produced by three α-dihydrazone ligands increases in the order BdH < PvdH < GdH. These data, inferred from the diffuse reflectance spectra of the complexes, demonstrate also that the field strengths produced by PvdH and GdH are greater than any reported previously for α-dimine and α-dihydrazone complexes of nickel(II); however, few Δ values for cobalt(II) complexes are available for comparison. These observations can be interpreted in terms of intraligand repulsion effects augmented by coordination to a central metal atom. Observations on the shifts in the position of the C═N stretching vibrations in the infrared spectra of these complexes provide additional data to support this proposal. Further support is found in the fact that the cobalt(II) complexes of PvdH and GdH exhibit anomalous Curie–Weiss behavior interpreted on the basis of an equilibrium mixture of high- and low-spin complexes; *i.e.*, the two ligands in which intraligand repulsions are least provide a ligand field splitting approximately equal to the electron pairing energy.

It is suggested that the unusual magnetic moments of the two 2:1 iron(II) complexes of GdH and PvdH (exhibiting normal Curie–Weiss behavior) result from a *trans* configuration and the unusually large ligand fields produced by the coplanar bidentate ligands.

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Chemistry of the Cyclopentadienylmetal Carbonyls. II. Cyclopentadienyliron Carbonyl Derivatives[1]

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Cyclopentadienyliron carbonyl triphenylphosphine halides ($C_5H_5Fe(CO)[(C_6H_5)_3P]X$, X = Cl, Br, or I) have been shown to be formed in the direct reaction of triphenylphosphine and the cyclopentadienyliron dicarbonyl halide in refluxing benzene, along with the ionic derivatives $C_5H_5Fe(CO)_2(C_6H_5)_3P^+X^-$ (X = Cl, I, not Br), previously reported to be formed in this reaction. Cyclopentadienyliron dicarbonyl methyl and triphenylphosphine under ultraviolet irradiation at 90–100° give mixtures of the new compounds $C_5H_5Fe(CO)[(C_6H_5)_3P]CH_3$ and $C_5H_5Fe(CO)[(C_6H_5)_3P]COCH_3$. Evidence suggests that the pathway of this reaction involves initial formation of the former compound only and subsequent carbonylation to give the acetyl derivative. The nature of the reactions between $C_5H_5Fe(CO)_2X$ and CH_3CN and pyridine is discussed. In the course of this study several new ionic compounds of the formulas $C_5H_5Fe(CO)_2L^+PF_6^-$ and $C_5H_5Fe(CO)L_2^+PF_6^-$ (L = $(C_6H_5)_3P$, CH_3CN, py) have been prepared and characterized. Carbonyl stretching frequencies and proton nmr spectra of these compounds are reported.

Substitution reactions involving metal carbonyls, or metal carbonyl halides and alkyls, and electron-pair donor ligands have been extensively studied,[2] but little work has yet been done on similar reactions of the cyclopentadienylmetal carbonyl systems, except in the case of cyclopentadienylmanganese tricarbonyl.[3] This work was initiated to determine similarities or differences in behavior between carbonyl derivatives and cyclopentadienylmetal carbonyl derivatives. Work on cyclopentadienyliron carbonyl systems is reported here.

Experimental Section[4]

Cyclopentadienyliron dicarbonyl dimer,[5,6] cyclopentadienyliron dicarbonyl halides,[7] and cyclopentadienyliron dicarbonyl methyl[5,7] were prepared by methods well established in the literature. Merck acid-washed alumina was used without purification in column chromatographic separations.

Infrared spectra of the compounds prepared here were run on a Beckman IR-10 grating spectrometer and are reported in Table I. Proton nmr spectra were recorded on a Varian A-60; these data are tabulated in Table II. All molecular weight determinations were made using a Mechrolab osmometer, on approximately 0.01 *m* solutions in benzene.

Reaction of $C_5H_5Fe(CO)_2I$ and Triphenylphosphine.[8]—Triphenylphosphine (6.0 g, 22.9 mmoles) and $C_5H_5Fe(CO)_2I$ (5.0 g, 16.5 mmoles) were refluxed in benzene under nitrogen for 18 hr. During this time a yellow precipitate formed. The reaction mixture was filtered while hot, giving a yellow solid and a green filtrate. The yellow solid was washed with several portions of hot benzene and finally rinsed with hexane and then dried, giving 4.70 g of $C_5H_5Fe(CO)_2[(C_6H_5)_3P]^+I^-$ (50.2% yield).

Anal. Calcd for $C_{25}H_{20}O_2PIFe$: C, 53.03; H, 3.56; P, 5.47; I, 22.42. Found: C, 52.83; H, 3.68; P, 5.55; I, 22.68.

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[1] Previous paper in this series: P. M. Treichel and G. Werber, *Inorg. Chem.*, **4**, 1098 (1965).

[2] This subject is summarized in an excellent review article. See T. A. Manuel, *Advan. Organometal. Chem.*, **3**, 181 (1966).

