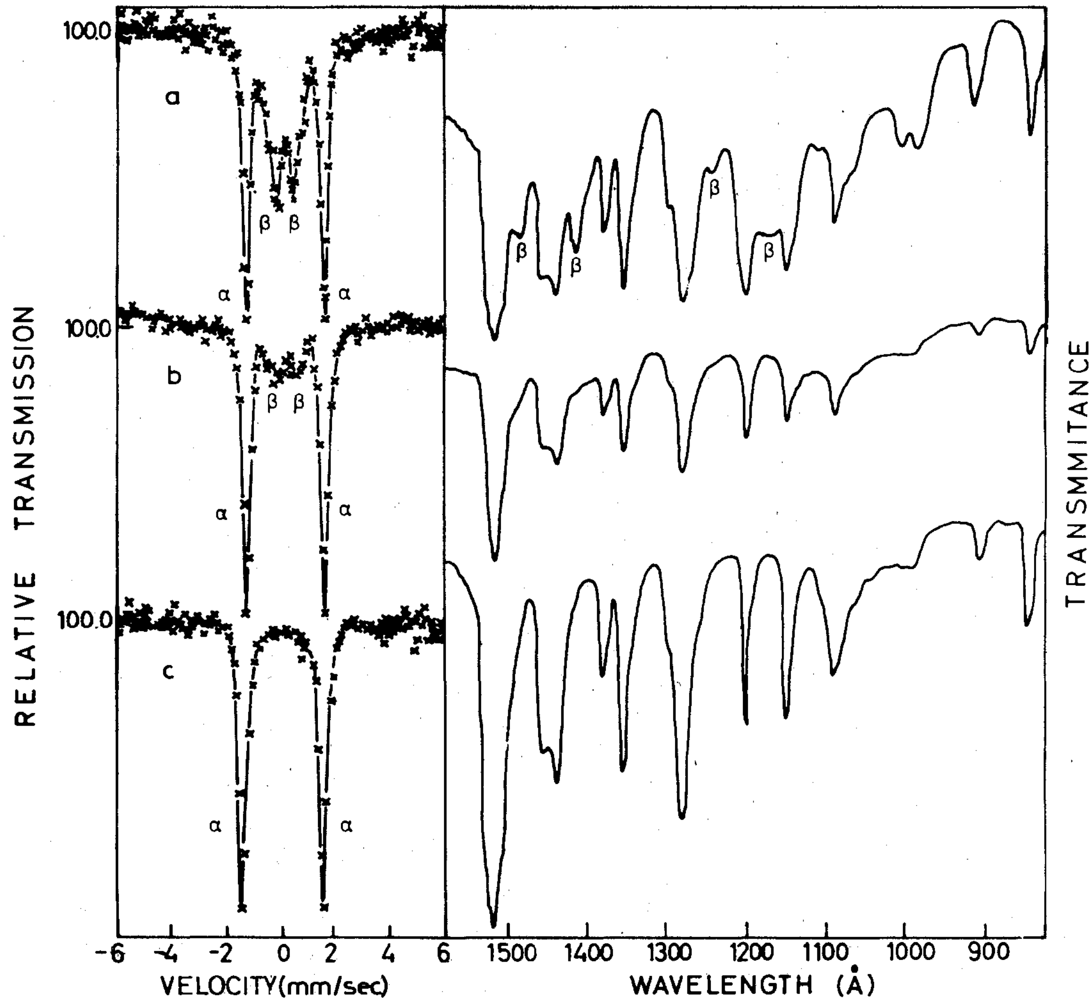

Figure 2. Room-temperature Mössbauer and ir spectra: (a) solid mixture of $Fe(dtc)_2Br$ and $(THF)Fe(dtc)_2Br$; (b) previous sample after 48-h heating at 50 °C; (c) pure $Fe(dtc)_2Br$.

