Dicarbonyl(η-cyclopentadienyl)iron(II) Derivatives of Pentaborane(9)

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The $[B_5H_8]^-$ anion reacts with $[Fe(\eta\text{-}C_5H_5)(CO)_2I]$ to give $[Fe(2\text{-}B_5H_8)(\eta\text{-}C_5H_5)(CO)_2]$ (1). This can be deprotonated with KH to give the anion $[Fe(2\text{-}B_5H_7)(\eta\text{-}C_5H_5)(CO)_2]^-$ which can react with another equivalent of $[Fe(\eta\text{-}C_5H_5)(CO)_2I]$ to give $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2(2,4\text{-}B_5H_7)]$ (3); this is the first example of a compound with two transition-metal atoms bound to the pentaborane skeleton. Boron-11 and ^1H n.m.r. and mass spectroscopic data confirm the structures assigned to (1) and (3): these are consistent with the hypothesis that *nido*-pentaborate anions act as 2—3-η ligands in 16-electron transition-metal compounds and as 2-σ ligands in 18-electron species. The electron-impact fragmentation of the compounds is briefly discussed.

METAL–BORANE compounds exhibit a wide diversity of bonding in which the borane moiety can act as a σ or η^2, η^3, η^4, or η^5 ligand to the metal atom, and the bonding may involve either direct metal–boron bonds or three-centre M–H–B bridge bonds or both.[1,2] Known metal derivatives of pentaborane(9) include those of manganese,[3] rhenium,[3] iridium,[4,5] nickel,[6] copper,[7,8] cadmium,[9] and the Group 4B semi-metals.[10-12] For the iridium and copper compounds, the mode of bonding in the solid state has been unequivocally established by

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X-ray diffraction analysis. In the 18-electron species $[Ir(2\text{-}B_5H_8)Br_2(CO)(PMe_3)_2]$ the boron ligand is σ bonded with the iridium(III) atom coplanar with the four basal boron atoms,[5] and n.m.r. evidence suggests that the manganese(I) and rhenium(I) compounds $[Mn(B_5H_8)(CO)_5]$ and $[Re(B_5H_8)(CO)_5]$ have similar structures.[3] In contrast, in the 16-electron species $[Cu(B_5H_8)(PPh_3)_2]$ the metal-boron bonding is 2—3-η with the copper(I) atom in the B(1)–B(2)–B(3) plane;[8] the cadmium(II) and nickel(II) compounds $[Cd(B_5H_8)Cl(PPh_3)]$ and $[Ni(B_5H_8)Cl(Ph_2PCH_2CH_2PPh_2)]$ probably also adopt this geometry,[6,9] although it is believed that in solution the latter compound is fluxional, with the bridging hydrogen atoms undergoing rapid intramolecular exchange with the nickel moiety.[9] In addition to these compounds, it should be noted that the metallahexaboranes $[Be(BH_4)(B_5H_{10})]$ [13] and $[Fe(B_5H_8)(CO)_3H]$,[14] in which the metal atoms are incorporated fully into the *nido*-borane cage structure, can also be formally regarded as pentaborane derivatives in which the borane moieties act now as η^5 and η^4 ligands to the metal atoms.

In view of this variety of ligation it is of considerable interest to prepare additional examples of metal–pentaborane compounds in order to delineate the factors which determine the structure to be adopted and to investigate the properties of these interesting compounds in detail. Accordingly we now report the synthesis and some properties of the mono- and bis-[dicarbonyl-(η-cyclopentadienyl)iron(II)] derivatives of pentaborane(9), $[Fe(2\text{-}B_5H_8)(\eta\text{-}C_5H_5)(CO)_2]$ and $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2(2,4\text{-}B_5H_7)]$, of which the latter is the first example of a compound with two transition-metal atoms bonded to a pentaborane skeleton. The only previously reported iron derivatives of boranes are the ferrahexaborane mentioned above,[14] and the compounds $[Fe(B_3H_8)(C_5H_5)(CO)_2]$,[15] $[Fe(B_4H_8)(CO)_3]$,[16] $[Fe(B_6H_{10})(CO)_4]$,[17] $[Fe(B_{10}H_{13}C_5H_5N)Br_2(NC_5H_5)]$,[18] and $[Fe(B_{10}H_{13})(C_5H_5)(CO)_2]$.[19]

EXPERIMENTAL

All the manipulations were carried out under rigorously dry oxygen-free conditions using standard vacuum-line, glove-box, and Schlenk techniques. Pentaborane(9) was obtained by courtesy of Dr. R. E. Williams (Chemical Systems Inc., California) and other substances were obtained from commercial sources or made by standard methods. Potassium hydride was freed from mineral oil by washing with pentane before use.

