

structure. The rate is close to the diffusion-controlled value one might expect for reaction between a ground state and an excited triplet. If we consider this interaction as leading to an excimer, then the rate of excimer formation for some given concentration of triplets is nearly the same for thymine and uracil. However, the fraction of these excimers which lead to dimers is about one-half in uracil and one-fifth in thymine. This fact, combined with a somewhat lower ϕ_{isc} in

thymine, accounts for the greatly reduced yield of photodimers of thymine in aqueous solution.

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Iron(II)- and Manganese(I)-Carborane Complexes Formed through Metal-Carbon σ Bonds

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Abstract: 1,2-Dicarba-*closo*-dodecaborane(12) and 1,10-dicarba-*closo*-decaborane(10) and their C-monosubstituted derivatives react with *n*-butyllithium in ethereal solvents to form the corresponding 1-lithiocarboranes. Reaction of these 1-lithiocarboranes with manganese pentacarbonyl bromide and cyclopentadienyliron dicarbonyl iodide gives rise to a series of stable neutral derivatives containing a metal-carbon σ bond. Reaction of 1,10-dilithio-1,10-dicarba-*closo*-decaborane(10), formed from 1,10-dicarba-*closo*-decaborane(10) and 2 mol equiv of *n*-butyllithium in ethereal solvents, with 2 mol equiv of cyclopentadienyliron dicarbonyl iodide, gives rise to an analogous derivative containing two nonchelating metal-carbon σ bonds. The preparation, characterization, reactions, and proposed structures of these complexes are discussed.

Numerous π -bonded transition metal complexes with $B_9C_2H_{11}^{2-}$, $B_8C_2H_{10}^{4-}$, $B_7C_2H_9^{2-}$, and $B_6C_2H_8^{4-}$ ligands have been prepared in this laboratory.¹⁻¹⁰ In addition, a series of extremely stable anionic chelated biscarborane-transition metal complexes containing unusually stable carbon-metal σ bonds has been reported.^{11,12} Complexes containing platinum(II)-carborane metal-carbon single σ bonds have also been reported.¹³ Preliminary evidence¹⁴ indicated that an extensive series of stable neutral iron(II)- and manganese(I)-carborane complexes incorporating the 1,2- $B_{10}C_2H_{11}^-$, 1,10- $B_8C_2H_9^-$, and 1,10- $B_6C_2H_8^{2-}$ ligands through metal-carbon σ bonds could be prepared. We now wish to report a compilation of results obtained on these two series of carborane complexes containing stable iron(II)- and manganese(I)-carbon σ bonds.

σ -Bonded Iron(II)-Dicarba-*closo*-decaborane(10) Complexes. When a solution of $(\pi-C_5H_5)Fe(CO)_2I^{15}$ in ethyl ether was treated with a solution of 1-Li-10- CH_3 -1,10- $B_8C_2H_8^{16}$ in ethyl ether at reflux for 0.5 hr, a deep brown color formed. Isolation of the products by rotary evaporation of the reaction mixture, elution of the yellow product from a silica gel column with hexane, and vacuum sublimation of the yellow solute afforded yellow, diamagnetic crystals of 1- $[(\pi-C_5H_5)Fe(CO)_2]$ -10- CH_3 -1,10- $(\sigma-B_8C_2H_8)$, mp 68–69°, in 75% yield. The mass spectral parent ion peak (Table I) was observed at m/e 310, corresponding to $^{10}B_2^{11}B_6^{12}C_{10}^1H_{16}^{16}O_2^{56}Fe_1^+$. Elemental analysis (Table I) supported this formulation. The infrared spectrum of a Nujol mull (Table II) exhibited a strong B—H stretching absorption at 2560 cm^{-1} and two sharp strong C=O stretching absorptions at 2040 and 1970 cm^{-1} , as expected for a $(\pi-C_5H_5)Fe(CO)_2$ -derivative having a single symmetry plane.¹⁷ No carborane C—H stretching absorption around 3060 cm^{-1} was observed, indicating the product to be a C-substituted cyclopentadienyl iron dicarbonyl derivative. A band indicative of the $\pi-C_5H_5$ group was observed at 845 cm^{-1} . The 60-MHz 1H nmr spectrum (Table III) consisted of a very sharp singlet of intensity 5.0 at τ 4.94, which was assigned to the $\pi-C_5H_5$ protons,¹⁷ and a sharp singlet of intensity 3.0 at τ 7.23,

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Table I. Elemental Analyses, Molecular Weights, Melting Points, and Yields of the σ -Bonded Neutral Iron(II)- and Manganese(I)-Carborane Complexes

Compound	Color	Mp, °C	Yield, %	Analyses, %	Mol wt
1-[(π -C ₅ H ₅)Fe(CO) ₂]-1,10-(σ -B ₈ C ₂ H ₈)	Gold	97–98	11 ^a 25 ^b	Calcd Fe, 18.83; B, 29.21; C, 36.44; H, 4.76 Found Fe, 19.02; B, 29.07; C, 36.54; H, 4.65	296.7 296 ^c
1-[(π -C ₅ H ₅)Fe(CO) ₂]-10-CH ₃ -1,10-(σ -B ₈ C ₂ H ₈)	Yellow	68–69	75 ^d	Calcd Fe, 17.98; B, 27.85; C, 38.67; H, 5.19 Found Fe, 18.00; B, 27.50; C, 38.67; H, 5.30	310.7 310 ^c
1,10-[(π -C ₅ H ₅)Fe(CO) ₂] ₂ -1,10-(σ -B ₈ C ₂ H ₈)	Yellow	203–204	61 ^a	Calcd Fe, 23.65; B, 18.31; C, 40.68; H, 3.81 Found Fe, 24.67; B, 18.82; C, 40.53; H, 3.88	474.1 474 ^c
1-[(π -C ₅ H ₅)Fe(CO) ₂]-10-[(π -C ₅ H ₅)Fe(CO)]P(C ₆ H ₅) ₃]-1,10-(σ -B ₈ C ₂ H ₈)	Red	184–186 dec	28 ^b	Calcd ^e Fe, 15.80; B, 12.25; C, 56.07; H, 4.70 Found Fe, 16.02; B, 12.11; C, 56.17; H, 4.65	706.9 713 ^f
1-[(π -C ₅ H ₅)Fe(CO) ₂]-2-CH ₃ -1,2-(σ -B ₁₀ C ₂ H ₁₀)	Gold	144–145	47 ^d	Calcd Fe, 16.72; B, 32.33; C, 35.92; H, 5.39 Found Fe, 16.90; B, 32.60; C, 35.62; H, 5.53	336.2 336 ^c
1-[(π -C ₅ H ₅)Fe(CO) ₂]-2-C ₆ H ₅ -1,2-(σ -B ₁₀ C ₂ H ₁₀)	Yellow	135–136	83 ^d	Calcd Fe, 14.09; B, 27.28; C, 45.46; H, 5.09 Found Fe, 14.30; B, 27.41; C, 45.29; H, 5.03	396.37 396 ^c
1-[Mn(CO) ₅]-10-CH ₃ -1,10-(σ -B ₈ C ₂ H ₈)	Yellow	57–59	63 ^d	Calcd Mn, 16.72; B, 26.32; C, 29.24; H, 3.37 Found Mn, 16.20; B, 27.79; C, 30.20; H, 2.70	328.7 328 ^c
1-[Mn(CO) ₅]-2-CH ₃ -1,2-(σ -B ₁₀ C ₂ H ₁₀)	White	85–87	57 ^d	Calcd Mn, 15.60; B, 30.69; C, 27.28; H, 3.72 Found Mn, 16.20; B, 29.72; C, 27.34; H, 3.85	352.3 352 ^c