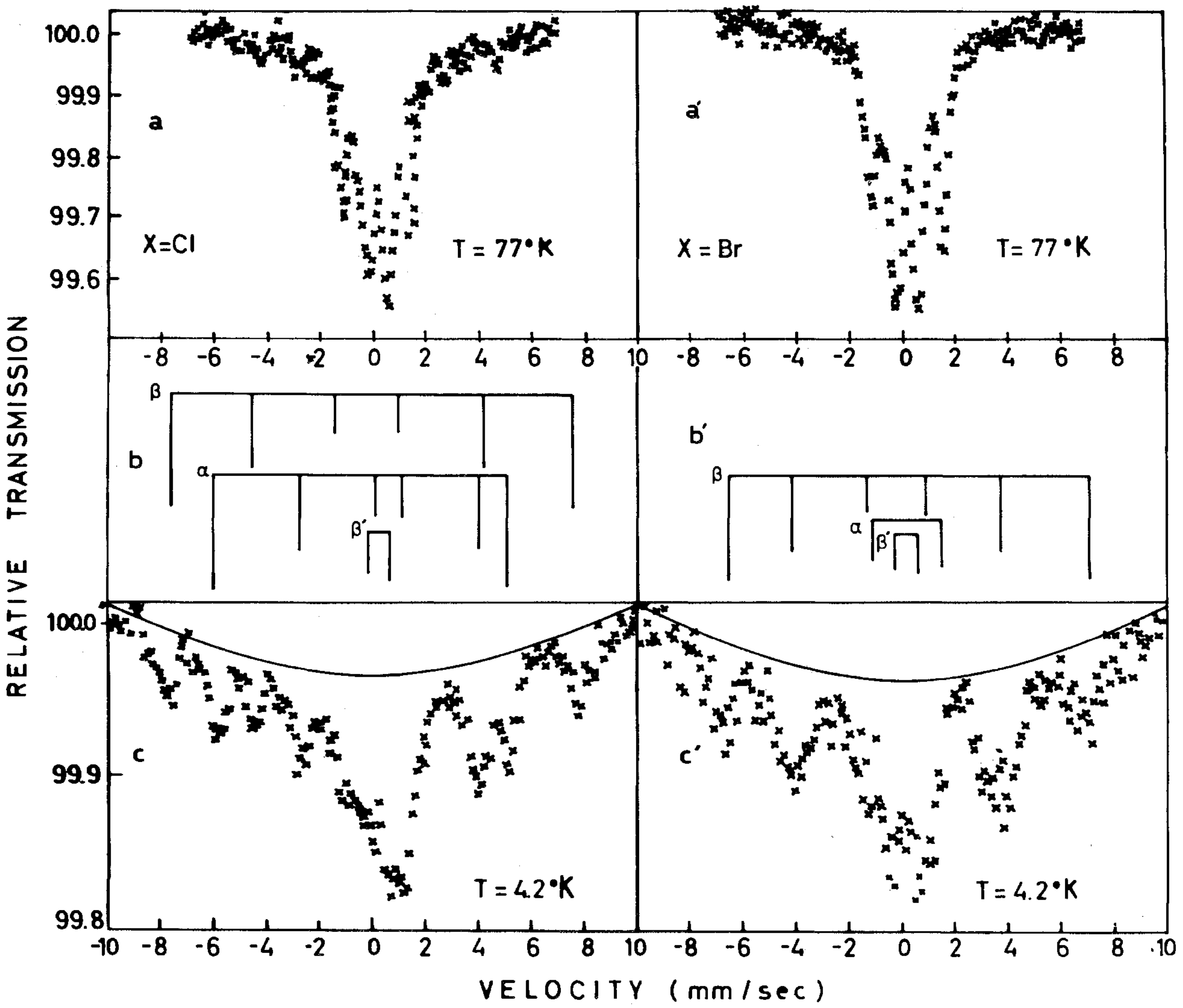

Figure 3. Mössbauer spectra of a 10^{-3} M ^{57}Fe(dtc)$_2$X solution in THF. [b and b' are calculated spectra at 4.2 K; β lines correspond to (THF)Fe(dtc)$_2$X microcrystallites.]