N.M.R. Measurements.—90-MHz ^1H and $^1H\text{-}\{^{11}B\}$ together with 28.9-MHz ^{11}B and $^{11}B\text{-}\{^1H\}$ n.m.r. spectra were recorded at 28 °C in the Fourier-transform mode on a Bruker HFX spectrometer modified with a Bruker BNC12 data system. Data accumulation and manipulation parameters were selected so that the digital resolution in the ^1H spectra was $\leqslant 0.25$ Hz and in the ^{11}B spectra was $\leqslant 3$ Hz, *i.e.* both somewhat less than the natural linewidths of the boron and boron hydride resonances observed. The reference standards used were tetramethylsilane for ^1H and a 50% v/v solution of $OEt_2{\cdot}BF_3$ in C_6D_6(external) for ^{11}B, and the chemical shifts are quoted as positive to high frequency (low field) of these. It may be noted that this recently recommended sign convention has the disadvantage that nuclear shielding and chemical shift have opposite signs.[20]

Mass Spectroscopy.—Mass spectra were recorded at a nominal ionising potential of 70 eV on an A.E.I. MS3074 single-beam instrument equipped with an all-glass heated inlet system and a peak-matching accessory.* Samples were introduced *via* the solid-sample introduction probe, and probe and cage temperatures were maintained at <80 °C. High-resolution mass measurements were carried out at resolutions in the range 15 000—18 000 and were accurate to *ca.* 5 p.p.m.; perfluorokerosene introduced *via* the heated inlet system was used as the mass-reference standard and also to calibrate the peak-matching device. Anisotopic spectra (Table 2 and 5) were obtained from high-resolution measurements of peak intensities and accurate mass within a multiplet at a given mass number (*e.g.* Tables 1 and 4), and scaled using the low-resolution spectra plus an assumed ^{11}B : ^{10}B ratio of 80 : 20.

Infrared Spectra.—These were recorded on a Perkin-Elmer 457 grating spectrometer and were calibrated using a polystyrene film; errors in the quoted band maxima are ± 5 cm^{-1}.

Preparation of Dicarbonyl(η-*cyclopentadienyl*)[*octahydropentaborato*(1−)]*iron*(II), $[Fe(2\text{-}B_5H_8)(\eta\text{-}C_5H_5)(CO)_2]$.—In a typical experiment, pentaborane(9) (5.00 mmol) and dimethyl ether (20 cm^3) were condensed at −196 °C on to potassium hydride (70% active, 0.285 g, corresponding to 5.0 mmol KH) and stirred at -60 ± 20 °C for 1 h to produce $K[B_5H_8]$.[21] The compound $[Fe(\eta\text{-}C_5H_5)(CO)_2I]$ (1.52 g, 5.0 mmol) was added and the mixture stirred at −40 °C for 4 h, yielding a deep red solution and a fine white precipitate. The more volatile components were removed under reduced pressure (0.1 mmHg, −40 °C, 2 h) and the resulting semi-solid was extracted with pentane (*ca.* 50 cm^3). Removal of pentane from the extract (0.1 mmHg, 20 °C, 6 h) yielded the product as an orange *solid* (0.9 g, 4.3 mmol, 86% yield), m.p. 21—22 °C, which was stable under dry nitrogen, moderately stable in air, and very soluble in most organic solvents. On storage it formed well crystallised yellow needles as the ambient temperature fluctuated around the melting point [Found: C, 35.4; H, 5.4; B, 21.9; Fe, 23.1; O (by difference) 14.2. $C_7H_{13}B_5FeO_2$ requires C, 35.2; H, 5.5; B, 22.6; Fe, 23.35; O, 13.4%]. Infrared: ν(B–H) at 2 575s; ν(C–O) at 2 012s and 1 956s; ν(B–H–B) at 1 812w and 1 784w (in CCl_4 solution); at 2 575s, 2 005s, 1 946s,

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* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J; 1 mmHg ≈ 13.6×9.8 Pa.

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[20] See, for example, *Pure Appl. Chem.*, 1972, **29**, 627; R. K. Harris in 'Nuclear Magnetic Resonance', *Specialist Periodical Reports*, The Chemical Society, London, 1975, vol. 4, p. iv.

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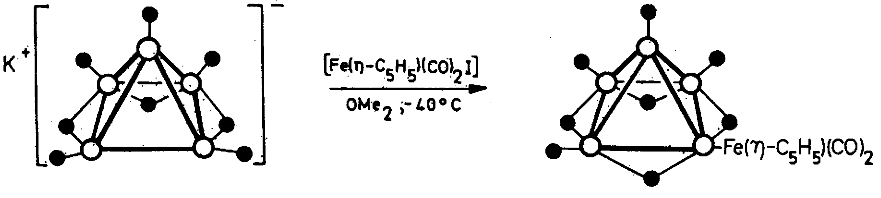
1 805w, and 1 779w cm^{-1} (in Nujol mull). Other spectroscopic data are presented and discussed below. Use of LiMe–OEt$_2$ instead of KH–OMe$_2$ in the above procedure gave yields of the product of 35—55%; use of sodium hydride and tetrahydrofuran (thf) gave yields of 40—45%.