^a Prepared from 1,10-Li₂-1,10-B₈C₂H₈. ^b Prepared from 1,10-[(π -C₅H₅)Fe(CO)₂]₂-1,10-(σ -B₈C₂H₈). ^c Mass spectral parent ion maximum peak. ^d Prepared from the corresponding 1-lithiocarborane. ^e P, calcd: 4.38; P, found: 4.41. ^f Osmometric in benzene.

Table II. Infrared Spectra of Nujol Mulls of the σ -Bonded Neutral Iron(II)- and Manganese(I)-Carborane Complexes

Compound	Absorbance, cm ⁻¹
1-[(π -C ₅ H ₅)Fe(CO) ₂]-1,10-(σ -B ₈ C ₂ H ₈)	3050 (m), 3565 (vs), 2005 (vs), 1969 (vs), 1454 (m), 1418 (s), 1370 (m), 1351 (m), 1142 (s), 1058 (w), 1012 (s), 1004 (s), 985 (m), 942 (m), 846 (vs), 832 (sh), 745 (w), 679 (m)
1-[(π -C ₅ H ₅)Fe(CO) ₂]-10-CH ₃ -1,10-(σ -B ₈ C ₂ H ₈)	2560 (s), 2040 (s), 1970 (s), 1162 (w), 1040 (w), 976 (m), 920 (w), 902 (w), 845 (s), 835 (s), 769 (m), 724 (m), 690 (m)
1,10-[(π -C ₅ H ₅)Fe(CO) ₂] ₂ -1,10-(σ -B ₈ C ₂ H ₈)	2565 (s), 2040 (vs), 1990 (vs), 1454 (s), 1431 (s), 1424 (sh), 1370 (m), 1352 (w), 1120 (w), 1058 (m), 1020 (m), 1005 (m), 940 (w), 992 (m), 875 (w), 858 (m), 847 (s), 836 (m), 815 (w), 702 (w)
1-[(π -C ₅ H ₅)Fe(CO) ₂]-10-[(π -C ₅ H ₅)Fe(CO)]P(C ₆ H ₅) ₃]-1,10-(σ -B ₈ C ₂ H ₈)	2560 (s), 2022 (vs), 1972 (vs), 1925 (vs), 1587 (w), 1482 (sh), 1452 (s), 1439 (m), 1370 (m), 1182 (w), 1093 (s), 1002 (s), 939 (w), 880 (m), 851 (sh), 845 (m), 830 (m), 758 (sh), 749 (m), 702 (s), 692 (sh), 682 (w)
1-[(π -C ₅ H ₅)Fe(CO) ₂]-2-CH ₃ -1,2-(σ -B ₁₀ C ₂ H ₁₀)	2565 (s), 2040 (vs), 1970 (vs), 1454 (s), 1438 (m), 1370 (s), 1092 (m), 1045 (m), 1031 (w), 1023 (w), 1017 (w), 945 (w), 872 (w), 848 (s), 810 (w), 729 (m)
1-[(π -C ₅ H ₅)Fe(CO) ₂]-2-C ₆ H ₅ -1,2-(σ -B ₁₀ C ₂ H ₁₀)	2560 (s), 2035 (s), 1979 (s), 1587 (w), 1165 (w), 1054 (w), 1017 (w), 1002 (w), 845 (m), 752 (w), 740 (w), 702 (m)
1-[Mn(CO) ₅]-10-CH ₃ -1,10-(σ -B ₈ C ₂ H ₈)	2570 (s), 2130 (s), 2030 (s), 2000 (s), 976 (m), 907 (w), 852 (w), 820 (w), 764 (m), 724 (m), 790 (w)
1-[Mn(CO) ₅]-2-CH ₃ -1,2-(σ -B ₁₀ C ₂ H ₁₀)	2560 (s), 2130 (s), 2030 (vs), 2002 (vs), 1195 (m), 1091 (s), 1040 (m), 1025 (m), 988 (w), 925 (w), 804 (m), 739 (s), 702 (w), 677 (sh)

which was assigned to the 10-methyl protons of a 10-CH₃-1,10-B₈C₂H₈ group by comparison with the singlet found in the spectrum of 1,10-(CH₃)₂-1,10-B₈C₂H₈ (τ 7.22).¹⁸ The 32.1-MHz ¹¹B nmr spectrum of the complex (Table IV) consisted of a doublet at +11.1 (J = 159 cps) ppm relative to BF₃·O(C₂H₅)₂, corre-

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sponding to fortuitous overlap of the two equal-intensity doublets expected for a 1-substituted-10-CH₃-1,10-B₈C₂H₈ compound. The electronic spectrum in cyclohexane (Table V) consisted of three maxima in the visible and ultraviolet regions. These bands were not assigned, but probably correspond to the various metal \rightarrow ligand charge-transfer phenomena.

From these analytical, infrared, and nmr data, the complex was assigned the structure depicted in Figure 1, where the metal ion is bonded to the carborane polyhedron through a Fe–C σ bond, and R = CH₃.

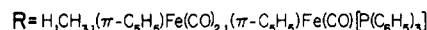
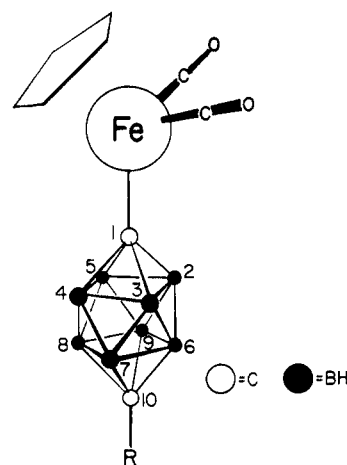


Figure 1. The proposed structure and numbering system for 1-[(π -C₅H₅)Fe(CO)₂]-1,10-(σ -B₈C₂H₈) and its 10-substituted derivatives.