[3] W. Strohmeier and J. F. Guttenberger, *Chem. Ber.*, **96**, 2112 (1963); **97**, 1256, 1871 (1964).

[4] Microanalyses were performed by A. Bernhardt, Microanalytical Laboratory, Mulheim, Germany.

[5] See procedures described in R. B. King, "Organometallic Syntheses," Vol. 1, Academic Press Inc., New York, N. Y., 1965.

[6] We thank the Antara Chemical Co. for their generous gift of iron pentacarbonyl, a precursor to this material.

[7] T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955); **3**, 104 (1956).

[8] This reaction has been reported but no experimental details were given: K. K. Joshi, P. L. Pauson, and W. L. Stubbs, *J. Organometal. Chem.*, **1**, 51 (1963).

TABLE I

INFRARED DATA FOR CYCLOPENTADIENYLIRON CARBONYL DERIVATIVES (CM^{-1})[a]

Compound	Terminal carbonyl str freq	Other bands
$C_5H_5Fe(CO)[(C_6H_5)_3P]I$	1938 vs[b]	1480 w, 1432 m, 1085 m, 1000 w, 850 w, 835 vw, 820 w, 755 w, 745 m, 692 s, 600 w, 567 w, 555 m, 538 m, 522 m, 512 m, 492 m[d]
$C_5H_5Fe(CO)[(C_6H_5)_3P]Br$[b]	1965 s	2990 m, 1485 w, 1435 m, 1090 m
$C_5H_5Fe(CO)[(C_6H_5)_3P]Cl$[d]	1960 s	1485 w, 1435 m, 1090 m, 840 w, 820 w, 745 m, 692 m, 556 m, 525 w
$C_5H_5Fe(CO)[(C_6H_5)_3P]CH_3$[b]	1905 s	3010 w, 1480 w, 1435 w, 1090 w
$C_5H_5Fe(CO)[(C_6H_5)_3P]COCH_3$[b]	1920 s	3000 m, 1595 s, 1485 m, 1435 m, 1330 w, 1090 m, 1065 w
$C_5H_5Fe(CO)_2[(C_6H_5)_3]P^+PF_6^-$	2055 s, 2010 s[c]	1435 s, 1090 s, 995 w, 880 m, 850–820 vs, br, 740 m, 700 m, 685 m, 605 m, 575 m, 555 m, 525 m, 500 w[d]
$C_5H_5Fe(CO)_2(CH_3CN)^+PF_6^-$	2080 s, 2035 s[c]	3125 m, 1000 w, 820 vs, br, 585 m, 565 w, 555 s, 525 s[d]
$C_5H_5Fe(CO)_2(py)^+PF_6^-$	2070 s, 2025 s[c]	835 vs, 600 w, 560 m, 535 w[d]
$[C_5H_5Fe(CO)_2]_2$-μ-$(C_6H_5)_2PC_2H_4P(C_6H_5)_2{}^{+2}PF_6^-$	2040 s, 1995 s[d]	1440 m, 1120 w, 1095 w, 1000 vw, 890 m, 880 m, 835 vs, br, 732 m, 718 m, 690 w, 610 m, 583 m, 557 s[d]
$C_5H_5Fe(CO)[(C_6H_5)_3P]_2{}^+PF_6^-$	1970 s[c]	1435 m, 1090 m, 1000 w, 830 vs, br, 750 w, 740 m, 690 s, 575 w, 555 s, 550 m, 530 w, 520 s, 505 w[d]
$C_5H_5Fe(CO)(CH_3CN)[(C_6H_5)_3P]^+PF_6^-$ [d]	1970 m	1480 w, 1438 m, 1092 m, 830 vs, br, 740 m, 690 m, 555 s, 523 s
$C_5H_5Fe(CO)(bipy)^+PF_6^-$	1990 s[c]	1610 m, 830 vs, br, 760 s, 730 w, 555 s, 530 w, 505 w[d]

[a] Spectra taken using a Beckman IR-10 grating spectrometer, with KBr plates or cells. [b] $CHCl_3$ solution. [c] CH_2Cl_2 solution. [d] Nujol mull spectra.