Deprotonation of $[Fe(2\text{-}B_5H_8)(\eta\text{-}C_5H_5)(CO)_2]$ *and Preparation of the* $[PPh_4]^+$ *and* $[NBu^n_4]^+$ *Salts of the Anion* $[Fe(2\text{-}B_5H_7)(\eta\text{-}C_5H_5)(CO)_2]^-$.—Monoglyme (20 cm^3) was distilled on to $[Fe(2\text{-}B_5H_8)(\eta\text{-}C_5H_5)(CO)_2]$ (1.2 g, 5.0 mmol) at −196 °C and KH (70% active, 0.285g, corresponding to 5 mmol KH) was added. The mixture was stirred at −40 °C for 4 h, during which time hydrogen (5.1 mmol) was evolved. Tetraphenylphosphonium iodide (2.3 g, 5 mmol) was added, the mixture stirred at −40 °C for another 2 h, and filtered. Addition of pentane (60 cm^3) to the filtrate precipitated the product $[PPh_4][Fe(2\text{-}B_5H_7)(\eta\text{-}C_5H_5)(CO)_2]$ which was filtered off, washed with diethyl ether (*ca.* 15 cm^3) at 0 °C, and dried *in vacuo* (0.1 mmHg, 20 °C, 3 h) yielding a yellow-orange *powder* (2.0 g, 3.5 mmol, 70%) [Found: C, 65.0; H, 5.7; B, 9.1; Fe, 9.8; O (by difference), 5.0; P, 5.4. $C_{31}H_{32}B_5FeO_2P$ requires C, 65.0; H, 5.6; B, 9.4; Fe, 9.7; O, 5.5; P, 5.4%]. The *tetra-n-butylammonium analogue* $[NBu^n_4][Fe(2\text{-}B_5H_7)(\eta\text{-}C_5H_5)(CO)_2]$ was made similarly and in similar yield using tetra-n-butylammonium iodide [Found: C, 57.6; H, 10.1; B, 10.9; Fe, 11.3; N, 2.8; O (by difference), 7.3. $C_{23}H_{48}FeB_5NO_2$ requires C, 57.5; H, 10.1; B, 11.3; Fe, 11.6; N, 2.9; O, 6.6%]. These complex salts were unchanged after 24 h under nitrogen at −15 °C and were thus somewhat more stable than the potassium salt, which under the same conditions showed signs of decomposition after 2 h (i.r. spectrum).



(1)

SCHEME 1

TABLE 1

Typical high-resolution measurements for the 70-eV mass spectrum of $[Fe(2\text{-}B_5H_8)(\eta\text{-}C_5H_5)(CO)_2]$

Nominal mass number	Observed relative mass (*m/e*)	Relative intensity within multiplet at a given mass no.	Assignment	Calculated relative mass (*m/e*)
240	240.073 5(10)	singlet	$[^{56}Fe(^{11}B_5H_8)(C_5H_5)(CO)_2]^+$	240.073 0
239	239.076 6(10)	singlet	$[^{56}Fe(^{11}B_4{}^{10}BH_8)(C_6H_5)(CO)_2]^+$	239.076 7
238	238.079 0(20)	singlet	$[^{56}Fe(^{11}B_3{}^{10}B_2H_8)(C_5H_5)(CO)_2]^+$	238.080 3
184	184.082 9(10)	singlet	$[^{56}Fe(^{11}B_5H_8)(C_5H_5)]^+$	184.083 2
183	183.086 7(10)	singlet	$[^{56}Fe(^{11}B_4{}^{10}BH_8)(C_5H_5)]^+$	183.086 8
182 *	182.089 5(10)	2	$[^{56}Fe(^{11}B_3{}^{10}B_2H_8)(C_5H_5)]^+$	182.090 5
	182.066 9(10)	3	$[^{56}Fe(^{11}B_5H_6)(C_5H_5)]^+$	182.067 6
181 *	181.094 3(10)	1	$[^{56}Fe(^{11}B_2{}^{10}B_3H_8)(C_5H_5)]^+$	181.094 1
	181.071 5(10)	10	$[^{56}Fe(^{11}B_4{}^{10}BH_6)(C_5H_5)]^+$	181.071 2
180 *	180.096 5(20)	trace	$[^{56}Fe(^{11}B^{10}B_4H_8)(C_5H_5)]^+$	180.097 7
	180.075 3(10)	2	$[^{56}Fe(^{11}B_3{}^{10}B_2H_6)(C_5H_5)]^+$	180.074 8
	180.052 5(10)	3	$[^{56}Fe(^{11}B_5H_4)(C_5H_5)]^+$	180.051 9

* The absence of fragments with odd numbers of H atoms on the boron fragment is notable.

Preparation of μ*-Heptahydropentaborato*(2—)*-bis*[*dicarbonyl*(η*-cyclopentadienyl*)*iron*(II)], $[\{Fe(\eta\text{-}C_5H_5)(CO_2\}_2(2,4\text{-}B_5H_7)]$.—A sample of $[Fe(2\text{-}B_5H_8)(\eta\text{-}C_5H_5)(CO)_2]$ (1.20 g, 5.0 mmol) was deprotonated with KH as described above, and cooled to −196 °C. The compound $[Fe(\eta\text{-}C_5H_5)(CO)_2I]$ (1.52 g, 5.0 mmol) was added, and the mixture stirred first for 8 h, during which time the temperature was allowed to rise from −78 to −20 °C, and then for 30 min at *ca.* 20 °C. The mixture was filtered, and the solvent removed from the filtrate under reduced pressure. The resulting dark red solid was extracted with thf (*ca.* 20 cm^3), the extracts were filtered, and the solvent again removed from the filtrate under reduced pressure. The resulting solid residue was dissolved in benzene (*ca.* 15 cm^3) and separated chromatographically on a 20 × 250 mm silica gel column at ambient temperatures using benzene as eluant. The first component was eluted as a yellow band, and removal of the solvent under reduced pressure gave the product $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2(2,4\text{-}B_5H_7)]$ as a yellow *solid* (0.23 g, 0.55 mmol, 11.0%). This could be recrystallised from dichloromethane as yellow needles, m.p. 110 °C (decomp.), which could be handled in air without apparent change and which were very soluble in polar organic solvents [Found: C, 40.8; H, 4.2; B, 12.7; Fe, 27.1; O (by difference), 15.2. $C_{14}H_{17}B_5Fe_2O_4$ requires C, 40.5; H, 4.1; B, 13.0; Fe, 26.9; O, 15.4%]. Infrared: ν(B–H) at 2 580s and 2 543s; ν(C–O) at 1 988s and 1 930s cm^{-1} (KCl disc). Other spectroscopic data are presented and discussed below. The other major identified product from the reaction was $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ (*ca.* 60% yield).