A derivative incorporating two (π -C₅H₅)Fe(CO)₂ groups, 1,10-[(π -C₅H₅)Fe(CO)₂]₂-1,10-(σ -B₈C₂H₈), was prepared by reaction of 2 mol equiv of (π -C₅H₅)Fe(CO)₂I with 1 mol equiv of 1,10-Li₂-1,10-B₈C₂H₈¹⁶ in ethyl ether for 4 hr. Elution of the products from a silica gel column with hexane gave two yellow fractions. The second of these, upon isolation of the solute, gave golden diamagnetic needles of 1,10-[(π -C₅H₅)-

Table III. ^1H Nmr Spectra (60 MHz) of the σ -Bonded Neutral Iron(II)- and Manganese(I)-Carborane Complexes

Compound	Feature ^b	τ	Rel peak intensity	Assignment ^a
1-[(π -C ₅ H ₅)Fe(CO) ₂]-1,10-(σ -B ₈ C ₂ H ₈)	Sh singlet	4.76	5.0	a
	Br singlet	3.17	1.0	b
1-[(π -C ₅ H ₅)Fe(CO) ₂]-10-CH ₃ -1,10-(σ -B ₈ C ₂ H ₈)	Sh singlet	4.94	5.0	a
	Sh singlet	7.23	3.0	c
1,10-[(π -C ₅ H ₅)Fe(CO) ₂] ₂ -1,10-(σ -B ₈ C ₂ H ₈)	Sh singlet	5.02		a
1-[(π -C ₅ H ₅)Fe(CO) ₂]-10-{(π -C ₅ H ₅)Fe(CO)-[P(C ₆ H ₅) ₃]}-1,10-(σ -B ₈ C ₂ H ₈)	Sh singlet	5.02	5.0	a
	Doublet ($J_{\text{H-P}} = 1.4$ cps)	5.55	5.0	a
	Multiplet	2.2-2.6	15.1	d
1-[(π -C ₅ H ₅)Fe(CO) ₂]-2-CH ₃ -1,2-(σ -B ₁₀ C ₂ H ₁₀)	Sh singlet	5.07	5.0	a
	Sh singlet	8.02	3.0	e
1-[(π -C ₅ H ₅)Fe(CO) ₂]-2-C ₆ H ₅ -1,2-(σ -B ₁₀ C ₂ H ₁₀)	Sh singlet	5.35	5.0	a
	Multiplet	2.58	5.0	d
1-[Mn(CO) ₅]-10-CH ₃ -1,10-(σ -B ₈ C ₂ H ₈)	Sh singlet	7.23		c
1-[Mn(CO) ₅]-2-CH ₃ -1,2-(σ -B ₁₀ C ₂ H ₁₀)	Sh singlet	7.91		e

^a a, cyclopentadienyl protons; b, 10-C-H proton of 1,10-B₈C₂H₈; c, 10-methyl protons of 10-CH₃-1,10-B₈C₂H₈; d, phenyl protons; e, 2-methyl protons of 2-CH₃-1,2-B₁₀C₂H₁₀. ^b Sh = sharp; br = broad.

Table IV. ^{11}B Nmr Spectra (32.1 MHz) of the σ -Bonded Neutral Iron(II)- and Manganese(I)-Carborane Complexes

Compound	Feature	δ , ppm ^a (J , cps) ^a	Rel peak intensity
1-[(π -C ₅ H ₅)Fe(CO) ₂]-1,10-(σ -B ₈ C ₂ H ₈)	Doublet	+10.8 (164)	4.0
	Doublet	+12.8 (158)	4.0
1-[(π -C ₅ H ₅)Fe(CO) ₂]-10-CH ₃ -1,10-(σ -B ₈ C ₂ H ₈)	Doublet	+11.1 (159)	8.0
1,10-[(π -C ₅ H ₅)Fe(CO) ₂] ₂ -1,10-(σ -B ₈ C ₂ H ₈)	Doublet	+11.6 (160)	8.0
1-[(π -C ₅ H ₅)Fe(CO) ₂]-10-{(π -C ₅ H ₅)Fe(CO)[P(C ₆ H ₅) ₃]}-1,10-(σ -B ₈ C ₂ H ₈)	Overlapping doublets	+10.5 (153)	8.0
1-[(π -C ₅ H ₅)Fe(CO) ₂]-2-CH ₃ -1,2-(σ -B ₁₀ C ₂ H ₁₀)	Overlapping doublets	+3.1 (165)	2.0
		+10.1 (157)	3.0
		+14.9 (154)	5.0
1-[(π -C ₅ H ₅)Fe(CO) ₂]-2-C ₆ H ₅ -1,2-(σ -B ₁₀ C ₂ H ₁₀)	Overlapping doublets	+3.8 (160)	5.0
		+10.6 (157)	5.0
		+15.2 (155)	
1-[Mn(CO) ₅]-10-CH ₃ -1,10-(σ -B ₈ C ₂ H ₈)	Doublet	+10.4 (158)	8.0
1-[Mn(CO) ₅]-2-CH ₃ -1,2-(σ -B ₁₀ C ₂ H ₁₀)	Overlapping doublets	+2.1 (143)	1.0
		+6.6 (141)	1.0
		+11.3 (169)	4.0
		+12.4 (160)	4.0

^a Relative to BF₃·O(C₂H₅)₂.

Fe(CO)₂]₂-1,10-(σ -B₈C₂H₈), mp 204–205°, in 61 % yield. The mass spectral parent ion peak (Table I) was observed at m/e 474, corresponding to $^{10}\text{B}_2^{11}\text{B}_6^{12}\text{C}_{16}^{1}\text{H}_{18}^{16}\text{O}_4^{56}\text{Fe}_2^+$. Elemental analysis (Table I) supported this formula. The infrared spectrum of a Nujol mull (Table II) exhibited a sharp strong B—H stretching absorption at 2565 cm⁻¹, and two sharp strong C=O stretching absorptions at 2040 and 1990 cm⁻¹, as expected for a complex with two equivalent (π -C₅H₅)Fe(CO)₂ groups. No carborane C—H stretching absorptions were observed, indicating the polyhedron to be substituted in both the 1 and 10 positions. The 60-MHz ^1H nmr spectrum (Table III) consisted of a single sharp resonance at τ 5.02, corresponding to the ten equivalent π -C₅H₅ protons. The 32.1-MHz ^{11}B nmr spectrum (Table IV) exhibited a single doublet at +11.6 (J = 160) ppm relative to BF₃·O(C₂H₅)₂, indicating the eight boron atoms to be equivalent. The electronic spectrum in cyclohexane (Table V) consisted of three maxima in the visible and ultraviolet regions.

These maxima were not assigned, but probably result from various metal \rightarrow ligand charge-transfer processes. From the analytical, infrared, and nmr data, the complex was assigned the structure shown in Figure 1, where the carborane polyhedron is σ bonded to two (π -C₅H₅)Fe(CO)₂ groups [R = (π -C₅H₅)Fe(CO)₂] through two Fe—C σ bonds.