Table I. Temperature Variation of Isomer Shift (IS), Quadrupole Splitting (QS), and Effective Field (H_{eff}) of (THF)Fe(DTC)$_2$X[a]

	(THF)Fe(dtc)$_2$Br			(THF)Fe(dtc)$_2$Cl		
T, K	IS, mm/s	QS, mm/s	$H_{eff}(\theta,\phi)$, kG	IS, mm/s	QS, mm/s	$H_{eff}(\theta,\phi)$, kG
300	0.34 ± 0.01	0.72 ± 0.01	0	0.35 ± 0.01	0.72 ± 0.01	0
240	0.35 ± 0.01	0.73 ± 0.01	0	0.35 ± 0.01	0.74 ± 0.01	0
140	0.42 ± 0.01	0.73 ± 0.01	0	0.42 ± 0.01	0.74 ± 0.01	0
77	0.45 ± 0.01	0.73 ± 0.01	0	0.45 ± 0.01	0.74 ± 0.01	0
4.2	0.48	0.72	440 ± 10 (30°, 0°)	0.48	0.72	470 ± 10 (30°, 0°)

[a] IS values are referred to the metallic iron standard. θ and ϕ are the polar angles of H_{eff} in the principal EFG system of the iron nucleus.

may be observed even in zero applied field. Only when the lowest Kramers doublet is a $|\pm^1/_2\rangle$ state, which has fast spin–spin relaxation, hyperfine interactions average to zero.[6]

In Figure 3c and c' the 4.2 K Mössbauer absorption spectra of 10^{-3} M solutions of ^{57}Fe(dtc)$_2$X in THF are shown. In these solutions, five- and six-coordinate complexes coexist, as indicated from their spectra at 77 K (Figure 3a and a'). In the case of ^{57}Fe(dtc)$_2$Br dissolved in THF, the 4.2 K Mössbauer spectrum (Figure 3c') consists of the hfs of (THF)^{57}Fe(dtc)$_2$Br (β) and a quadrupole doublet (α) corresponding to ^{57}Fe(dtc)$_2$Br, since this complex, having a $|\pm^1/_2\rangle$ ground state,[7] does not demonstrate any hfs.

Fe(dtc)$_2$Cl, on the other hand, with the $|\pm^3/_2\rangle$ doublet as its ground Kramers state,[7] demonstrates hfs at 4.2 K. This structure is observed in Figure 3c (α) and is identical with previously reported spectra.[7] The rest of the absorption lines in Figure 3c represent the hfs of (THF)^{57}Fe(dtc)$_2$Cl (β). The 4.2 K parameters (Table I) were calculated by computer fitting line spectra (Figure 3b and b') to the absorption positions of the experimental spectra using the nuclear spin Hamiltonians (1) and (2) for the ground and excited nuclear states, respectively, all symbols having their usual meaning.

$$\mathcal{H}_N = -g_N\mu_N I\cdot H_{eff}(\theta,\phi) \qquad (1)$$

$$\mathcal{H}_N = -g_N{}^*\mu_N I^*\cdot H_{eff}(\theta,\phi) + (e^2qQ/4)[3I^*{}_x{}^2 - I^*(I^*+1) + \eta(I^*{}_x{}^2 - I^*{}_y{}^2)] \qquad (2)$$

spectively, all symbols having their usual meaning. The experimental magnitudes of the effective field, H_{eff} = 440 kG for the bromo and 470 kG for the chloro derivative, are characteristic of high-spin Fe^{3+} complexes with considerable 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}

$$H_{\mathrm{eff}} = H_{\mathrm{c}}\langle \mathrm{S}\rangle \tag{3}$$

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.

