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Reactions of Metal Carbonyl Derivatives. I. Monosubstituted Derivatives of Tetracarbonyldi-π-cyclopentadienyldiiron and Their Iodination Reactions[1,2]

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Tetracarbonyldi-π-cyclopentadienyldiiron reacts with the ligands L = $P(C_2H_5)_3$, $P(n\text{-}C_3H_7)_3$, $P(n\text{-}C_4H_9)_3$, $P(C_6H_5)_2C_2H_5$, $P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(O\text{-}i\text{-}C_3H_7)_3$, $P(O\text{-}n\text{-}C_4H_9)_3$, and $P(OC_6H_5)_3$ in refluxing benzene to afford the monosubstituted complexes $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3L$. On the basis of infrared spectroscopic evidence it is shown that the compounds $(\pi\text{-}C_5H_5)_2$-$Fe_2(CO)_3L$ [L = $P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(O\text{-}i\text{-}C_3H_7)_3$, $P(O\text{-}n\text{-}C_4H_9)_3$, $P(OC_6H_5)_3$, and $P(C_6H_5)_3$] occur as a mixture of isomers in solution whereas the derivatives $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3L$ [L = $P(C_2H_5)_3$, $P(n\text{-}C_3H_7)_3$, $P(n\text{-}C_4H_9)_3$, and $P(C_6H_5)_2C_2H_5$] are present in solution as a single isomer. Possible structures for these isomers are discussed. The reaction of $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3L$ [L = $P(C_2H_5)_3$, $P(O\text{-}i\text{-}C_3H_7)_3$, and $P(OC_6H_5)_3$] with iodine involves asymmetric cleavage of the parent compounds to yield the ionic derivatives $[\pi\text{-}C_5H_5Fe(CO)_2L]I$ as well as symmetric cleavage to give the complexes $\pi\text{-}C_5H_5Fe(CO)LI$ and $\pi\text{-}C_5H_5$-$Fe(CO)_2I$.

Introduction

Substitution reactions of tetracarbonyldi-π-cyclopentadienyldiiron with several tertiary group Va donor ligands have been reported but in general relate to reactions at elevated temperatures. For instance the ligands $P(C_6H_5)_3$, $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (diphos), and terpyridyl (terpy) have been shown to react with $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ at temperatures greater than 160°, to replace the cyclopentadienyl ring and to form $Fe(CO)_3$-$\{P(C_6H_5)_3\}_2$,[4] $Fe(CO)_3$diphos, and $Fe(CO)_2$terpy,[5] respectively. Furthermore it has been observed that only amorphous decomposition products could be isolated from the reaction of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ with $P\{N(CH_3)_2\}_3$ in refluxing xylene.[6]

The reactions of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ with the tetrasubstituted diphosphines $L_2 = (CH_3)_4P_2$ and $(C_6H_5)_4P_2$ and the diarsine $L_2 = (CH_3)_4As_2$ in toluene under reflux conditions have also been studied and shown to afford products of the type $[\pi\text{-}C_5H_5Fe(CO)L]_2$ in which the groups L are bridging and the carbonyls are terminal.[7] The analogous reactions with the fluorinated diarsines $L_2 = (CF_3)_4As_2$[8] and $(C_6F_5)_4As_2$[9] afforded the derivatives $\pi\text{-}C_5H_5Fe(CO)_2L$. Ultraviolet irradiation of these compounds was necessary to effect carbonyl substitution and to form $[\pi\text{-}C_5H_5Fe(CO)L]_2$.

It has been recently found that reactions of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ with the ditertiary phosphines $(C_6H_5)_2P$-$(CH_2)_nP(C_6H_5)_2$ ($n = 1\text{--}3$) in refluxing benzene yield products of the type $[\pi\text{-}C_5H_5Fe(CO)]_2(C_6H_5)_2P(CH_2)_n$-$P(C_6H_5)_2$ which contain both bridging carbonyl groups

and a bridging ditertiary phosphine ligand as well as a metal–metal bond.[10] As an extension of this study, the reactions of various monodentate tertiary phosphines and tertiary phosphites with $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ have been studied and the results are presented here.

Experimental Section

The ligands $P(C_2H_5)_3$, $P(n\text{-}C_3H_7)_3$, and $P(C_6H_5)_2C_2H_5$ were synthesized by established methods. All other ligands as well as $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ were obtained commercially. All experiments were performed under a nitrogen atmosphere. The photochemical reactions employed a Hanau TQ81 lamp. Petroleum ether refers to that boiling at 40–60°. The infrared spectra were recorded on a Perkin-Elmer Model 621 grating spectrophotometer. The nmr spectra were obtained with a Varian A-60 instrument. Conductivities were determined by conventional methods. The elemental analyses were performed by the Bernhardt Microanalytical Laboratory, Mühlheim, West Germany, and by Mr. K. P. Kunz, National Chemical Research Laboratory, CSIR, Pretoria.