Reaction of 1,10-[(π -C₅H₅)Fe(CO)₂]₂-1,10-(σ -B₈C₂H₈) with an excess of (C₆H₅)₃P in refluxing tetrahydrofuran gave a mixture of two products. Elution of the reaction mixture from a silica gel column with hexane gave a red and a fast-moving yellow fraction. Crystallization of the red fraction from dichloromethane–hexane afforded red diamagnetic needles of 1-[(π -C₅H₅)Fe(CO)₂]-10-{(π -C₅H₅)Fe(CO)[P(C₆H₅)₃]}-1,10-(σ -B₈C₂H₈), mp 184–186° dec, in 28 % yield. Analytical and molecular weight data are presented in Table I. The infrared spectrum of a Nujol mull (Table II) of the complex exhibited a strong B—H stretching absorption at 2560 cm⁻¹, three sharp strong C=O stretching absorptions at

Table V. Electronic Spectra in Cyclohexane of the σ -Bonded Neutral Iron(II)- and Manganese(I)-Carborane Complexes

Compound	Maxima, $m\mu$ (ϵ)
1-[(π -C ₅ H ₅)Fe(CO) ₂]-1,10-(σ -B ₈ C ₂ H ₉)	239 (12, 600) 288 (sh, 2980) 364 (930)
1-[(π -C ₅ H ₅)Fe(CO) ₂]-10-CH ₃ -1,10-(σ -B ₈ C ₂ H ₉)	245 (sh, 12, 200) 288 (sh, 2040) 363 (690)
1,10-[(π -C ₅ H ₅)Fe(CO) ₂]-1,10-(σ -B ₈ C ₂ H ₉)	252 (19, 500) 290 (sh, 12, 500) 360 (2200)
1-[(π -C ₅ H ₅)Fe(CO) ₂]-10-[(π -C ₅ H ₅)Fe(CO)[P(C ₆ H ₅) ₃]]-1,10-(σ -B ₈ C ₂ H ₉) ^a	256 (20, 200) 415 (sh, 2200) 503 (sh, 550)
1-[(π -C ₅ H ₅)Fe(CO) ₂]-2-CH ₃ -1,2-(σ -B ₁₀ C ₂ H ₁₀)	259 (sh, 9400) 290 (sh, 3200) 367 (740)
1-[(π -C ₅ H ₅)Fe(CO) ₂]-2-C ₆ H ₅ -1,2-(σ -B ₁₀ C ₂ H ₁₀)	253 (10, 700) 297 (sh, 2800) 369 (795)
1-[Mn(CO) ₅]-10-CH ₃ -1,10-(σ -B ₈ C ₂ H ₉)	342 (9300)
1-[Mn(CO) ₅]-2-CH ₃ -1,2-(σ -B ₁₀ C ₂ H ₁₀)	310 (2650)

^a Acetonitrile solution.

2022, 1972, and 1929 cm^{-1} , corresponding to the three C=O groups of the complex. Bands at 1587 and 1482 cm^{-1} indicative of the P(C₆H₅)₃ ligand were observed. The 60-MHz ¹H nmr spectrum (Table III) consisted of a very sharp singlet of intensity 5.0 at τ 5.02, a doublet of intensity 5.0 at τ 5.55 (J = 1.4 cps), and a multiplet of total intensity 15.1 centered at τ 2.4. These resonances were assigned to the 1-(π -C₅H₅)Fe(CO)₂ ring protons, the 10-[(π -C₅H₅)Fe(CO)P(C₆H₅)₃] ring protons, and the P(C₆H₅)₃ protons, respectively. The doublet at τ 5.55 was presumed due to coupling of the ring protons with the ligand ³¹P atom. Coupling of other ligands through transition metal ions by ³¹P has been observed in other systems.^{19,20} The 32.1-MHz ¹¹B nmr spectrum (Table IV) consisted of a set of two closely spaced overlapping doublets centered at +10.5 (J = 153) ppm, relative to BF₃·O(C₂H₅)₂. The electronic spectrum in acetonitrile (Table V) was substantially different from that of the other iron(II) derivatives. Its three maxima were not assigned. The proposed structure of this complex is basically the same as in Figure 1, where R = (π -C₅H₅)Fe(CO)[P(C₆H₅)₃].

The first yellow fraction from the preparation of 1,10-[(π -C₅H₅)Fe(CO)₂]-1,10-(σ -B₈C₂H₉) and the fast-moving yellow fraction from the preparation of 1-[(π -C₅H₅)Fe(CO)₂]-10-[(π -C₅H₅)Fe(CO)[P(C₆H₅)₃]]-1,10-(σ -B₈C₂H₉) were both found to be 1-[(π -C₅H₅)Fe(CO)₂]-1,10-B₈C₂H₉. Yellow crystals, mp 97–98°, of the diamagnetic complex were formed as a side-product in 10 and 25% yield, depending upon the method used. The mass spectral parent ion peak (Table I) was observed at m/e 296, corresponding to ¹⁰B₂¹¹B₆¹²C₉¹H₁₄-¹⁶O₂⁵⁶Fe⁺. Elemental analysis (Table I) supported this formula. The infrared spectrum of a Nujol mull (Table II) contained a sharp B—H stretching absorption at 2565 cm^{-1} , two strong sharp C=O stretching absorptions at 2005 and 1969 cm^{-1} , a carborane C—H stretch-

ing absorption at 3050 cm^{-1} , and bands indicative of a π -C₅H₅ group at 1431 and 847 cm^{-1} . The 60-MHz ¹H nmr spectrum (Table III) consisted of a very sharp singlet of intensity 5.0 at τ 4.76, which was assigned to the π -C₅H₅ protons, and a broad singlet of intensity 1.0 at τ 3.17, which was assigned to the 10-C—H proton of a 1,10-B₈C₂H₉ group by comparison with 1,10-B₈C₂H₁₀ (τ 3.1).¹⁶ The 32.1-MHz ¹¹B nmr spectrum (Table IV) consisted of two overlapping doublets of equal intensity 4.0 at +10.8 (J = 164) and +12.8(158) ppm, relative to BF₃·O(C₂H₅)₂, and corresponded nicely to the two sets of four equivalent boron atoms in the complex. The electronic spectrum of a cyclohexane solution of this complex exhibited the three familiar maxima due to various charge transfer phenomena. The proposed structure for this complex is depicted in Figure 1, where R = H.