RESULTS

We have found that $K[B_5H_8]$ reacts readily with $[Fe(\eta\text{-}C_5H_5)(CO)_2I]$ in dimethyl ether to give $[Fe(2\text{-}B_5H_8)(\eta\text{-}C_5H_5)(CO)_2]$ in essentially quantitative yield as a reasonably air-stable yellow crystalline solid of low melting point (Scheme 1). With other solvents and counter ions the yield is reduced. The molecular formula of the product was confirmed by high-resolution mass spectrometry (Table 1): the molecular ion at nominal *m/e* 240 had a

TABLE 2

Principal peaks in the anisotopic mass spectrum of $[Fe(2\text{-}B_5H_8)(\eta\text{-}C_5H_5)(CO)_2]$ at 70 eV

Ion group	Percentage total ion content (Σ_{33})
$[Fe(B_5H_8)(C_5H_5)(CO)_2]^+$	0.79
$[Fe(B_5H_8)(C_5H_5)(CO)]^+$	8.54
$[Fe(B_5H_8)(C_5H_5)]^+$	9.45
$[Fe(B_5H_6)(C_5H_5)]^+$	10.10
$[Fe(B_5H_4)(C_5H_5)]^+$	10.75
$[Fe(B_5H_2)(C_5H_5)]^+$	7.63
$[Fe(B_5)(C_5H_5)]^+$	2.24
$[Fe(B_4H_n)(C_5H_5)]^+$ fragments	*ca.* 3.0
$[Fe(C_5H_5)(CO)H]^+$	1.05
$[Fe(C_5H_5)(CO)]^+$	2.30
$[Fe(C_5H_5)(H)]^+$	1.27
$[Fe(C_5H_5)]^+$	6.41
$[C_5H_7]^+$	0.63
$[C_5H_6]^+$	4.46
$[C_5H_5]^+$	1.86
Fe^+	4.20
$[B_nH_m]^+$ fragments	<0.6

precise *m/e* of 240.073 5 ± 0.001 0 ($^{12}C_7{}^1H_{13}{}^{11}B_5{}^{56}Fe^{16}O_2$ requires 240.073 0), and the fragmentation pattern (Table 2) is consistent with the proposed structure (1).

That the iron atom is bonded to the pentaborane cage in the basal terminal (2) position (structure 1) follows from the ^{11}B and $^{11}B\text{-}\{^1H\}$ n.m.r. spectra (Figure 1 and Table 3). The nucleus of the apical (1) boron atom resonates at δ −48.5 p.p.m. and shows a coupling $^1J(^{11}B\text{–}^1H)$ of 170 Hz, and there are three resonances due to basal boron atoms at δ +7.9, −10.6, and −14.3 p.p.m. of relative intensity 1 : 2 : 1. Of these, the resonance at δ +7.9 is a singlet (B–Fe), whereas the other two show couplings $^1J(^{11}B\text{–}^1H)$ of *ca.* 160 Hz. Additional confirmation of this structure comes from the results of ^1H and $^1H\text{-}\{^{11}B\}$ n.m.r. spectroscopy (Table 3); in particular, the two resonances of equal intensity for the bridging hydrogen atoms indicate substitution in the 2 position and eliminate the possibility of the 2,3-bridge-bonded isomer [structure (2)].

The monoiron compound $[Fe(2\text{-}B_5H_8)(\eta\text{-}C_5H_5)(CO)_2]$ can

TABLE 3

Boron-11 and ^1H n.m.r. parameters for $[Fe(2\text{-}B_5H_8)(\eta\text{-}C_5H_5)(CO)_2]$ [a]

	^{11}B and $^{11}B\text{-}\{^1H\}$ spectra			^1H and $^1H\text{-}\{^{11}B\}$ spectra		
Position assigned	$\delta(^{11}B)$ [b]	multiplicity [c] and relative intensity	$^1J(^{11}B\text{–}^1H)$/Hz	$\delta(^1H)$ [d]	relative intensity	$^1J(^{11}B\text{–}^1H)$/Hz
1	−48.5(2)	d, 1	170(5)	+0.9(1)	1	168(2)
2	+7.9(2)	s, 1				
3,4	−10.6(2)	d, 2	150(10)	+2.7(2) [e]	3	156(4) [e]
5	−14.3(2)	d, 1	160(20)			
Bridging				A −0.8(1)	2	
				B −1.9(1)	2	
C_5H_5				−4.95(10)	5	

[a] Measured for a 50% v/v solution in C_6D_6 at 28 °C. [b] In p.p.m. to high frequency (low field) of $OEt_2{\cdot}BF_3$. [c] d = Doublet; s = singlet. [d] In p.p.m. to high frequency (low field) of $SiMe_4$. [e] Apparent values: resonance positions and coupling constants for protons at positions 3—5 are almost identical.