General Method for the Preparation of the Monosubstituted Derivatives.—$[\pi\text{-}C_5H_5Fe(CO)_2]_2$ and the appropriate ligand were allowed to react in refluxing benzene (*ca.* 80 ml); the course of the reaction was monitored by means of infrared spectroscopy. On completion, the solution was filtered and the solvent was removed under reduced pressure. The residue was crystallized and the pure crystalline product washed with petroleum ether (room temperature or −78°) and dried *in vacuo*.

Tricarbonyltriethylphosphinedi-π-cyclopentadienyldiiron.—The product obtained by allowing $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (0.8 g, 2.2 mmol) and triethylphosphine (0.8 g, 6.8 mmol) to react for 10 hr as described above was dissolved in benzene and crystallization was effected by the addition of a little petroleum ether.

Tricarbonyltri-*n*-propylphosphinedi-π-cyclopentadienyldiiron.—The product obtained by allowing $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (1.0 g, 2.8 mmol) and tri-*n*-propylphosphine (1.0 g, 6.5 mmol) to react for 20 hr as described above was dissolved in petroleum ether and the solution was filtered. The filtrate was cooled to −78° to afford dark green crystals.

Tricarbonyltri-*n*-butylphosphinedi-π-cyclopentadienyldiiron.—The product obtained by allowing $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (1.0 g, 2.8 mmol) and tri-*n*-butylphosphine (0.69 g, 3.4 mmol) to react for 16 hr as described above was dissolved in petroleum

(1) A preliminary communication of this work has been presented: *Chem. Commun.*, 1513 (1968).

(2) Taken in part from the M.S. thesis of A. L. du Preez presented to the University of Pretoria, Nov 1968.

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(6) R. B. King, *Inorg. Chem.*, **2**, 936 (1963).

(7) R. G. Hayter, *J. Am. Chem. Soc.*, **85**, 3120 (1963).

(8) W. R. Cullen and R. G. Hayter, *ibid.*, **86**, 1030 (1964).

(9) M. Cooke, M. Green, and D. Kirkpatrick, *J. Chem. Soc., A*, 1507 (1968).

(10) R. J. Haines, A. L. du Preez, and G. T. W. Wittmann, *Chem. Commun.*, 611 (1968).

ether and crystallization was effected as for the tripropylphosphine complex.

Tricarbonyldiphenylethylphosphinedi-π-cyclopentadienyldiiron.—The product obtained by allowing $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (0.5 g, 1.4 mmol) and diphenylethylphosphine (1.5 g, 7.1 mmol) to react for 36 hr as described above was washed with petroleum ether to remove excess ligand. Crystallization of the resultant green oil could not be effected.

Tricarbonyl(trimethyl phosphite)di-π-cyclopentadienyldiiron.—Petroleum ether was added to the product obtained by allowing $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (1.1 g, 3.2 mmol) and trimethyl phosphite (0.46 g, 3.7 mmol) to react for 20 hr as described above and the mixture was kept at 0° for 12 hr. The dark red crystals which separated were recrystallized from benzene–petroleum ether.

Tricarbonyl(triethyl phosphite)di-π-cyclopentadienyldiiron.—The product obtained by allowing $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (0.5 g, 1.5 mmol) and triethyl phosphite (0.3 g, 1.8 mmol) to react for 13 hr as described above was crystallized as described for the trimethyl phosphite complex.

Tricarbonyl(triisopropyl phosphite)di-π-cyclopentadienyldiiron.—The product obtained by allowing $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (0.56 g, 1.6 mmol) to react with triisopropyl phosphite (0.4 g, 1.9 mmol) for 24 hr as described above was crystallized as described for the trimethyl phosphite complex.

Tricarbonyl(tri-*n*-butyl phosphite)di-π-cyclopentadienyldiiron.—The product obtained by allowing $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (0.98 g, 2.8 mmol) and tri-*n*-butyl phosphite (0.78 g, 3.1 mmol) to react for 20 hr as described above was dissolved in petroleum ether and the solution was filtered. The filtrate was cooled to $-78°$ to afford a low yield of dark red crystals.

Tricarbonyl(triphenyl phosphite)di-π-cyclopentadienyldiiron.—The product obtained by allowing $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (1.4 g, 4.0 mmol) and triphenyl phosphite (1.4 g, 4.6 mmol) to react for 24 hr as described above was dissolved in benzene and crystallization was effected by the addition of a little petroleum ether.

Photochemical Synthesis of Tricarbonyltriphenylphosphinedi-π-cyclopentadienyldiiron.—A benzene solution of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (1.0 g, 2.8 mmol) and triphenylphosphine (3.5 g, 13 mmol) kept at *ca.* 25° was irradiated with ultraviolet light for 3 hr. Solvent was removed under reduced pressure to afford a green-brown residue. Unreacted $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ and excess triphenylphosphine were removed by washing the residue with cyclohexane. Crystallization of the product was effected from benzene–petroleum ether but extensive decomposition took place. The final green product could consequently only be obtained in low yield and in a slightly impure form.