σ -Bonded Iron(II)-Dicarba-closo-dodecaborane(12) Complexes. When a solution of (π -C₅H₅)Fe(CO)₂I in 1,2-dimethoxyethane was treated with a solution of 1-Li-2-CH₃-1,2-B₁₀C₂H₁₀²¹ in 1,2-dimethoxyethane for 1 hr at reflux, a brown mixture formed. The products were separated by elution from a silica gel column with 1:3 benzene-hexane. Collection and concentration of a yellow fraction afforded golden diamagnetic needles of 1-[(π -C₅H₅)Fe(CO)₂]-2-CH₃-1,2-(σ -B₁₀C₂H₁₀), which gave a mass spectral parent ion peak at m/e 336, corresponding to ¹⁰B₂¹¹B₈¹²C₁₀¹H₁₈¹⁶O₂⁵⁶Fe⁺. Elemental analysis (Table I) supported this formula. The infrared spectrum of a Nujol mull (Table II) exhibited a strong B—H absorption at 2565 cm^{-1} , two strong C=O absorptions at 2040 and 1970 cm^{-1} , and bands characteristic of the π -C₅H₅ ligand at 1438 and 848 cm^{-1} . No carborane C—H stretching absorption was observed, indicating the product to be a C(1)-substituted complex. The 60-MHz ¹H nmr spectrum (Table III) exhibited a very sharp singlet of intensity 5.0 at τ 5.07 due to the π -C₅H₅ protons and a sharp singlet of intensity 3.0 at τ 8.02 which was assigned to the 2-methyl protons of the carborane ligand, by comparison with singlets found in the spectra of 1-CH₃-1,2-B₁₀C₂H₁₁ (τ 8.02) and 1,2-(CH₃)₂-1,2-B₁₀C₂H₁₀ (τ 7.98).²² The 32.1-MHz ¹¹B nmr (Table IV) was not interpreted. The electronic spectrum of a cyclohexane solution (Table V) contained three maxima due to the various metal \rightarrow ligand charge-transfer processes. From these analytical, infrared, and nmr data, we proposed the structure in Figure 2 for 1-[(π -C₅H₅)Fe(CO)₂]-2-CH₃-1,2-(σ -B₁₀C₂H₁₀), where the metal ion is bonded to the icosahedron through an iron-carbon(1) σ bond and R = CH₃.

The corresponding 2-phenyl derivative was made in 83% yield in analogous fashion, by reaction of (π -C₅H₅)Fe(CO)₂I with 1-Li-2-C₆H₅-1,2-B₁₀C₂H₁₀ in refluxing 1,2-dimethoxyethane. Its properties are presented in Tables I–V. Its proposed structure is depicted in Figure 2, where R = C₆H₅.

σ -Bonded Manganese(I)-Carborane Complexes. When a solution of 1-Li-10-CH₃-1,10-B₈C₂H₉¹⁶ in ethyl ether was treated with a suspension of Mn(CO)₅Br in ethyl ether for 1 hr, a dark solution formed. Elution

(19) S. O. Grim and R. A. Ference, *Inorg. Nucl. Chem. Lett.*, **2**, 205 (1966).(20) T. H. Brown and P. J. Green, *J. Amer. Chem. Soc.*, **91**, 3378 (1969).(21) T. L. Heying, J. W. Ager, Jr., S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *Inorg. Chem.*, **2**, 1097 (1963).(22) M. F. Hawthorne, T. D. Andrews, P. M. Garrett, M. Reintjes, F. N. Tebbe, L. F. Warren, Jr., P. A. Wegner, and D. C. Young, *Inorg. Syn.*, **10**, 91 (1967).

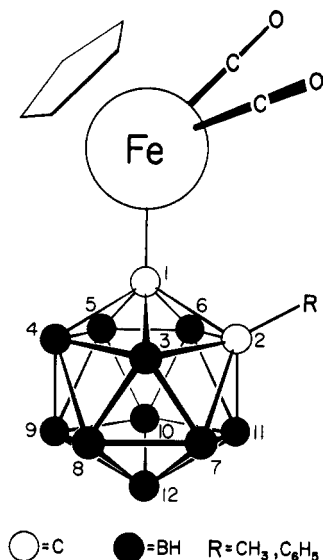


Figure 2. The proposed structure and numbering system for 1-[(π -C₅H₅)Fe(CO)₂]-2-CH₃-1,2-(σ -B₁₀C₂H₁₀) and its 2-phenyl derivative.

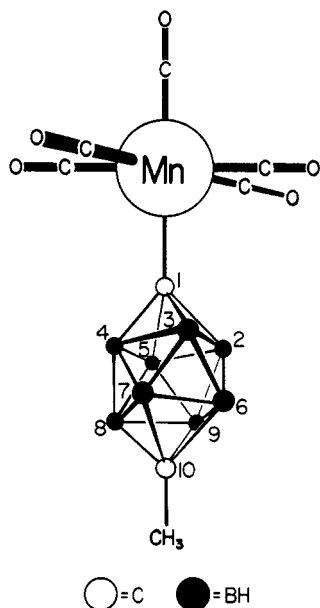


Figure 3. The proposed structure and numbering system for 1-[Mn(CO)₅]-10-CH₃-1,10-(σ -B₈C₂H₈).

of the products from a polyamide column with hexane afforded bright yellow diamagnetic 1-[Mn(CO)₅]-10-CH₃-1,10-(σ -B₈C₂H₈), mp 57–59°, in 64% yield. The mass spectral parent ion peak (Table I) was observed at m/e 328, corresponding to $^{10}\text{B}_2^{11}\text{B}_6^{12}\text{C}_8^{1}\text{H}_{11}^{16}\text{O}_5^{55}\text{Mn}_1^+$. Elemental analysis (Table I) supported this formula. The infrared spectrum of a Nujol mull (Table II) exhibited a strong B—H stretching absorption at 2570 cm^{-1} and three sharp strong C=O stretching absorptions at 2130, 2030, and 2000 cm^{-1} , indicative of a Mn(CO)₅ derivative possessing C_{4v} symmetry.²³ No carborane C—H stretching absorption around 3060 cm^{-1} was observed, indicating the product to be a C(1)-substituted derivative. The 60-MHz ^1H nmr spectrum (Table III) consisted of a single sharp resonance at τ 7.23 which was assigned, as before, to the methyl protons of the 10-CH₃-1,10-B₈C₂H₈ ligand. The 32.1-MHz ^{11}B nmr spectrum (Table IV) exhibited only one doublet

(23) W. F. Edgell, J. W. Fisher, G. Asato, and W. M. Risen, Jr., *Inorg. Chem.*, **8**, 1103 (1969).