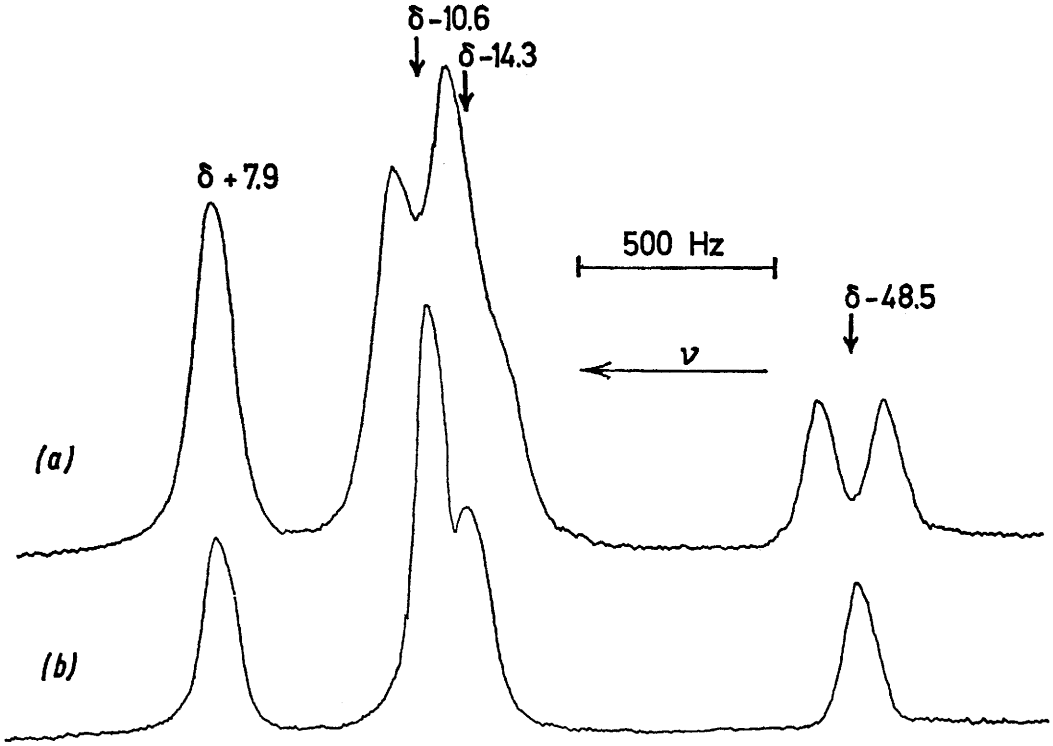


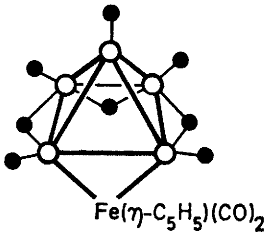
FIGURE 1 28.87-MHz ^{11}B n.m.r. spectra of $[Fe(2\text{-}B_5H_8)(\eta\text{-}C_5H_5)(CO)_2]$ (1): (*a*) normal ^{11}B spectrum showing coupling to protons; (*b*) $^{11}B\text{-}\{^1H\}$ spectrum (at reduced spectrometer gain) with proton coupling removed by simultaneous broad-band irradiation at the ^1H frequency

TABLE 4

Typical high-resolution mass measurements from the 70-eV mass spectrum of $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2(2,4\text{-}B_5H_7)]$

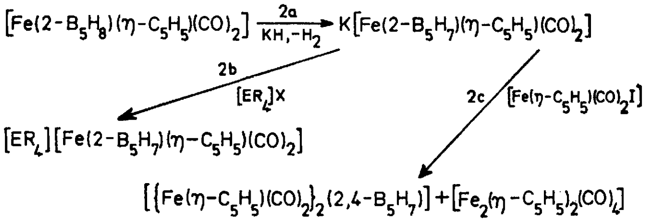
Nominal mass number	Observed relative mass (*m/e*)	Relative intensity within a multiplet at a given mass no.	Assignment	Calculated relative mass (*m/e*)
416	416.032(3)	singlet	$[^{56}Fe_2(^{11}B_5H_7)(C_5H_5)_2(CO)_4]^+$	416.029
415	415.035(3)	singlet	$[^{56}Fe_2(^{11}B_4{}^{10}BH_7)(C_5H_5)_2(CO)_4)]^+$	415.033
414	414.036(3)	singlet	$[^{56}Fe_2(^{11}B_3{}^{10}B_2H_7)(C_5H_5)_2(CO)_4]^+$	414.036
183	183.087(2)	trace	$[^{56}Fe(^{11}B_4{}^{10}BH_8)(C_5H_5)]^+$	183.087
	183.076(2)	major component	$[^{56}Fe(^{11}B_5H_7)(C_5H_5)]^+$	183.075
182	182.092(2)	trace	$[^{56}Fe(^{11}B_3{}^{10}B_2H_8)(C_5H_5)]^+$	182.090
	182.080(2)	major component	$[^{56}Fe(^{11}B_4{}^{10}BH_7)(C_5H_5)]^+$	182.079
	182.068(20)	trace	$[^{56}Fe(^{11}B_5H_6)(C_5H_5)]^+$	182.068
181	181.095(20)	trace	$[^{56}Fe(^{11}B_2{}^{10}B_3H_8)(C_5H_5)]^+$	181.094
	181.083(20)	1	$[^{56}Fe(^{11}B_3{}^{10}B_2H_7)(C_5H_5)]^+$	181.082
	181.073(20)	trace	$[^{56}Fe(^{11}B_4{}^{10}BH_6)(C_5H_5)]^+$	181.071
	181.061(20)	>10	$[^{56}Fe(^{11}B_5H_5)(C_5H_5)]^+$	181.060

be deprotonated quantitatively by KH (Scheme 2a) to give the monoanion $[Fe(2\text{-}B_5H_7)(\eta\text{-}C_5H_5)(CO)_2]^-$ of which the



(2)

unstable tetraphenylphosphonium and tetra-n-butylammonium salts have been isolated (Scheme 2b, $[ER_4]^+ = [PPh_4]^+$ or $[NBu^n{}_4]^+$). Reaction of the monoanion with $[Fe(\eta\text{-}C_5H_5)(CO)_2I]$ (Scheme 2c) gives the air-stable di-iron compound $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2(2,4\text{-}B_5H_7)]$ in low yield together with larger amounts of the well known dimer $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$.