General Procedure for the Reaction of the Monosubstituted Complexes with Iodine.—Iodine in toluene (*ca.* 20 ml) was added dropwise to a stirred solution of $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3L$ [L = P(C$_2$-H$_5$)$_3$, P(O-*i*-C$_3$H$_7$)$_3$, P(OC$_6$H$_5$)$_3$] in toluene (*ca.* 60 ml) at 0°. A yellow-brown compound separated. The mother liquor was decanted off and the residue was washed with benzene. This solid was dissolved in acetone and an acetone solution containing excess sodium tetraphenylboron was added. The product was precipitated by the addition of water and crystallized from acetone–water.

Dicarbonyltriethylphosphine-π-cyclopentadienyliron Tetraphenylborate.—The compound was obtained by allowing iodine (0.06 g, 0.24 mmol) to react with $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3P(C_2H_5)_3$ (0.15 g, 0.24 mmol) and isolating it as the pure tetraphenylborate by the method described above.

Dicarbonyl(triisopropyl phosphite)-π-cyclopentadienyliron Tetraphenylborate.—The compound was obtained by allowing iodine (0.29 g, 1.1 mmol) to react with $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3P\text{-}(O\text{-}i\text{-}C_3H_7)_3$ (0.67 g, 1.1 mmol) and isolating it as the pure tetraphenylborate by the method described above.

Dicarbonyl(triphenyl phosphite)-π-cyclopentadienyliron Tetraphenylborate.—The compound was obtained by allowing iodine (0.13 g, 0.51 mmol) to react with $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3P(OC_6H_5)_3$ (0.32 g, 0.51 mmol) and isolating it as the pure tetraphenylborate by the method described above.

Results and Discussion

The tertiary phosphines $P(C_2H_5)_3$, $P(n\text{-}C_3H_7)_3$, $P(n\text{-}C_4H_9)_3$, and $P(C_6H_5)_2C_2H_5$ and the tertiary phosphites $P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(O\text{-}i\text{-}C_3H_7)_3$, $P(O\text{-}n\text{-}C_4H_9)_3$, and $P(OC_6H_5)_3$ have been found to react with $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ in refluxing benzene, to effect substitution of a single carbonyl group and to form in good yield products of the type $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3L$ (L = ligand). With the exception of $P(OCH_3)_3$ further replacement of carbonyl groups by these ligands could not be effected in spite of increasing the reaction time and the ligand to parent carbonyl ratio. When equimolar amounts of $P(OCH_3)_3$ and $[\pi\text{-}C_5H_5Fe(CO_2]_2$ were allowed to react, the monosubstituted derivative $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3P(OCH_3)_3$ was formed. When a large excess of this ligand was used, however, three further products were identified by monitoring the reaction using infrared spectroscopy. Attempts to separate these products by employing fractional crystallization and column chromatographic techniques proved unsuccessful. It should be noted that the tetrasubstituted derivative $[\pi\text{-}C_5H_5Fe\{P(OC_6H_5)_3\}_2]_2$ has been previously synthesized but not directly from $[\pi\text{-}C_5H_5Fe(CO)_2]_2$.[11]

All of the monosubstituted derivatives synthesized are unstable in solution in air while, apart from $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3L$ [L = $P(C_2H_5)_3$, $P(n\text{-}C_3H_7)_3$, and $P(OC_6H_5)_3$], they are also air sensitive in the crystalline state. Furthermore, the derivatives $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3L$ [L = $P(n\text{-}C_4H_9)_3$, $P(C_6H_5)_2C_2H_5$, $P(C_6H_5)_3$, and $P(O\text{-}n\text{-}C_4H_9)_3$] decompose in solution under a nitrogen atmosphere; this accounts for the extreme difficulty encountered in obtaining pure crystals of these compounds. The complex $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3P(C_6H_5)_3$ is particularly unstable in solution at temperatures greater than 50° and could not be synthesized by thermal methods. Its synthesis was effected by irradiating a benzene solution of the two reactants at room temperature with ultraviolet light.

The chemical composition of the monosubstituted derivatives was established by elemental analysis and from a comparison of the integrated intensities of the cyclopentadienyl and ligand proton peaks in the nmr spectra. The diamagnetism of the compounds was demonstrated by the sharpness of the nmr spectral peaks. Conductance measurements show the complexes to be neutral.

The nmr spectra exhibit two cyclopentadienyl proton resonances of equal intensity. This is consistent with an asymmetric molecular structure containing two nonequivalent cyclopentadienyl rings; three possible structures are shown in Figure 1. The peak to higher field is assigned to the cyclopentadienyl ring bonded to the same iron atom as the phosphorus donor ligand. For most compounds this peak was found to be split into a doublet due to phosphorus–hydrogen coupling. The coupling constant could only be measured for $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3P(C_6H_5)_2C_2H_5$, however.