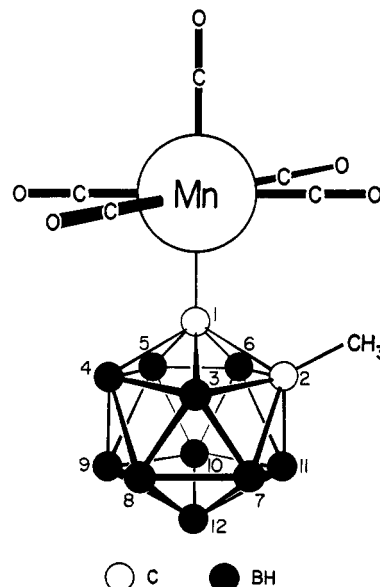


Figure 4. The proposed structure and numbering system for 1-[Mn(CO)₅]-2-CH₃-1,2-(σ -B₁₀C₂H₁₀).

at +10.4 ($J = 158$) ppm, relative to $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$, corresponding to fortuitous overlap of the two equal-intensity doublets expected for a 1-substituted-10-CH₃-B₈C₂H₈ derivative. The electronic spectrum in cyclohexane (Table V) consisted of a single maximum at 342 $m\mu$ (ϵ 9300) which was not assigned. From these analytical, infrared, and nmr data, we proposed the structure in Figure 3 for this derivative, where the metal ion is joined to the ligand polyhedron through a Mn—C(1) σ bond.

When a solution of 1-Li-2-CH₃-1,2-B₁₀C₂H₁₀ in ethyl ether was treated with a suspension of Mn(CO)₅Br in ethyl ether for 1 hr at room temperature, a dark solution formed. Elution of the products from a polyamide column with hexane, and concentration of the yellow eluent, afforded white diamagnetic needles of 1-[Mn(CO)₅]-2-CH₃-1,2-B₁₀C₂H₁₀, mp 85–87°, in 57% yield. Concentration of the mother liquor gave a mixture of the white product and yellow Mn₂(CO)₁₀. The mass spectral parent ion peak (Table I) was observed at m/e 352, corresponding to $^{10}\text{B}_2^{11}\text{B}_8^{12}\text{C}_8^{1}\text{H}_{13}^{16}\text{O}_6^{55}\text{Mn}_1^+$. Elemental analysis (Table I) supported this formula. The infrared spectrum of a Nujol mull (Table II) exhibited a strong B—H stretching absorption at 2560 cm^{-1} , and three strong sharp C=O stretching absorptions at 2130, 2030, and 2002 cm^{-1} . No sharp carborane C—H stretching absorption around 3060 cm^{-1} was observed, indicating that the product was a C(1)-substituted derivative. The 60-MHz ^1H nmr spectrum (Table III) of the complex consisted of a single sharp resonance at τ 7.91, which was assigned to the methyl protons of a 2-CH₃-1,2-B₁₀C₂H₁₀ group by comparison with other 2-methylated-1,2-carborane derivatives.²² The 32.1-MHz spectrum (Table IV) consisted of a set of overlapping doublets of relative intensities 1:1:4:4. This compares favorably with the 1:1:2:2:2:2 pattern expected for a 1,2-B₁₀C₂H₁₀RR' derivative possessing a single symmetry plane. The electronic spectrum of the complex in cyclohexane solution consisted of a single maximum at 310 $m\mu$ (ϵ 2650) which was not assigned. From these analytical, infrared, and nmr data we proposed the structure in Figure 4 for this complex, where

the metal ion is joined to the icosahedron through a Mn-C(1) σ bond.

This series of σ -bonded iron(II) and manganese(I) derivatives, together with the chelated biscarborane-cobalt, -nickel, -copper, and -zinc derivatives, extends to six the number of first-row transition metals which may be σ bonded to a polyhedral carborane ligand. Thus the number and complexity of the σ -bonded derivatives now rivals, and may surpass in the future, the number and complexity of the corresponding π -bonded derivatives.

Experimental Section

Methods and Materials. The majority of solvents were of reagent grade and were used without further purification. Ethyl ether and THF were further purified by distillation from lithium aluminum hydride, while 1,2-dimethoxyethane was further purified by distillation from sodium-benzophenone. $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$, 1-Li-2-CH₃-1,2-B₁₀C₂H₁₀, 1-Li-2-C₆H₅-1,2-B₁₀C₂H₁₀, 1-Li-10-CH₃-1,10-B₁₀C₂H₈, 1,10-Li₂-1,10-B₁₀C₂H₈, and Mn(CO)₅Br were prepared by literature methods.^{15,16,21} All reactions involving lithiocarboranes were carried out under nitrogen atmospheres. Silica gel was obtained from J. T. Baker Co. and was dried before use. Alumina was Matheson Coleman and Bell reagent grade. Polyamide was obtained from Machery, Nagel and Co. Infrared spectra were obtained as Nujol mulls with a Perkin-Elmer Model 137 sodium chloride spectrometer. Proton nmr spectra were obtained using a Varian A-60 spectrometer, while 32.1-MHz ¹¹B nmr were obtained using a Varian HA-100 spectrometer. Electronic spectra were obtained using a Beckman DB spectrometer. Melting points were determined using a Thomas-Hoover capillary melting point apparatus. Osmometric molecular weights were obtained on a Mechrolab Model 301 osmometer. Mass spectra were obtained on a RMU-6D Hitachi Perkin-Elmer low-resolution mass spectrometer. Elemental analyses were made by Elek Microanalytical Laboratories of Torrance, Calif., and Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

1-[($\pi\text{-C}_5\text{H}_5$)Fe(CO)₂]-10-CH₃-1,10-($\sigma\text{-B}_5\text{C}_2\text{H}_5$). A solution of 3.10 g (10.2 mmol) of $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ in 40 ml of anhydrous ethyl ether was added slowly under a nitrogen atmosphere to a stirred solution of 10.55 mmol of 1-Li-10-CH₃-1,10-B₁₀C₂H₈ in 100 ml of anhydrous ethyl ether. After stirring at reflux for 0.5 hr, the reaction mixture was cooled and rotary evaporated onto 5 g of dried silica gel. This mixture was placed atop a 1 in. \times 16 in. column of dried silica gel in hexane and a yellow band was eluted with hexane. The eluent was rotary evaporated at room temperature and the product was sublimed at 80° under high vacuum to give 1.56 g (5 mmol) of the desired product, 1-[($\pi\text{-C}_5\text{H}_5$)Fe(CO)₂]-10-CH₃-1,10-($\sigma\text{-B}_5\text{C}_2\text{H}_5$). Further elution of the column with dichloromethane afforded 0.95 g (3.12 mmol) of product. The product was further purified by several sublimations at 80° under high vacuum and elution from an alumina column with benzene. The yield of pure product was 2.5 g (75%). The yellow crystals melted at 68–69°. Analytical data and the infrared, ¹H nmr, ¹¹B nmr, and electronic spectra are presented in Tables I–V.