SCHEME 2

The molecular formula of the di-iron compound $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2(2,4\text{-}B_5H_7)]$ was confirmed by high-resolution mass spectrometry (Table 4), and the electron-impact fragmentation pattern (Table 5) is consistent with a structure in which the two dicarbonylcyclopentadienyliron groups are pendant from the pentaborane cage. The results from the ^{11}B n.m.r. spectra (Figure 2 and Table 6) show that the pentaborane skeleton is bis(basal-terminal) substituted, and the presence of only one bridging proton resonance in the ^1H n.m.r. spectrum (Table 6) suggests that the substituents are in mutually *trans* (2,4) positions [structure (3)]. A single bridging proton resonance would only be consistent with a *cis* (2,3) substituted structure (4) in the unlikely circumstance that the ^1H resonances of the different types of bridging hydrogen were accidently coincident.

TABLE 5

Principal peaks in the anisotopic mass spectrum of $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}(2,4\text{-}B_5H_7)]$ at 70 eV

Ion group	Percentage total ion content (Σ_{33})
$[Fe_2(B_5H_7)(C_5H_5)_2(CO)_4]^+$	0.33
$[Fe_2(B_5H_7)(C_5H_5)_2(CO)_3]^+$	1.65
$[Fe_2(B_5H_7)(C_5H_5)_2(CO)_2]^+$	2.90
$[Fe_2(B_5H_7)(C_5H_5)_2(CO)]^+$	2.97
$[Fe_2(B_5H_7)(C_5H_5)_2]^+$	<0.2
$[Fe_2(B_5H_6)(C_5H_5)_2]^+$	<0.2
$[Fe_2(B_5H_5)(C_5H_5)_2]^+$	15.18
$[Fe_2(B_5H_3)(C_5H_5)_2]^+$	*ca.* 1.5
$[Fe(B_5H_7)(C_5H_5)(CO)_2]^+$	3.56
$[Fe(B_5H_7)(C_5H_5)(CO)]^+$	2.64
$[Fe(C_5H_5)_2]^+$	1.49
$[Fe(B_5H_7)(C_5H_5)]^+$	3.10
$[Fe(B_5H_6)(C_5H_5)]^+$	<0.1
$[Fe(B_5H_5)(C_5H_5)]^+$	0.95
$[Fe(C_5H_5)(CO)_2]^+$	4.17
$[Fe(C_5H_5)(CO)]^+$	4.00
$[Fe(C_5H_5)]^+$	5.71
$[C_5H_6]^+$	0.52
Fe^+	3.81

TABLE 6

Boron-11 and ^1H n.m.r. parameters for $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2(2,4\text{-}B_5H_7)]$ [a]

	^{11}B and $^{11}B\text{-}\{^1H\}$ spectra			$^1H\text{-}\{^{11}B\}$ spectrum	
Position assigned	$\delta(^{11}B)$ [b]	multiplicity [c] and relative intensity	$^1J(^{11}B–^1H)$/Hz	$\delta(^1H)$ [d]	relative intensity
1	−45.0(2)	d, 1	168(8)	+0.2(1)	1
2.4	+1.4(2)	s, 2			
3,5	−8.6(2)	d, 2	127(8)	+2.2(1)	2
Bridging				−1.5(1)	4
C_5H_5				+4.9(1)	10

[a] Measured for a saturated solution in CD_2Cl_2 at 28 °C. [b] In p.p.m. to high frequency (low field) of $OEt_2{\cdot}BF_3$. [c] d = Doublet; s = singlet. [d] In p.p.m. to high frequency (low field) of $SiMe_4$.

DISCUSSION

Preparation and Properties.—The formation of [Fe(2-B_5H_8)(η-C_5H_5)(CO)$_2$], in which the iron substituent is on the 2 position of *nido*-pentaborane, is noteworthy. The [B_5H_8]$^-$ anion (see structure in Scheme 1) is formed by the abstraction of a bridge proton from B_5H_9,[21] and a straightforward mechanistic rationale would predict than an initial metathetical reaction would produce a substituent in the 2,3-bridging position [structure (2)]. This occurs for all the other pentaborane compounds of transition elements so far prepared by this method.[6-12] A possible mechanism is that a compound with structure (2) forms initially in the reaction represented by Scheme 1, but that this subsequently isomerises to give a product with structure (1). However, monitoring the reaction at low temperatures by ^{11}B n.m.r. spectroscopy showed no evidence for such an intermediate, implying that any isomerisation is rapid. For a number of Group 4B metal derivatives the metal-bridged structure can be isolated as an initial stable product, and then subsequently be isomerised under very mild Lewis-base catalysis to give the substituent in the 2 position.[10] However, Group 4B metals bonded to electropositive substituents are not particularly labile species, and it is probable that an analogous isomerisation of a transition-metal species would occur much more readily. The observed metal–pentaborane products from many such reactions may therefore be the consequence of thermodynamic rather than kinetic control, and here it may be relevant that in all the 18-electron transition-metal–pentaborane species so far reported (refs. 3—5 and the compounds described in this work) the pentaborate anion acts as a σ ligand at the basal B(2) position, whereas in all the 16-electron species [6-9] it is a 2—3-η donor. This suggests that the 2—3-η structure may therefore result from an attempt to mitigate the electronic unsaturation of the 16-electron metal species.