TABLE II

PROTON NMR SPECTRA OF SOME CYCLOPENTADIENYLIRON CARBONYL COMPOUNDS PREPARED IN THIS STUDY

	C_5H_6 resonance			Other resonances		
Compound	τ	Mult	$J_{P,H}$ cps	τ	Mult	Assignment
$C_5H_5Fe(CO)_3{}^+PF_6^-$ [a]	3.86	Singlet	...	...	...	...
$C_5H_5Fe(CO)_2[(C_6H_5)_3P]^+PF_6^-$ [a]	4.38	Doublet	1.5	2.32	Multiplet	Phenyl
$C_5H_5Fe(CO)[(C_6H_5)_3P]_2{}^+PF_6^-$ [a]	5.05	1:2:1 triplet	1.5	2.58	Multiplet	Phenyl
$C_5H_5Fe(CO)_2(CH_3CN)^+PF_6^-$ [a]	4.34	Singlet	...	7.53	Singlet	CH_3CN
$C_5H_5Fe(CO)_2(C_5H_5N)^+PF_6^-$ [a]	4.34[d]	Singlet	...	2.5	Multiplet	C_5H_5N
$C_5H_5Fe(CO)(CH_3CN)[(C_6H_5)_3P]^+PF_6^-$ [b]	5.02	Doublet	1.5	7.78	Doublet $J = 1.5$ cps	CH_3CN
				2.45	Multiplet	Phenyl
$C_5H_5Fe(CO)(bipy)^+PF_6^-$[b]	4.79	Singlet	...	...[c]	...	...
$C_5H_5Fe(CO)_2CH_3$	5.27	Singlet	...	9.83	Singlet	CH_3
$C_5H_5Fe(CO)[(C_6H_5)_3P]CH_3$	5.75	Singlet	...	2.67	Multiplet	Phenyl
				10.17	Doublet $J = 6.5$ cps	CH_3

[a] Deuterioacetone solution. [b] Deuteriochloroform solution. [c] Solution was too dilute to obtain complete information on the bipyridine protons. [d] Literature value −352 cps from TMS; or τ 4:13. We do not understand this discrepancy of values.

The green filtrate was concentrated and octane added. Slow evaporation of the benzene using a rotary evaporator caused precipitation of a green solid which when collected and dried gave 3.0 g of $C_5H_5Fe(CO)[(C_6H_5)_3P]I$ (33.7% yield). This product was purified by recrystallization from a chloroform–octane mixture.

Anal. Calcd for $C_{24}H_{20}FeOPI$: C, 53.6; H, 3.25; P, 5.77; mol wt, 537. Found: C, 53.1; H, 3.79; P, 6.04; mol wt, 550.

The relative yields in other reactions run under similar conditions varied somewhat from the above values; in general the reaction could be said to give approximately equimolar quantities of the two products.

Reaction of $C_5H_5Fe(CO)_2Br$ and Triphenylphosphine.—This reaction was run in a manner similar to that with the iodide, described above. From 1.0 g of $C_5H_5Fe(CO)_2Br$ (4.1 mmoles) and 1.0 g of triphenylphosphine (3.9 mmoles), the only product obtained was $C_5H_5Fe(CO)[(C_6H_5)_3P]Br$ (1.05 g, 51.2% yield).

Anal. Calcd for $C_{24}H_{20}OBrPFe$: C, 58.7; H, 4.07; P, 6.31; Br, 16.3; mol wt, 491. Found: C, 57.7; H, 4.09; P, 6.34; Br, 16.5; mol wt, 499.

Reaction of $C_5H_5Fe(CO)_2Cl$ and Triphenylphosphine.—Triphenylphosphine (1.23 g, 4.7 mmoles) and $C_5H_5Fe(CO)_2Cl$ (1.0 g, 4.7 mmoles) were refluxed under nitrogen for 0.5 hr in benzene. Filtration gave 1.45 g (85% yield) of yellow $C_5H_5Fe(CO)_2[(C_6H_5)_3P]^+Cl^-$ reported by Davison, Green, and Wilkinson.[9] The green filtrate was concentrated, heptane was added, and then the solution was further concentrated until 0.25 g of a green solid precipitated. This compound could not be purified by the standard techniques of crystallization or chromatography. These procedures always caused some decomposition to give a mixture of the product and small amounts of triphenylphosphine oxide. The infrared spectrum of the green compound, however, is identical with that of $C_5H_5Fe(CO)[(C_6H_5)_3P]I$ and $C_5H_5Fe(CO)[(C_6H_5)_3P]Br$ (Table I).

Reaction of $C_5H_5Fe(CO)_2CH_3$ and Triphenylphosphine.—Triphenylphosphine (7.0 g, 0.0268 mole) and $C_5H_5Fe(CO)_2CH_3$ (5.0 g, 0.026 mole) were refluxed in a quartz flask in petroleum ether (bp 90–100°) for 20 hr under nitrogen, while the sample was irradiated with a 150-w Hanovia ultraviolet source at a distance of 4 cm. The solvent was then removed using a rotary evaporator and the resulting red-orange solid was dissolved in 1:1 chloroform–benzene and chromatographed on an alumina column. Two bands, the first red and the second a bright yellow, were observed to develop using 1:1 chloroform–benzene as an eluent. The first band was collected and the solvent evaporated off, and the solid residue recrystallized from a chloroform–octane mixture. This red crystalline compound was identified as $C_5H_5Fe(CO)[(C_6H_5)_3P]CH_3$, mp 152° (3.25 g, 29.1% yield).

Anal. Calcd for $C_{25}H_{23}OPFe$: C, 70.28; H, 5.40; P, 7.26; mol wt, 426. Found: C, 69.82; H, 5.45; P, 6.65; mol wt, 417.

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[9] A. Davison, M. L. H. Green, and G. Wilkinson, *J. Chem. Soc.*, 3172 (1961).