(11) A. N. Nesmeyanov, Yu. A. Chapovsky, and Yu. A. Ustynyuk, *J. Organometal. Chem.* (Amsterdam), **9**, 345 (1967).

TABLE I

Colors, Conductivity, Nmr, and Analytical Data

No.	Compound[a]	Color	Conductivity,[b] ohm^-1 cm^2 mol^-1	C5H5 proton resonance,[c] ppm	Anal, % Found			Calcd		
					C	H	Others	C	H	Others
I	(π-C5H5)2Fe2(CO)3P(C2H5)3	Green	8.5	5.29, 5.55	51.1	5.8	P, 6.8	51.4	5.7	P, 7.0
II	(π-C5H5)2Fe2(CO)3P(n-C3H7)3	Green	7.8	5.43, 5.71	54.2	6.5		54.3	6.3	
III	(π-C5H5)2Fe2(CO)3P(n-C4H9)3	Green	9.1	5.26, 5.53	56.7	7.0		56.9	7.1	
IV	(π-C5H5)2Fe2(CO)3P(C6H5)2C2H5	Green oil		5.34, 5.82[d]						
V	(π-C5H5)2Fe2(CO)3P(OCH3)3	Dark red	4.1	5.30, 5.43	42.7	4.3	P, 8.6	42.7	4.3	P, 8.8
VI	(π-C5H5)2Fe2(CO)3P(OC2H5)3	Dark red	9.3	5.31, 5.46	46.4	5.2		46.4	5.1	
VII	(π-C5H5)2Fe2(CO)3P(O-i-C3H7)3	Dark red	5.2	5.28, 5.49	49.5	5.8		49.5	5.9	
VIII	(π-C5H5)2Fe2(CO)3P(O-n-C4H9)3	Dark red	8.4	5.33, 5.48	51.3	6.4		52.2	6.5	
IX	(π-C5H5)2Fe2(CO)3P(OC6H5)3	Dark red	1.7	5.21, 5.90	58.2	4.0	P, 4.7	58.5	4.0	P, 4.9
XI	[π-C5H5Fe(CO)2P(C2H5)3][B(C6H5)4]	Yellow	95	e	72.4	6.6		72.3	6.6	
XII	[π-C5H5Fe(CO)2P(O-i-C3H7)3][B(C6H5)4]	Yellow	82	5.68[f]	68.5	6.7	Fe, 7.7	68.2	6.6	Fe, 7.9
XIII	[π-C5H5Fe(CO)2P(OC6H5)3][B(C6H5)4]	Yellow	90	5.99	72.7	5.0		73.0	5.0	

[a] All compounds are diamagnetic; decomposition temperatures are poorly defined. [b] Solutions 10^{-3} M in acetone. [c] τ scale measured in CDCl3, at 38°. [d] J_{P-H} = 1.2 cps. [e] Insufficiently soluble; value for [π-C5H5Fe(CO)2P(C2H5)3]I in acetone is 4.16 ppm; J_{P-H} = 1.6 cps. [f] J_{P-H} = 1.4 cps.
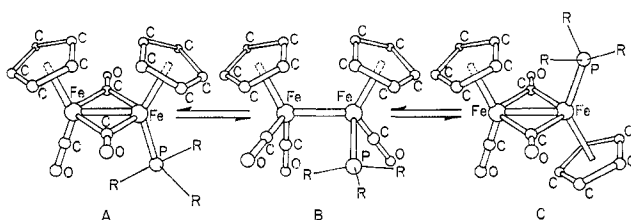

Figure 1.—Possible structures for (π-C5H5)2Fe2(CO)3L (L = phosphorus donor ligand) in solution showing the stereochemistry of the iron atoms only.

The solution infrared spectra of all of the monosubstituted complexes contain peaks corresponding to both terminal and bridging carbonyl stretching modes, the frequencies and relative intensities of which are given in Table II. A single peak is observed in the terminal carbonyl stretching region in the spectra of the compounds (π-C5H5)2Fe2(CO)3L [L = P(C2H5)3, P(n-C3H7)3, P(n-C4H9)3, and P(C6H5)2C2H5]. This is consistent with the compounds having a molecular structure with one terminal and two bridging carbonyl groups. In contrast the spectra of the complexes (π-C5H5)2Fe2(CO)3L [L = P(C6H5)3, P(OCH3)3, P(OC2H5)3, P(O-i-C3H7)3, P(O-n-C4H9)3, and P(OC6H5)3] contain two terminal carbonyl stretching peaks as well as a bridging carbonyl stretching mode. This can be explained in terms of more than one isomer being present in solution. The structures of the three most likely isomers are represented in Figure 1. Isomers A and C belong to the point group C_s for which one terminal carbonyl stretching mode is predicted. Isomer B belongs to the point group C_1, however, and for this three terminal carbonyl stretching modes are expected. An analysis of the infrared spectrum of (π-C5H5)2Mo2(CO)3L (L = phosphorus donor ligand) in the carbonyl stretching region has shown it to correspond to the superposition of the spectra of π-C5H5Mo(CO)3Y and π-C5H5Mo(CO)2LY.[12] Assuming a similar correlation for isomer B of (π-

(12) R. J. Haines, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc., A,* 43 (1968).