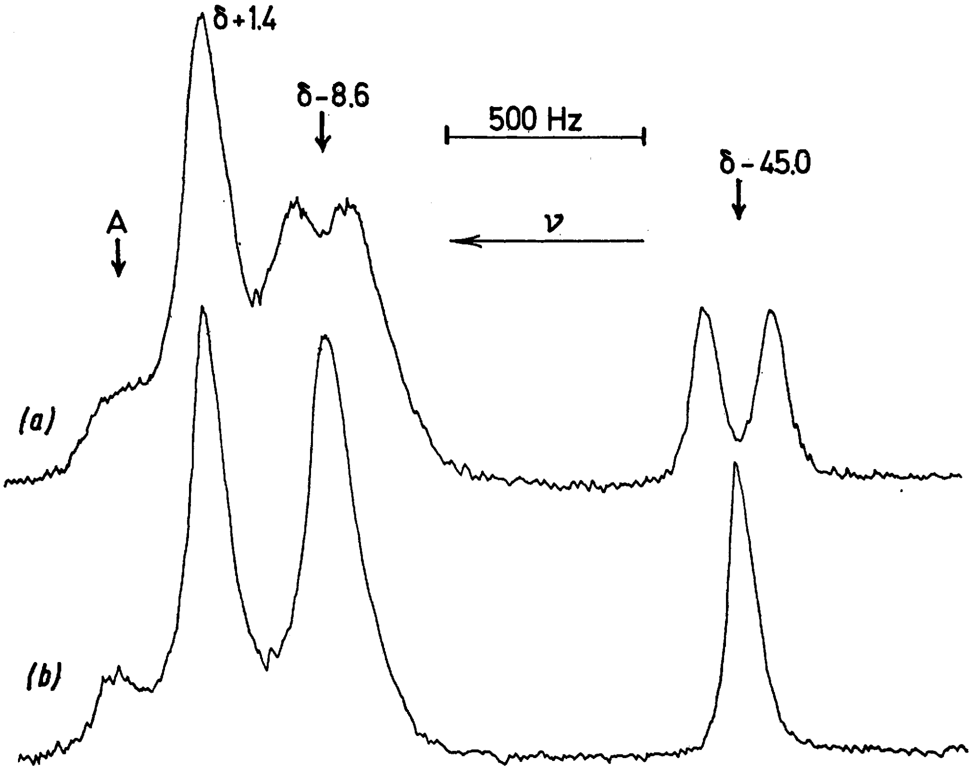
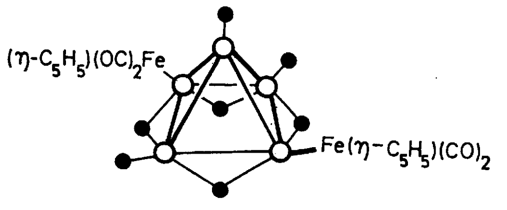


FIGURE 2 28.87-MHz ^{11}B n.m.r. spectra of [{Fe(η-C_5H_5)(CO)$_2$}$_2$(2,4-B_5H_7)] (3): (*a*) normal ^{11}B spectrum showing coupling to protons; (*b*) ^{11}B-{^{1}H} spectrum with proton coupling removed by simultaneous broad-band irradiation at the ^{1}H frequency. Resonance A is due to an impurity which develops on storage of the sample in solution in CD_2Cl_2



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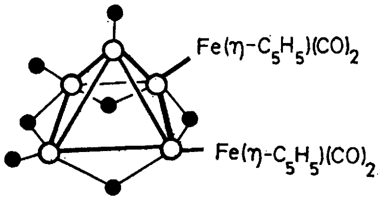


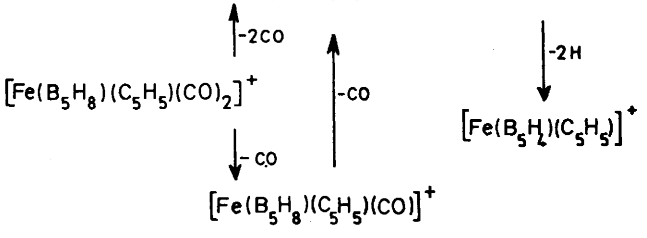
(4)

It is probable that deprotonation of [Fe(2-B_5H_8)-

(η-C_5H_5)(CO)$_2$] to give the anion [Fe(2-B_5H_7)(η-C_5H_5)-(CO)$_2$]$^-$ also occurs by abstraction of one of the bridging positions (Scheme 2a). The elimination of the dimer [Fe_2(η-C_5H_5)$_2$(CO)$_4$], either directly or *via* an intermediate such as (4), is most likely to result from attack by [Fe(η-C_5H_5)(CO)$_2$I] on the pentaboratometal anion at the sterically unfavoured 2,3 and 2,5 bridging positions. This may imply that deprotonation is most favoured at these positions, but this conclusion is speculative in the absence of other evidence. Examination of models based on reasonable estimates of bond distances and angles shows that there are no gross non-bonded interactions in a structure such as (4), but we could find no evidence for its existence in the product mixture.