The second product, a yellow crystalline solid, was identified as $C_5H_5Fe(CO)[(C_6H_5)_3P]COCH_3$, mp 146° (6.60 g, 59.7% yield).

Anal. Calcd for $C_{26}H_{23}O_2PFe$: C, 68.87; H, 5.07; P, 6.21; mol wt, 454. Found: C, 69.66; H, 5.42; P, 6.21; mol wt, 464.

The effect of length of reaction time on the ratio of the products was investigated. Results are summarized in Table III.

TABLE III
EFFECT OF REACTION TIME ON YIELDS
OF $C_5H_5Fe(CO)[(C_6H_5)_3P]CH_3$ (A) AND
$C_5H_5Fe(CO)[(C_6H_5)_3P]COCH_3$ (B)

Time, hr	% A	% B	% $C_5H_5Fe(CO)_2CH_3$
6	67	16	16
12	63	31	6
20	33	66	0

Attempted Decarbonylation of $C_5H_5Fe(CO)[(C_6H_5)_3P]COCH_3$.—Ultraviolet irradiation of a solution of $C_5H_5Fe(CO)[(C_6H_5)_3P]COCH_3$ (1.0 g, 2.2 mmoles) in refluxing petroleum ether (bp 90–100°) for 20 hr, followed by a workup involving chromatography on alumina, failed to show any evidence of decarbonylation of this material to the methyl compound. Some decomposition was evident, and only 60% of the starting material (0.6 g) was recovered.

Reaction of $C_5H_5Fe(CO)[(C_6H_5)_3P]CH_3$ and Carbon Monoxide.—Carbon monoxide was slowly bubbled into a solution of 0.4 g of $C_5H_5Fe(CO)[(C_6H_5)_3P]CH_3$ (0.95 mmole) in petroleum ether for 18 hr, while maintaining the solution at 90–100°. Some solid decomposition product was observed at this point. Evaporation of the solvent followed by chromatography on alumina gave two products. The product eluting first, present in exceedingly small quantity, was shown by its infrared spectrum to be a mixture of $C_5H_5Fe(CO)_2CH_3$ and triphenylphosphine. The second product eluted much slower; it was identified as the acetyl compound $C_5H_5Fe(CO)[(C_6H_5)_3P]COCH_3$ (0.10 g, 25% yield). No starting material was detected among the products.

It is interesting to note that under similar conditions $C_5H_5Fe(CO)_2CH_3$ will not add carbon monoxide.

Reaction of $C_5H_5Fe(CO)[(C_6H_5)_3P]CH_3$ and Bromine.—Bromine (0.25 g, 1.6 mmoles) and $C_5H_5Fe(CO)[(C_6H_5)_3P]CH_3$ (0.6 g, 1.4 mmoles) were stirred in 75 ml of chloroform for 20 min under nitrogen. Excess bromine was consumed by shaking the chloroform solution with an aqueous solution of $Na_2S_2O_3$. The chloroform solution was dried over Na_2SO_4 for 2 hr and solvent removed on a rotary evaporator. The resultant green solid was chromatographed on silica gel using benzene as eluent; the green solution was caught under nitrogen with Na_2SO_4 in the receiving flask as a drying agent. Solvent was removed at reduced pressure and the resultant solid crystallized from chloroform–heptane to yield 0.15 g of green crystals, which were identified as $C_5H_5Fe(CO)[(C_6H_5)_3P]Br$ (22% yield).

Reaction of $C_5H_5Fe(CO)[(C_6H_5)_3P]CH_3$ and Iodine.—This reaction was carried out in a manner similar to the reaction with bromine described above. From 0.55 g of $C_5H_5Fe(CO)[(C_6H_5)_3P]CH_3$ (1.3 mmoles) and 0.35 g of I_2 (1.4 mmoles) the compound $C_5H_5Fe(CO)[(C_6H_5)_3P]I$ could be obtained in 36.8% yield (0.26 g).

The analogous reaction with chlorine, run at 0°, led only to decomposition; no $C_5H_5Fe(CO)[(C_6H_5)_3P]Cl$ was obtained.

Although the direct reaction of $C_5H_5Fe(CO)_2Cl$ and triphenylphosphine led primarily to the ionic product $C_6H_5Fe(CO)_2[(C_6H_5)_3P]^+Cl^-$, direct reactions with other ligands failed to give either an analogous ionic product or the covalent derivative $C_5H_5Fe(CO)LCl$. No reaction was observed between 1.5 g of $C_5H_5Fe(CO)_2Cl$ (7.0 mmoles) and 5 ml of acetonitrile in benzene for 48 hr. At reflux for 2.5 hr, however, these reagents led to formation of an 11.5% yield of ferrocene and a 6.1% yield of the cationic species $C_5H_5Fe(CO)_3^+$ isolated as the hexafluorophosphate. The latter species did not react further with acetonitrile, with loss of carbon monoxide. An inorganic residue was obtained but not investigated. It should be noted that no reaction was observed to occur if $C_5H_5Fe(CO)_2I$ was used, even at reflux (80°).