1,10-[($\pi\text{-C}_5\text{H}_5$)Fe(CO)₂]₂-1,10-($\sigma\text{-B}_5\text{C}_2\text{H}_5$). A solution of 2.64 g (8.66 mmol) of $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ in 50 ml of anhydrous ethyl ether was added slowly under nitrogen to a stirred suspension of 4.33 mmol of 1,10-Li₂-1,10-B₁₀C₂H₈ in 100 ml of anhydrous ethyl ether. After stirring for 4 hr at room temperature, the reaction mixture was rotary evaporated to a dark oil. The oil thus obtained was dissolved in 100 ml of dry benzene, the resulting mixture was rotary evaporated onto 5 g of dried silica gel, and this mixture was placed atop a 1 in. \times 16 in. column of dried silica gel in hexane. Elution with hexane separated two yellow bands. The first was eluted with hexane and saved. The second band was then eluted with 20% benzene-hexane, and evaporation of the eluent gave 1.25 g (61%) of gold crystals of 1,10-[($\pi\text{-C}_5\text{H}_5$)Fe(CO)₂]₂-1,10-($\sigma\text{-B}_5\text{C}_2\text{H}_5$), mp 203–204°. The complex was further purified by recrystallization from benzene-heptane. Analytical data and the infrared ¹H nmr, ¹¹B nmr, and electronic spectra are presented in Tables I–V.

1-[($\pi\text{-C}_5\text{H}_5$)Fe(CO)₂]-1,10-($\sigma\text{-B}_5\text{C}_2\text{H}_5$). The first yellow eluent from above was rotary evaporated at room temperature to give 0.12 g (10%) of gold crystals of 1-[($\pi\text{-C}_5\text{H}_5$)Fe(CO)₂]-1,10-B₁₀C₂H₈, mp 97–98°. The complex was further purified by sublimation at room temperature under high vacuum. Analytical data and the

infrared, ¹H nmr, ¹¹B nmr, and electronic spectra are presented in Tables I–V.

1-[($\pi\text{-C}_5\text{H}_5$)Fe(CO)₂]-10-[($\pi\text{-C}_5\text{H}_5$)Fe(CO)[P(C₆H₅)₃]-1,10-($\sigma\text{-B}_5\text{C}_2\text{H}_5$). A solution of 0.53 g (2 mmol) of P(C₆H₅)₃ and 0.475 g (1 mmol) of 1,10-[($\pi\text{-C}_5\text{H}_5$)Fe(CO)₂]-1,10-($\sigma\text{-B}_5\text{C}_2\text{H}_5$) in 10 ml of THF was refluxed for 48 hr under a nitrogen atmosphere. The reaction mixture was cooled and rotary evaporated onto 2 g of alumina. The resulting mixture was placed atop a 1 in. \times 18 in. column of alumina in hexane and a yellow band was eluted with hexane. The yellow eluent was rotary evaporated to dryness to give 0.075 g (25%) of 1-[($\pi\text{-C}_5\text{H}_5$)Fe(CO)₂]-1,10-($\sigma\text{-B}_5\text{C}_2\text{H}_5$), identified by its infrared spectrum and melting point. Elution with dichloromethane developed a red band. The red eluent was combined with 100 ml of dry hexane and rotary evaporated at room temperature to approximately 50 ml, at which time long red needles of 1-[($\pi\text{-C}_5\text{H}_5$)Fe(CO)₂]-10-[($\pi\text{-C}_5\text{H}_5$)Fe(CO)[P(C₆H₅)₃]-1,10-($\sigma\text{-B}_5\text{C}_2\text{H}_5$), mp 184–186° dec, separated. The yield of red product was 0.20 g (28%). It was purified by recrystallization from dichloromethane-hexane. Analytical data and the infrared, ¹H nmr, ¹¹B nmr, and electronic spectra are presented in Tables I–V.

1-[($\pi\text{-C}_5\text{H}_5$)Fe(CO)₂]-2-CH₃-1,2-($\sigma\text{-B}_{10}\text{C}_2\text{H}_{10}$). A solution of 1.94 g (6.32 mmol) of $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ in 50 ml of anhydrous 1,2-dimethoxyethane was added under a nitrogen atmosphere to a stirred, refluxing solution of 6.32 mmol of 1-Li-2-CH₃-1,2-B₁₀C₂H₁₀ in 150 ml of anhydrous 1,2-dimethoxyethane. After stirring at reflux for 1 hr, the reaction mixture was cooled and rotary evaporated to a dark oil. This oil was mixed with 50 ml of benzene and the resultant product was rotary evaporated onto 8 g of silica gel. Chromatography from a 1 in. \times 20 in. silica gel column in hexane with hexane gave an orange fraction which was discarded and a yellow fraction. Elution of this yellow fraction with 25:75 benzene-hexane gave a yellow solution which was rotary evaporated at room temperature to give 0.87 g of gold crystals of 1-[($\pi\text{-C}_5\text{H}_5$)Fe(CO)₂]-2-CH₃-1,2-($\sigma\text{-B}_{10}\text{C}_2\text{H}_{10}$), mp 144–145°. Collection of a trailing brown fraction followed by rechromatography from an identical column gave 0.24 g of additional product. The total yield of gold crystals was 1.11 g (47.5%). The compound was further purified by recrystallization from benzene-heptane and sublimation at 130° under high vacuum. Analytical data and the infrared, ¹H nmr, ¹¹B nmr, and electronic spectra are presented in Tables I–V.

1-[($\pi\text{-C}_5\text{H}_5$)Fe(CO)₂]-2-C₆H₅-1,2-($\sigma\text{-B}_{10}\text{C}_2\text{H}_{10}$). A solution of 1.88 g (6.2 mmol) of $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ in 50 ml of anhydrous 1,2-dimethoxyethane was added under a nitrogen atmosphere to a stirred, refluxing solution of 6.2 mmol of 1-Li-2-C₆H₅-1,2-B₁₀C₂H₁₀ in 150 ml of anhydrous 1,2-dimethoxyethane. After refluxing for 1 hr, the reaction mixture was cooled and rotary evaporated to a dark oil. The resulting oil was dissolved in 20 ml of benzene and this mixture was poured onto a 1 in. \times 22 in. column of silica gel in hexane. Elution with 50% benzene-hexane gave merging yellow and brown fractions. The yellow fraction was collected and rotary evaporated to give 2.0 g (5.1 mmol, 83%) of crude 1-[($\pi\text{-C}_5\text{H}_5$)Fe(CO)₂]-2-C₆H₅-1,2-($\sigma\text{-B}_{10}\text{C}_2\text{H}_{10}$). Recrystallization of the complex from benzene-heptane gave gold crystals, mp 135–136°. Analytical data and the infrared, ¹H nmr, ¹¹B nmr, and electronic spectra are presented in Tables I–V.