C5H5)2Fe2(CO)3L (L = ligand) and from a comparison of the energies and relative intensities of the carbonyl stretching modes of π-C5H5Fe(CO)2X and π-C5H5Fe(CO)LX (L = ligand; X = halogen), it is expected (i) that the three carbonyl stretching modes of this isomer would be of comparable intensity and (ii) that the energy of the carbonyl stretching vibration corresponding to the π-C5H5Fe(CO)L moiety would be much lower (ca. 50–100 cm⁻¹) than the higher energy mode associated with the π-C5H5Fe(CO)2 moiety. The observed spectra for the compounds (π-C5H5)2Fe2(CO)3L [L = P(C6H5)3, P(OCH3)3, P(OC2H5)3, P(O-i-C3H7)3, P(O-n-C4H9)3, and P(OC6H5)3] are not consistent with these considerations and therefore the possibility of isomer B occurring in solution for these complexes is eliminated. It is thus concluded that they exist primarily as a mixture of the two carbonyl-bridged isomers in solution, viz., A and C. This isomeric equilibrium is analogous to that postulated for [π-C5H5Fe(CO)2]2. Based on a study of the influence of solvents on the intensities of the C–O and M–C stretching modes and on the M–C–O bending modes, it was suggested that the parent dimer exists primarily as a mixture of the cis and trans carbonyl-bridged isomers in solution.[13] From the reasons presented above it is also evident that the complexes (π-C5H5)2Fe2(CO)3L [L = P(C2H5)3, P(n-C3H7)3, P(n-C4H9)3, and P(C6H5)2C2H5] exist as either isomer A or isomer C in solution but from the available data it is not possible to assign the structure uniquely.

The appearance of a single peak in the bridging carbonyl stretching region of the infrared spectra of all the monosubstituted derivatives is inconsistent with the above structures as two infrared-active bridging carbonyl stretching modes are predicted by group theory for both isomer A and isomer C. It is thus assumed that for either isomer the symmetric and asymmetric modes are accidentally degenerate or that the symmetric mode is of negligible intensity. A further assumption is that the frequency of the bridging carbonyl stretching

(13) A. R. Manning, *ibid., A,* 1319 (1968).