$$\mathcal{H}_{\mathrm{s}} = D[S_z^{\,2} - S(S+1)/3] + E[S_x^{\,2} - S_y^{\,2}] \tag{4}$$

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 (THF)Fe(dtc)$_2$X 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 $|D| \geq 1.4$ 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 FeF$_3$[10] to 460 kG in highly covalent (pyrr(dtc))$_3$Fe.[11]

Further evidence supporting the high-spin assignment for (THF)Fe(dtc)$_2$X 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 ($^2T_2$) causes substantial temperature variation of the QS,[12] in high-spin ($^6A_1$) Fe^{3+} complexes, the magnitude of the QS is expected to be independent of the temperature. This is the case for the six-coordinate (THF)Fe(dtc)$_2$X 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 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 Fe^{3+} d orbitals giving rise to the EFG.

Typical isomer shift values for low-spin 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 (THF)Fe(dtc)$_2$X 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 (THF)Fe(dtc)$_2$X compared to Fe(dtc)$_2$X. 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 Fe(dtc)$_2$X $\rightleftharpoons$ (THF)Fe(dtc)$_2$X.

Registry No. Fe(dtc)$_2$Br, 54163-77-8; (THF)Fe(dtc)$_2$Br, 58815-46-6; (THF)Fe(dtc)$_2$Cl, 58815-47-7.

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Iron–Hydrogen and Iron–Cobalt Metallocarboranes. Synthesis and Chemistry of $[(CH_3)_2C_2B_4H_4]_2Fe^{II}H_2$ and a Novel Tetracarbon Carborane System, $(CH_3)_4C_4B_8H_8$

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The reaction of Na$^+$(CH$_3$)$_2$C$_2$B$_4$H$_5$$^-$ with FeCl$_2$ below −30 °C produces red [*C*,*C*′-(CH$_3$)$_2$C$_2$B$_4$H$_4$]$_2$Fe$^{\mathrm{II}}$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 Co$^{\mathrm{III}}$H counterpart, the compound was not observed to convert to a nido,closo species, but treatment with NaH in THF forms the [(CH$_3$)$_2$C$_2$B$_4$H$_4$]$_2$Fe$^{\mathrm{II}}$H$^-$ ion, which on air oxidation produces the [(CH$_3$)$_2$C$_2$B$_4$H$_4$]$_2$Fe$^{\mathrm{III}-}$ ion. Reaction of the latter species with HCl gas generates [*C*,*C*′-(CH$_3$)$_2$C$_2$B$_4$H$_4$]$_2$Fe$^{\mathrm{II}}$H$_2$ and a novel air-stable carborane, (CH$_3$)$_4$C$_4$B$_8$H$_8$; this latter product is also formed in high yield on air oxidation of the commo species [(CH$_3$)$_2$C$_2$B$_4$H$_4$]$_2$Fe$^{\mathrm{II}}$H$_2$. The compound (CH$_3$)$_4$C$_4$B$_8$H$_8$ 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 (CH$_3$)$_2$C$_2$B$_4$H$_4$ 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*′-(CH$_3$)$_2$C$_2$B$_4$H$_4$]$_2$Fe$^{\mathrm{II}}$H$_2$ with (η^5-C$_5$H$_5$)Co(CO)$_2$ yields (η^5-C$_5$H$_5$)Co[(CH$_3$)$_2$C$_2$B$_3$H$_3$]Fe(CO)$_3$, in which the metal atoms are proposed to occupy the apexes of a pentagonal-bipyramidal cage, and a structurally novel compound, [(CH$_3$)$_4$C$_4$B$_8$H$_8$]FeCo(η^5-C$_5$H$_5$), 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*′-(CH$_3$)$_2$C$_2$B$_4$H$_4$)$_2$Co$^{\mathrm{III}}$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*′-(CH$_3$)$_2$C$_2$B$_4$H$_4$]$^{2-}$ ligand[2] developed some interesting contrasts with the cobalt system and also led to the preparation of two