Ferrocene (0.35 g, 80% yield) was obtained in the reaction of 1.0 g of $C_5H_5Fe(CO)_2Cl$ (4.7 mmoles) and 0.38 ml of pyridine (4.7 mmoles) in benzene after 18 hr at reflux. No $C_5H_5Fe(CO)_3^+X^-$ was isolated however. Similarly ferrocene and $Fe(bipy)_3^{2+}2X^-$ were isolated in the rcaction of $C_5H_5Fe(CO)_2Cl$ and 2,2′-bipyridine.

Preparation of $C_5H_5Fe(CO)_2(CH_3CN)^+PF_6^-$.—$C_5H_5Fe(CO)_2Cl$ (2.1 g, 10 mmoles) was dissolved in 50 ml of benzene, and 4.0 g of $AlCl_3$ (30 mmoles) and 5 ml of CH_3CN were added. This mixture was refluxed under nitrogen for 1 hr. The solvent and excess CH_3CN were then removed on the rotary evaporator followed by vacuum at 0.1 mm. Water was carefully added to the residue. The aqueous solution (50 ml) was filtered to give a clear orange solution. Excess NH_4PF_6 solution was added dropwise, causing immediate precipitation of yellow solid. The product was collected, dried, and then recrystallized from acetone–ether; yield 1.25 g (35.4%), mp 142°.

Anal. Calcd for $C_9H_8FeO_2NPF_6$: C, 29.78; H, 2.22; N, 3.86; F, 31.41. Found: C, 30.04; H, 2.22; N, 3.88; F, 31.22.

A similar reaction with 1.0 g of $C_5H_5Fe(CO)_2Cl$ (4.7 mmoles), 0.63 g of $AlCl_3$ (4.7 mmoles), and 0.37 g of pyridine (4.7 mmoles) led to ferrocene (0.2 g, 46% yield) and $C_5H_5Fe(CO)_3^+$ isolated as the hexafluorophosphate salt (0.2 g, 12% yield).

Preparation of $C_5H_5Fe(CO)_2(py)^+PF_6^-$.—$C_5H_5Fe(CO)_3^+PF_6^-$ (0.5 g, 1.42 mmoles) was stirred under nitrogen at room temperature with 0.17 ml of pyridine (2.16 mmoles) in 50 ml of acetone for 18 hr. The addition of 50 ml of ether caused precipitation of 0.1 g of starting material. The filtrate was concentrated to a red oil which was subsequently redissolved in 5 ml of acetone. Slow addition of ether (100 ml) with stirring gradually precipitated 0.25 g of bright yellow crystals which did not melt but darkened above 135° (yield 44%). Recrystallization was accomplished from an acetone–ether mixture.

Anal. Calcd for $C_{12}H_{10}FeO_2NPF_6$: C, 35.94; H, 2.51; P, 7.73; F, 28.43; N, 3.49. Found: C, 36.11; H, 2.71; P, 6.53; F, 28.20; N, 3.67.

It is interesting to note that $C_5H_5Fe(CO)_2(CH_3CN)^+PF_6^-$ and $C_5H_5Fe(CO)_2(py)^+PF_6^-$ resisted further substitution by more CH_3CN or pyridine, respectively, under a wide variety of conditions. Neither did significant decomposition occur on treatment with these reagents. For example, when $C_5H_5Fe(CO)_2(CH_3CN)^+PF_6^-$ was refluxed in acetonitrile for 3 hr, only starting material was recovered. Similarly when $C_5H_5Fe(CO)_2(py)^+PF_6^-$ was refluxed in acetone containing excess pyridine for 12 hr the starting compound was recovered in 85% yield.

Preparation of $C_5H_5Fe(CO)[(C_6H_5)_3P]_2^+PF_6^-$.—To a solution of 1.6 g of $C_5H_5Fe(CO)[(C_6H_5)_3P]I$ (2.97 mmoles) in 50 ml of benzene was added 2.5 g of $AlBr_3$ (10.4 mmoles) and 2.6 g of triphenylphosphine (9.0 mmoles). The mixture was stirred under nitrogen for 18 hr at room temperature. The solvent was then removed on a rotary evaporator and the residue extracted with hot water followed by benzene. The remaining orange, insoluble residue was dissolved in acetone–water and excess NH_4PF_6 solution added. Crystallization of the product without oiling was difficult, but was finally effected by slow evaporation of an acetone–water solution. The orange powder gradually darkens on heating and melts at 186°. Starting material (0.9 g) was recovered from the benzene layer. The total yield based on a starting material used in the reaction was 19% (0.2 g).

Anal. Calcd for $C_{42}H_{35}FeOP_3F_6$: C, 61.63; H, 4.31; P, 11.35; F, 13.93. Found: C, 61.49; H, 4.28; P, 11.21; F, 13.74.