Table II

Infrared Spectroscopic Data

Compound	C–O str freq,[a] cm^{-1} (rel intens in parentheses)	Other peaks,[a,d] cm^{-1}
[π-C$_5$H$_5$Fe(CO)$_2$]$_2$	2005 s, 1961 vs, 1793 vs[b]	
I (π-C$_5$H$_5$)$_2$Fe$_2$(CO)$_3$P(C$_2$H$_5$)$_3$	1934 (5.9), 1747 (10)[b]	3118 w, 3096 w, 2966 w, 2937 w, 2908 w, 2880 w, 1455 w, 1427 w, 1375 m, 1258 w, 1237 w, 1119 w, 1038 m, 1014 w, 844 m, 826 m, 763 m, 713 s, 646 vs, 617 s, 591 w, 556 m, 537 w, 519 w, 418 w
II (π-C$_5$H$_5$)$_2$Fe$_2$(CO)$_3$P(n-C$_3$H$_7$)$_3$	1932 (5.7), 1745 (10)[b]	3108 w, 3100 w, 2953 s, 2912 m, 2864 m, 1450 m, 1418 m, 1075 m, 1067 m, 1037 w, 1008 w, 858 w, 841 w, 817 m, 803 m, 770 w, 725 w, 641 vs, 607 m, 589 m, 551 m, 536 w, 518 w, 422 w
III (π-C$_5$H$_5$)$_2$Fe$_2$(CO)$_3$P(n-C$_4$H$_9$)$_3$	1933 (8.7), 1746 (10)[b]	3114 w, 3104 w, 2948 s, 2924 m, 2863 m, 1456 m, 1422 w, 1406 w, 1368 w, 1350 w, 1300 w, 1209 w, 1110 w, 1093 w, 1060 w, 1008 w, 908 w, 895 w, 848 w, 819 s, 803 m, 783 w, 767 w, 749 w, 720 w, 640 vs, 608 m, 590 w, 547 m, 533 w, 520 w, 443 w
IV (π-C$_5$H$_5$)$_2$Fe$_2$(CO)$_3$P(C$_6$H$_5$)$_2$C$_2$H$_5$	1940 (9.7), 1743 (10)[b]	
V (π-C$_5$H$_5$)$_2$Fe$_2$(CO)$_3$P(OCH$_3$)$_3$	1964 (7.7), 1944 (2.3), 1750 (10)[b]	3110 w, 3092 w, 2988 w, 2943 w, 2840 w, 1458 w, 1437 w, 1417 w, 1355 w, 1176 w, 1054 m, 1019 vs, 855 w, 835 w, 818 w, 790 s, 750 s, 638 vs, 606 m, 594 m, 540 m, 523 w
VI (π-C$_5$H$_5$)$_2$Fe$_2$(CO)$_3$P(OC$_2$H$_5$)$_3$	1963 (6.4), 1942 (3.1), 1749 (10)[b]	3100 w, 2900 w, 1472 w, 1436 w, 1412 w, 1386 w, 1354 w, 1151 w, 1094 w, 1054 w, 1018 vs, 943 s, 932 s, 860 w, 845 w, 821 m, 804 w, 783 m, 747 m, 638 vs, 602 m, 549 m, 539 m, 517 w, 450 w
VII (π-C$_5$H$_5$)$_2$Fe$_2$(CO)$_3$P(O-i-C$_3$H$_7$)$_3$	1961 (6.7), 1939 (1.8), 1753 (10)[b]	3108 w, 3100 w, 2982 m, 2968 m, 2933 m, 2862 w, 1448 w, 1429 w, 1417 w, 1379 m, 1370 m, 1173 m, 1137 w, 1102 s, 1001 vs, 972 vs, 954 vs, 910 w, 890 w, 876 m, 847 w, 835 w, 822 m, 802 m, 760 m, 740 w, 722 w, 638 vs, 603 m, 592 w, 538 s, 514 w, 495 w, 445 w, 400 w
VIII (π-C$_5$H$_5$)$_2$Fe$_2$(CO)$_3$P(O-n-C$_4$H$_9$)$_3$	1965 (6.6), 1944 (3.0), 1750 (10)[b]	3086 w, 2958 s, 2930 m, 2868 m, 1462 w, 1455 w, 1425 w, 1377 w, 1356 w, 1140 w, 1115 w, 1055 m, 1018 s, 960 s, 883 m, 810 m, 795 w, 780 w, 716 w, 650 vs, 608 m, 592 m, 563 w, 540 w, 519 w
IX (π-C$_5$H$_5$)$_2$Fe$_2$(CO)$_3$P(OC$_6$H$_5$)$_3$	1971 (6.8), 1948 (4.2), 1760 (10)[b]	3090 w, 3060 w, 3032 w, 1583 s, 1480 s, 1450 s, 1218 s, 1185 vs, 1158 s, 1068 m, 1020 m, 1003 m, 911 vs, 878 s, 823 m, 767 s, 730 m, 719 m, 687 s, 640 vs, 610 m, 590 s, 547 m, 500 m
X (π-C$_6$H$_5$)$_2$Fe$_2$(CO)$_3$P(C$_6$H$_5$)$_3$	1960 (4.5), 1936 (4.5), 1740 (10)[b]	
XI [π-C$_5$H$_5$Fe(CO)$_2$P(C$_2$H$_5$)$_3$][B(C$_6$H$_5$)$_4$]	2051 s, 2008 s[c]	3100 w, 3088 w, 3077 w, 3048 s, 3020 w, 3006 w, 2986 m, 2978 m, 2930 w, 2900 w, 2872 w, 1575 w, 1473 m, 1450 w, 1423 m, 1410 m, 1257 w, 1178 w, 1147 w, 1062 w, 1030 m, 1007 w, 1000 w, 863 w, 842 w, 755 m, 742 s, 733 s, 727 s, 705 vs, 622 m, 610 s, 600 s, 592 w, 578 s, 560 s, 506 w, 475 w, 455 w, 418 w
XII [π-C$_5$H$_5$Fe(CO)$_2$P(O-i-C$_3$H$_7$)$_3$][B(C$_6$H$_5$)$_4$]	2064 s, 2018 s[c]	3098 w, 3078 w, 3046 w, 2975 m, 2926 w, 1573 w, 1472 m, 1444 w, 1423 m, 1410 w, 1380 m, 1370 m, 1330 w, 1312 w, 1172 w, 1133 w, 1091 m, 990 vs, 968 vs, 879 w, 863 w, 844 w, 756 m, 739 s, 728 s, 704 s, 695 w, 620 w, 610 m, 600 m, 583 s, 562 m, 500 w, 473 w, 453 w, 428 w
XIII [π-C$_5$H$_5$Fe(CO)$_2$P(OC$_6$H$_5$)$_3$][B(C$_6$H$_5$)$_4$]	2075 s, 2034 s[c]	3086 w, 3052 m, 2998 w, 2980 w, 1583 m, 1479 vs, 1451 w, 1424 m, 1204 s, 1173 s, 1154 s, 1070 w, 1020 m, 1003 w, 930 vs, 868 w, 770 vs, 761 w, 748 w, 733 vs, 720 m, 707 vs, 689 s, 609 s, 601 s, 574 s, 559 s, 496 m, 463 w
π-C$_5$H$_5$Fe(CO)P(C$_2$H$_5$)$_3$I	1944[c]	
π-C$_5$H$_5$Fe(CO)P(O-i-C$_3$H$_7$)$_3$I	1960[c]	
π-C$_5$H$_5$Fe(CO)P(OC$_6$H$_5$)$_3$I	1979[c]	
π-C$_5$H$_5$Fe(CO)$_2$I	2040 s, 1996 s[c]	