1-[Mn(CO)₅]-10-CH₃-1,10-($\sigma\text{-B}_5\text{C}_2\text{H}_5$). Under nitrogen, 7.55 mmol of a solution of 1-Li-10-CH₃-1,10-B₁₀C₂H₈ in 80 ml of anhydrous ethyl ether was slowly added to a stirred suspension of 0.575 g (7.55 mmol) of Mn(CO)₅Br in 150 ml of anhydrous ethyl ether. After stirring for 1 hr at room temperature, the reaction mixture was rotary evaporated to a brown oil. The oil was mixed with 50 ml of dry hexane and the resulting mixture was rotary evaporated onto 2 g of polyamide. The resulting mixture was placed atop a 1 in. \times 12 in. column of polyamide in hexane and was chromatographed with 1:9 ethyl ether-hexane. The yellow band so eluted was rotary evaporated to near dryness and the residue was sublimed at room temperature under high vacuum to give 1.58 g (4.8 mmol, 64%) of bright yellow 1-[Mn(CO)₅]-10-CH₃-1,10-($\sigma\text{-B}_5\text{C}_2\text{H}_5$), mp 57–59°. The product was further purified by chromatography from polyamide with hexane and sublimation of the yellow product. Analytical data and the infrared, ¹H nmr, ¹¹B nmr, and electronic spectra are presented in Tables I–V.

1-[Mn(CO)₅]-2-CH₃-1,2-($\sigma\text{-B}_{10}\text{C}_2\text{H}_{10}$). A solution of 6.45 mmol of 1-Li-2-CH₃-1,2-B₁₀C₂H₁₀ in 40 ml of anhydrous ethyl ether was slowly added in a nitrogen atmosphere to a rapidly stirred suspension of 1.8 g (6.45 mmol) of Mn(CO)₅Br in 150 ml of anhydrous ethyl ether. After stirring for 1 hr at room temperature, the reaction mixture was evaporated to a dark oil. The oil was dissolved in 50 ml of dry benzene, the resulting solution was rotary evaporated onto 2 g of polyamide, this mixture was placed on a 1 in. \times 6 in.

polyamide column in hexane, and a yellow band was eluted from the column with hexane. An additional 100 ml of eluent was collected. Rotary evaporation of the eluent to 50 ml gave white crystalline needles of 1-[Mn(CO)₅]-2-CH₃-1,2-(σ -B₁₀C₂H₁₀), mp 85–87°. A total of 1.30 g (3.68 mmol, 57%) was collected. Rotary evaporation to dryness gave 0.30 g of a mixture of the product and Mn₂(CO)₁₀. This was discarded. The white crystals were sublimed and recrystallized from hexane. Analytical data and the infrared,

¹H nmr, ¹¹B nmr, and electronic spectra are presented in Tables I–V.

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Acyl, Alkyl, and Aryl Complexes of Iridium from Acid Chlorides

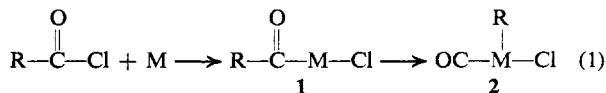
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Abstract: Acyl chlorides react with *trans*-chlorobis(triphenylphosphine)dinitrogeniridium(I) to form alkyl and aryl iridium complexes, [P(C₆H₅)₃]₂Cl₂(CO)IrR, where R is CH₃, C₂H₅, C₆H₅CH₂, C₆H₅, C₆F₅, etc. These reactions proceed *via* molecular rearrangement of intermediate acyl-iridium complexes. Various aspects of the acyl-alkyl (aryl) rearrangement, including stereochemical and solvent effects, have been investigated. New acyl complexes, L₂Cl₂(CO)IrC(O)R, where L is triphenylphosphine, methyldiphenylphosphine, tri-*p*-tolylphosphine, or triphenylarsine, are described and their proclivity to decarbonylation has been investigated. Carbonylation of [P(C₆H₅)₃]₂-Cl₂(CO)IrCH₃ is rapid in dichloromethane-methanol solution, but the reaction is negligible in benzene solution.

Information on the role of metal atoms in the facilitation of interaction of attached reactant groups is relevant to the elucidation of mechanisms of reactions which are homogeneously catalyzed by complexes of transition metals. Proposals for the mechanism of decarbonylation of acid chlorides catalyzed by rhodium complexes, for example, have been advanced following the isolation of intermediate acyl and alkyl complexes.^{1,2} The interaction of alkyl or aryl groups with carbon monoxide or the rearrangement of acyl groups at a metal site has been extensively studied in the context of CO insertion into metal-alkyl bonds or migration of alkyl to CO attached to a metal atom.³

Oxidative addition reactions of carboxylic acid chlorides with complexes of metals with d⁸ or d¹⁰ electronic configuration lead to formation of acyl-metal complexes **1** (M represents a metal atom with its appro-



priate ligands).^{1,2,4–19} σ -Alkyl or aryl carbonyl-metal

complexes **2** may be obtained by molecular rearrangement of the acyl complex **1** presumably by migration of R to the metal atom. Five-coordinated acyl complexes, [(C₆H₅)₃P]₂Cl₂RhC(O)R, where R is cyclohexyl or CH₃-(CH₂)_x (x = 1, 4, 5, 14) are obtained in the reaction of acyl halides RC(O)Cl with chlorotris(triphenylphosphine)rhodium(I).^{1,16} Acetyl and benzoyl chloride, on the other hand, react^{15,16} with chlorotris(triphenylphosphine)rhodium(I) to give the six-coordinated methyl and phenyl carbonyl complexes, [(C₆H₅)₃P]₂-Cl₂(CO)Rh-R. Six-coordinated acetyl-rhodium complexes, [C₆H₅(CH₃)P]₂Cl₂(CO)RhC(O)CH₃ and [C₆H₅-(C₂H₅)₂P]₂Cl₂(CO)RhC(O)CH₃, have also been reported.^{14,18} Other five- and six-coordinated acyl complexes of rhodium have also been isolated by Blum and coworkers.²

The tendency for migration of R, given as C₆H₅ > CH₃ > C₂H₅, has been related to the stability of C-Rh(III) bonds and the promotional energy for the Rh(I)-to-Rh(III) process.^{12,16} From the greater tendency of iridium(I) complexes to undergo oxidation,¹⁹ and from the known stabilities of iridium-alkyl or -aryl complexes,¹⁶ it might be expected that acyl-iridium complexes may be readily converted to the corresponding alkyl or aryl complexes. This expectation has not as yet been demonstrated.

Acyl chlorides react with complexes L₂Ir(CO)X (L = PCH₃(C₆H₅)₂,⁴ P(CH₃)₂C₆H₅,⁶ P(C₂H₅)₃,⁵ or P(C₂H₅)₂C₆H₅)⁵ to give the six-coordinated acyl complexes L₂XCl(CO)IrC(O)R. The decarbonylation of an acyl-iridium complex under forcing conditions has been reported only in one instance;⁵ namely, the thermolysis of [P(C₆H₅)(C₂H₅)₂]₂Br₂(CO)IrC(O)CH₃ at 200–210° gave the six-coordinated methyl-iridium complex

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