Preparation of $C_5H_5Fe(CO)[(C_6H_5)_3P]CH_3CN^+PF_6^-$.—A solution of 1.0 g of $C_5H_5Fe(CO)[(C_6H_5)_3P]I$ (1.86 mmoles), 0.75 g of $AlCl_3$ (5.58 mmoles), and 4 ml of acetonitrile (75 mmoles) in 50 ml of benzene was refluxed for 12 hr. Then 25 ml of water was added carefully. The mixture was separated after shaking and the benzene layer dried over Na_2SO_4. Hexane was added and 0.1 g of reddish brown solid precipitated. Infrared and nmr spectra indicated that this product is $C_5H_5Fe(CO)[(C_6H_5)_3P]$-

$CH_3CN^+X^-$. The product was converted to the PF_6^- salt and crystallized from aqueous acetone (yield 9%).

Preparation of $C_5H_5Fe(CO)(bipy)^+PF_6^-$.—$C_5H_5Fe(CO)_2Cl$ (1.0 g, 4.7 mmoles), 0.625 g of $AlCl_3$ (4.7 mmoles), and 0.735 g of bipyridine (4.7 mmoles) were refluxed in 50 ml of benzene for 3 hr. Water was added and the layers separated. Excess NH_4PF_6 solution was added to the aqueous layer and bright red crystalline $Fe(bipy)_3^{2+}2PF_6^-$ (0.65 g) precipitated. On recrystallization from acetone–ether, however, a slight color was noted in the filtrate. Evaporation to dryness gave a red-orange crystalline material. Infrared and proton nmr spectra suggested that this compound was $C_5H_5Fe(CO)(bipy)^+PF_6^-$, but due to the small quantity of material no analyses were obtained.

Preparation of $[C_5H_5Fe(CO)_2]_2$-μ-$(C_6H_5)_2PC_2H_4P(C_6H_5)_2^{2+}$-$2PF_6^-$.—A mixture of 1.0 g of $C_5H_5Fe(CO)_2Cl$ (4.7 mmoles), 1.88 g of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (4.7 mmoles), and 0.625 g of $AlCl_3$ (4.7 mmoles) was refluxed in 50 ml of benzene under nitrogen for 3 hr. The mixture was cooled and 30 ml of water added. The mixture was evaporated to dryness and the residue dissolved in acetone. Excess aqueous NH_4PF_6 solution was added dropwise. There was no immediate precipitation so 20 ml of water was slowly added. A yellow-brown solid precipitated. Recrystallization from acetone–ether gave 0.85 g of yellow crystals (35% yield).

Anal. Calcd for $C_{40}H_{34}Fe_2P_4O_4F_{12}$: C, 46.09; H, 3.29; P, 11.89. Found: C, 45.35; H, 3.52; P, 12.42.

Discussion

Substitution reactions between methylmanganese pentacarbonyl[10] or alkylcobalt tetracarbonyl compounds[11] and triphenylphosphine have been shown to occur with carbon monoxide insertion into the alkyl–metal bond. In contrast to these observations we have found that $C_5H_5Fe(CO)_2CH_3$ reacts with triphenylphosphine to give the direct substitution product $C_5H_5Fe(CO)[(C_6H_5)_3P]CH_3$. Evidence toward this end was indirect because this product is readily carbonylated to give the acetyl derivative which was thus present among the products, but it appeared to us fairly convincing.

The following points were noted to substantiate our belief that the compound $C_5H_5Fe(CO)[(C_6H_5)_3P]CH_3$ was the only direct product of this reaction. First, the relative yields of this compound and the corresponding acetyl product were dependent on the length of time of the reaction. When the reaction was run over short reaction times (~6 hr) the methyl compound was the major product. The acetyl compound was the major product when the reaction was run for a longer time (~20 hr). The relative amount of the acetyl product appeared to be a linear function of time though this must be recognized to be approximate only, since 100% of the starting material could not be accounted for. Second, the facile carbonylation of $C_5H_5Fe(CO)[(C_6H_5)_3P]CH_3$ to give the acetyl compound serves to rationalize how this compound came to be formed in the reaction. Carbon monoxide under low pressure, bubbled into the reaction mixture at 80°, is sufficient to effect this conversion. Presumably with both the substitution reaction and decomposition to provide a source of carbon monoxide, a sufficient quantity of this reagent would be present to carry out a smooth slow reaction giving $C_5H_5Fe(CO)[(C_6H_5)_3P]COCH_3$. Third, the acetyl product $C_5H_5Fe(CO)[C_6H_5)_3P]COCH_3$ could not be decarbonylated under the given conditions of the reaction,[12] proving that this is not the route by which the methyl compound is formed. This failure to be decarbonylated precludes the only other plausible route by which the methyl derivative could arise, assuring us that the direct reaction to give $C_5H_5Fe(CO)[(C_6H_5)_3P]CH_3$ is a major reaction involved, if not the only reaction.