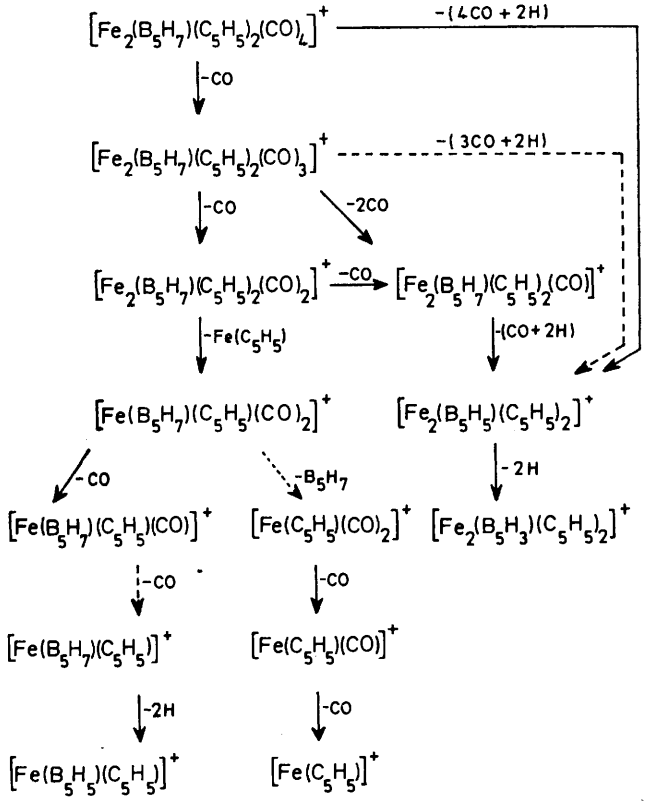
Mass Spectrometry.—In the 70-eV mass spectrum of [Fe(2-B_5H_8)(η-C_5H_5)(CO)$_2$] the identity of the major boron-containing fragments was confirmed by high-resolution mass measurements (Table 1) and the anisotopic spectrum calculated from these results is given in Table 2; those fragmentations which were confirmed by the observation of metastable peaks are given in Scheme 3.

It is of interest to note that the loss of two CO molecules from the molecular ion occurs before fragmentation of the pentaborane cluster, and that the Fe(C_5H_5) group then remains bound to the cluster during the fragmentation of the latter. Indeed, comparison of the fragmentation pattern of the [Fe(B_5H_8)(C_5H_5)]$^+$ ion (*i.e.* from *m/e* 184 to 130) with that of [B_5H_9]$^+$ itself [22,23] shows that the replacement of a hydrogen atom by the Fe(C_5H_5) residue apparently has little effect on the gross fragmentation behaviour of the borane cluster. In particular, the stepwise loss of successive pairs of hydrogen atoms from B_5 fragments is very similar for the two species. This may derive from the stability of the FeB_5 structure, but this conclusion is necessarily tentative since such fragmentations are often kinetically controlled.

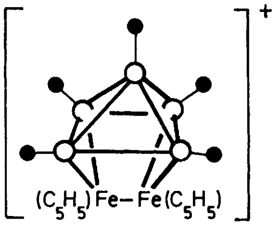


SCHEME 3

The anisotopic 70-eV mass spectrum of [{Fe(η-C_5H_5)-(CO)$_2$}$_2$(2,4-B_5H_7)] is given in Table 5. The identity of the major boron-containing fragments was confirmed by high-resolution mass measurement (Table 4) and those fragmentations which were confirmed by the presence of metastable peaks are given in Scheme 4, in which broken lines represent very weak metastable peaks or ambiguous assignments. The general features are similar to those for the monoiron compound and the absence of any di-iron non-boron-containing fragments favours the *trans* (2,4) formulation [structure (3)] since a *cis* geometry [structure (4)] may be expected to give preferential elimination of such species. A unique feature is the favoured formation of [Fe_2(B_5H_5)(C_5H_5)$_2$]$^+$, which constitutes the base peak in the anisotopic spectrum, and accounts for >15% of the total ion current. The formation of this from a variety of precursor ions is confirmed by metastable peaks, the most remarkable of these confirming the loss from the molecular ion of no fewer than four CO molecules and two hydrogen atoms. It is noteworthy in this context that the incidence of [Fe_2(B_5H_7)(C_5H_5)$_2$]$^+$ is very low indeed, and it is tempting to ascribe this to the favoured formation of a stable diferraheptaborane cluster such as (5).



SCHEME 4



(5)

The spectra of both [Fe(2-B_5H_8)(η-C_5H_5)(CO)$_2$] and

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[22] A. Quayle, *J. Appl. Chem.*, 1959, **9**, 395.

[23] J. J. Kaufman, W. S. Koski, L. J. Kulins, and S. S. Wright, *J. Amer. Chem. Soc.*, 1963, **85**, 1369.

$[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2(2,4\text{-}B_5H_7)]$ show that the borane units in each case fragment by loss of pairs of hydrogen atoms. In particular, comparison of the fragmentation of the $[Fe(B_5H_7)(C_5H_5)]^+$ ion from the di-iron compound with that of the $[Fe(B_5H_8)(C_5H_5)]^+$ ion from the mono-iron compound shows that this process, rather than any inherent stability of species $[Fe(B_5H_n)(C_5H_5)]^+$ for a particular value of n, governs the decompositions.

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