[a] Abbreviations: w, weak; m, medium; s, strong; vs, very strong.   [b] Measured in cyclohexane.   [c] Measured in dichloromethane.
[d] Measured in KBr disks.

band of one isomer is approximately equal to the frequency of the corresponding mode of the other isomer. Similar explanations have been used to account for the single bridging carbonyl stretching peak in the spectrum of [π-C$_5$H$_5$Fe(CO)$_2$]$_2$.[13–15]   The fact that only two peaks are observed in the nmr spectra of (π-C$_5$H$_5$)$_2$-Fe$_2$(CO)$_3$L [L = P(C$_6$H$_5$)$_3$, P(OCH$_3$)$_3$, P(OC$_2$H$_5$)$_3$, P(O-i-C$_3$H$_7$)$_3$, P(O-n-C$_4$H$_9$)$_3$, and P(OC$_6$H$_5$)$_3$] at 38° must also be reconciled with the isomerism proposed above. It is thus suggested, by analogy with the explanation proposed to account for the single peak in the spectra of [π-C$_5$H$_5$Fe(CO)$_2$]$_2$ and [π-C$_5$H$_5$Ru(CO)$_2$]$_2$, that a rapid exchange between the isomers occurs.[13,14]

The infrared spectra of the monosubstituted deriva-

tives in KBr disks contain one peak in the terminal region and one peak in the bridging carbonyl stretching region; this latter peak is split slightly for most compounds. This indicates that in the "solid solution" phase all of the compounds are present as either the carbonyl-bridged isomer A or as the bridged isomer C. The halocarbon mull spectra are in general more complex than the corresponding KBr spectra and show splitting of the terminal and the bridging carbonyl peaks. This can be attributed to different molecular sites in the unit cell, as is the case found for [π-C$_5$H$_5$Fe(CO)$_2$]$_2$.[16] The solid-state spectrum of (π-C$_5$H$_5$)$_2$Fe$_2$(CO)$_3$P-(OC$_6$H$_5$)$_3$ is unusual in that the splitting of the carbonyl peaks is much larger than that normally associated with different molecular site symmetries (see Figure 2).

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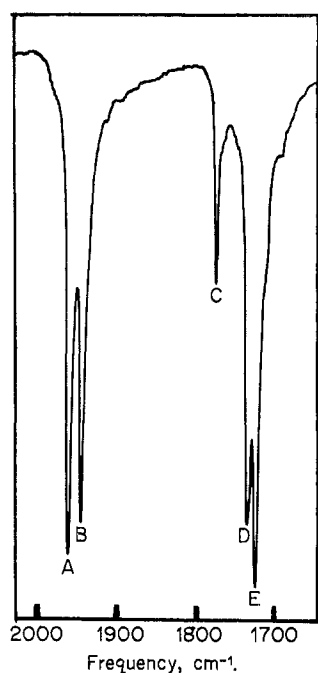
Figure 2.—Infrared spectrum of $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3P(OC_6H_5)_3$ in the C–O stretching region (Nujol mull): A, 1962 cm^{-1}; B, 1945 cm^{-1}; C, 1779 cm^{-1}; D, 1737 cm^{-1}; E, 1725 cm^{-1}.

With the difference in the frequency of the two terminal carbonyl stretching peaks being of the same order as the difference between the two terminal carbonyl peaks in the solution infrared spectrum of this compound, it is tempting to suggest that two different isomers occur in the unit cell as has recently been found for $Fe_3(CO)_{11}$-$P(C_6H_5)_3$.[17] It should be noted that the KBr spectra revert to the corresponding halocarbon mull spectra with time.

It has been previously noted that the replacement of the terminal carbonyl groups in $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ by the bidentate ligands $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ (n = 1–3) lowers the frequency of the bridging carbonyl stretching band considerably.[10] Table II shows that substitution of a single terminal carbonyl in the iron dimer by a tertiary phosphine or tertiary phosphite also lowers the frequency of this band but not to the same extent. A similar lowering of the frequency of terminal and ketonic carbonyl stretching modes in carbonyl derivatives as a result of carbonyl replacement has been explained in terms of an increase in π-bonding between the metal atom and the remaining carbonyl groups. The increase in the electron density on the metal atom as a result of the over-all stronger (σ–π) donor ability of the phosphorus donor ligand compared with carbon monoxide is redistributed into the antibonding orbitals of the carbonyl groups.[18] It is now suggested that a similar π-bonding mechanism operates between the metal atom and the bridging carbonyl groups in the above compounds.