The ease of carbonylation of $C_5H_5Fe(CO)[(C_6H_5)_3P]CH_3$ relative to $C_5H_5Fe(CO)_2CH_3$, and the difficulty of decarbonylation of $C_5H_5Fe(CO)[(C_6H_5)_3P]COCH_3$ relative to $C_5H_5Fe(CO)_2COCH_3$, serve as an interesting contrast. The same effect for a decarbonylation reaction has also been observed for the perfluoroacylcobalt carbonyl derivatives such as $CF_3COCo(CO)_3L$ (L = CO, decarbonylation occurs above 30°; L = $(C_6H_5)_3P$, decarbonylation only above 130°).[13] However, $CH_3COMn(CO)_4[(C_6H_5)_3P]$ loses carbon monoxide to give the methyl compound at room temperature,[14] whereas a temperature of over 80° is required for the analogous reaction of $CH_3COMn(CO)_5$. Clearly no definite statement on the effect of the triphenylphosphine ligand on this reaction can be made until more comparisons can be presented. It is reasonable to assume that both electronic effects related to the back-bonding capability of the ligand[15,16] and steric effects due to the bulkiness of the triphenylphosphine ligand may be involved.

The triphenylphosphine ligand is also notable for its ability to form metal complexes containing hydrido or alkyl groups, which are more stable thermally than the corresponding carbonyl compounds. Compare, for example, $CH_3Co(CO)_4$ *vs.* $CH_3Co(CO)_3[(C_6H_5)_3P]$, or $HCo(CO)_4$ *vs.* $HCo(CO)_3[(C_6H_5)_3P]$. The higher thermal stability of $C_5H_5Fe(CO)[(C_6H_5)_3P]CH_3$ relative to $C_5H_5Fe(CO)_2CH_3$ parallels these observations.

In conjunction with these studies on reactions of $C_5H_5Fe(CO)_2CH_3$ with triphenylphosphine and other ligands we have also investigated similar reactions of cyclopentadienyliron dicarbonyl halides. The reported reactions of these halides contrast with substitution reactions of other metal carbonyl halides[2] in that they often proceed with displacement of a halide ion, rather

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[10] R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 3996 (1964).

[11] R. F. Heck and D. S. Breslow, *ibid.*, **84**, 2499 (1962).

[12] These conditions were successful for most decarbonylations which have been run to date. See R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **2**, 15 (1964).

[13] W. Hieber, W. Beck, and E. Lindner, *Z. Naturforsch.*, **16b**, 229 (1962); W. Hieber and E. Lindner, *Chem. Ber.*, **95**, 2042 (1962).

[14] R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 5043 (1964).

[15] F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

[16] Triphenylphosphine does not back-bond to metals as well as does carbon monoxide, and thus the remaining carbonyls in such a compound must be back-bonded to a greater extent; this is observable in the infrared carbonyl stretching frequencies of related compounds. Electron density is also delocalized from the metal to the acyl carbonyl ($M{-}\overset{\overset{O}{\|}}{C}R \longleftrightarrow M^{+}{=}\overset{\overset{O^-}{|}}{C}R$). This extent of effect can be seen in the ketonic stretching frequencies in $C_5H_5Fe(CO)_2COCH_3$ and $C_5H_5Fe(CO)[(C_6H_5)_3P]COCH_3$ which are observed at 1640 and 1595 cm^{-1}, respectively. Depending on the decarbonylation mechanism both electronic effects might be significant.

than a carbonyl, to give an ionic derivative. Thus, cyclopentadienyliron dicarbonyl chloride is reported to react with triphenylphosphine in refluxing tetrahydrofuran to give the ionic compound $C_5H_5Fe(CO)_2[(C_6H_5)_3P]^+Cl^-$;[9] the iodide reacted with triphenylphosphine to give both the ionic compound $C_5H_5Fe(CO)_2[(C_6H_5)_3P]^+I^-$ and the covalent compound $C_5H_5Fe(CO)[(C_6H_5)_3P]I$, however.[8] The reaction of $C_5H_5Fe(CO)_2I$ and tris(dimethylamino)phosphine (tdp) is reported to give exclusively the ionic product $C_5H_5Fe(CO)_2tdp^+I^-$,[17] and the reaction of $C_5H_5Mo(CO)_3Cl$ and ammonia or hydrazine is reported to form $C_5H_5Mo(CO)_3(am)^+Cl^-$.[18]

In the course of this work we reinvestigated the triphenylphosphine reaction with $C_5H_5Fe(CO)_2X$ (X = Cl, Br, I). Ionic products were found in the reactions involving both the chloride and iodide, as reported, but $C_5H_5Fe(CO)[(C_6H_5)_3P]Br$ was found to be the only product of the reaction with $C_5H_5Fe(CO)_2Br$.[18a] A small amount of $C_5H_5Fe(CO)[(C_6H_5)_3P]Cl$, previously unreported, was obtained in the reaction of $C_5H_5Fe(CO)_2Cl$ and triphenylphosphine. The reactions of $C_5H_5Fe(CO)_2X$ (X = I, Cl) with donor molecules other than triphenylphosphine proved to be unusual, however, since neither the ionic product ($C_5H_5Fe(CO)_2L^+X^-$) nor the covalent product ($C_5H_5Fe(CO)LX$) were obtained. Excess acetonitrile and $C_5H_5Fe(CO)_2I$ did not react even in refluxing benzene for 18 hr. With $C_5H_5Fe(CO)_2Cl$, no reaction was observed at room temperature in a 48-hr period, but a reaction did occur in refluxing benzene. The products, surprisingly, were ferrocene and the ion $C_5H_5Fe(CO)_3^+$, which was isolated subsequently as the hexafluorophosphate salt. Notably, the ion $C_5H_5Fe(CO)_3^+$ did not react with excess acetonitrile present.

In the presence of aluminum chloride, cyclopentadienyliron dicarbonyl chloride and acetonitrile react to give the ionic compound $C_5H_5Fe(CO)_2(CH_3CN)^+AlX_4^-$. The reaction can best be interpreted as proceeding by way of formation of an intermediate complex such as $C_5H_5Fe(CO)_2ClAlCl_3$ from which the $AlCl_4^-$ anion is displaced by acetonitrile. Such a complex has been postulated in similar reactions of a metal carbonyl halide, the aluminum halide, and a donor molecule.[19]

The pyridine derivative $C_5H_5Fe(CO)_2(py)^+X^-$ could not be prepared in an analogous reaction to that used to prepare the acetonitrile product. We were able to prepare this compound by a simple displacement reaction between pyridine and $C_5H_5Fe(CO)_3^+PF_6^-$. This reaction reflects the relative base properties of pyridine as compared to acetonitrile.

We have also prepared complexes of the formula $C_5H_5Fe(CO)[(C_6H_5)_3P]L^+PF_6^-$ (L = $(C_6H_5)_3P$, CH_3CN) by the reaction of $C_5H_5Fe(CO)[(C_6H_5)_3P]X$, an aluminum halide, and the respective ligand.

Among the derivatives of the formula $C_5H_5Fe(CO)_2L^+PF_6^-$ and $C_5H_5Fe(CO)L_2^+PF_6$ prepared here a remarkable consistency in the position of the cyclopentadienyl resonance in the nmr spectra was noted. The cyclopentadienyl resonance was constant within about 5 cps regardless of the nature of L (except L = CO) for the former compounds.[20] A slightly larger variation between $CpFe(CO)L_2^+PF_6^-$ derivatives was observed. This resonance at τ 4.36 ± 0.02 for the $C_5H_5Fe(CO)_2L^+$ cations and at τ 4.92 ± 0.13 for the $C_5H_5Fe(CO)L_2^+$ cations can be contrasted to the resonance of the $C_5H_5Fe(CO)_3^+$ cyclopentadienyl protons which were observed at τ 3.86. This shift to higher τ value on increased substitution reflects the higher electron density on the ring. This would be expected since the phosphine or other ligand can accept electron density from the metal less effectively than either CO or C_5H_5. The near coincidence of the C_5H_5 proton resonance positions in $C_5H_5Fe(CO)_2L^+$ complexes is somewhat unexpected nonetheless.

The carbonyl stretching frequencies among the ionic products differ more significantly. The compound $C_5H_5Fe(CO)_3^+PF_6^-$ has two carbonyl resonances at 2120 and 2070 cm^{-1} (Nujol).[9] Two absorptions in the $C_5H_5Fe(CO)_2L^+PF_6^-$ complexes are shifted somewhat to lower wavenumbers, and the single absorption of $C_5H_5Fe(CO)[(C_6H_5)_3P]_2^+PF_6^-$ at 1970 cm^{-1} is the lowest among the compounds discussed here. Again these differences reflect the different degrees of back-bonding to the carbon monoxide ligand.

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[17] R. B. King, *Inorg. Chem.*, **2**, 936 (1963).

[18] E. O. Fisher and E. Moser, *J. Organometal. Chem.*, **2**, 230 (1964).

[18a] NOTE ADDED IN PROOF.—Since writing this paper we have had occasion to repeat this reaction and in several instances (three times of eight reactions attempted) we have isolated the ionic product in addition to the reported covalent species. We are unable to explain the apparent inconsistency in these results in terms of reaction time or temperature or reagent purity.

[19] E. O. Fischer and K. Fichtel, *Chem. Ber.*, **94**, 1200 (1961); **95**, 2063 (1962).

[20] The cyclopentadienyl resonance in the spectrum of $C_5H_5Fe(CO)_2(py)^+PF_6^-$ reported by Fischer and co-workers[18] differed somewhat from the value we found for the same compound. So also is their value for the cyclopentadienyl resonance of the benzonitrile complex ($C_5H_5Fe(CO)_2C_6H_5CN^+PF_6^-$) at somewhat higher τ than that for our acetonitrile complex. However, most of the olefin complexes ($C_5H_5Fe(CO)_2(olefin)^+X^-$) reported do have cyclopentadienyl resonances in the given range.