Previous studies on the substitution reactions of the

dinuclear metal carbonyls $Mn_2(CO)_{10}$,[19] $Co_2(CO)_8$,[20] and $[\pi\text{-}C_5H_5Mo(CO)_3]_2$[12] with various tertiary phosphines in solution have shown that neutral or ionic bis-substituted complexes are readily formed. Monosubstituted derivatives of the above dinuclear carbonyl compounds have been isolated but their syntheses either employed indirect methods or were performed under carefully controlled experimental conditions.[12,21,22] Furthermore many monosubstituted complexes disproportionate in solution to the bis-substituted derivatives and the parent compounds.[12] The inability of the phosphorus donor ligands studied here to replace more than one carbonyl group in $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ under the experimental conditions employed is thus unusual. It is suggested that when one terminal carbonyl group in $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ is replaced by a stronger donor ligand, the resultant increase in electron density on the iron atom to which this ligand is bonded is transmitted *via* the bridging carbonyl groups to the other iron atom. As a consequence the remaining terminal carbonyl will be more strongly bonded; an increase in the metal–carbon bond order will be reflected in the frequency of the terminal carbonyl stretching mode and an over-all lowering of frequency of this mode from $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ to $(\pi\text{-}C_2H_5)_2Fe_2(CO)_3L$ is indeed found. Although other factors might be operative, a strengthening of the metal–terminal carbonyl bond serves as a possible explanation for the inability to replace more than one carbonyl group above. The retention of the bridging carbonyl groups of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ on substitution by phosphorus donor ligands is a further unusual feature associated with this study. In contrast, while the isomer of $Co_2(CO)_8$ containing bridging carbonyl groups is present in about equimolar amounts with the nonbridged form in solution,[23] the substituted derivatives occur in most cases exclusively as the nonbridged isomer in solution.[20,24]

It is well established that the reaction of neutral dinuclear metal carbonyl derivatives containing a metal–metal bond with iodine involves symmetric cleavage of the parent compound to form neutral iodo derivatives. For instance, the derivatives $Mn(CO)_5I$,[25] $\pi\text{-}C_5H_5Mo$-$(CO)_3I$,[26] and $\pi\text{-}C_5H_5Fe(CO)_2I$[27] are synthesized by this method from $Mn_2(CO)_{10}$, $[\pi\text{-}C_5H_5Mo(CO)_3]_2$, and $[\pi\text{-}C_5H_5Fe(CO)_2]_2$, respectively. It is thus expected that treatment of $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3L$ (L = ligand) with iodine would afford $\pi\text{-}C_5H_5Fe(CO)_2I$ and $\pi\text{-}C_5H_5Fe(CO)LI$ in equimolar amounts. The reaction of $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3L$ [L = $P(C_2H_5)_3$, $P(O\text{-}i\text{-}C_3H_7)_3$,

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$P(OC_6H_5)_3$] with iodine in dichloromethane was shown by infrared spectroscopy to afford a third product in addition to $\pi\text{-}C_5H_5Fe(CO)_2I$ and $\pi\text{-}C_5H_5Fe(CO)LI$; these three compounds were formed in approximately equal amounts. When this iodination was performed in benzene, however, the unknown product separated out while trace quantities of $\pi\text{-}C_5H_5Fe(CO)_2I$ and $\pi\text{-}C_5H_5Fe(CO)LI$ remained in the benzene solution. The precipitate was shown to be ionic and characterization of the tetraphenylborate derivative showed it to be $[\pi\text{-}C_5H_5Fe(CO)_2L]B(C_6H_5)_4$. The neutral compounds $\pi\text{-}C_5H_5Fe(CO)LI$ were identified by comparing their infrared spectra with the spectra of authentic samples previously synthesized from $\pi\text{-}C_5H_5Fe(CO)_2I$.[28]

The physical and spectroscopic data for the ionic complexes are given in the tables. Conductivity data and spectroscopic evidence show, respectively, these derivatives to be 1:1 electrolytes in acetone and diamagnetic. The infrared spectra of these compounds in solution contain two peaks corresponding to C–O stretching modes; the frequencies decrease with the increase of the over-all (σ–π) donor ability of the phos-

phorus donor ligand as expected. The single cyclopentadienyl proton resonance in the nmr spectra of these ionic compounds is split into a doublet due to phosphorus–hydrogen coupling. The coupling constant could only be measured for the compounds containing the ligands $P(C_2H_5)_3$ and $P(O\text{-}i\text{-}C_3H_7)_3$.

The formation of both ionic and neutral compounds in the iodination of the monosubstituted derivatives demonstrates that this reaction occurs by at least two mechanistic pathways, one involving a symmetric cleavage and the other an asymmetric cleavage of the dinuclear parent. A similar scheme has been proposed for the halogenation of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ on the basis of the isolation of $[\pi\text{-}C_5H_5Fe(CO)_3]X$ and $\pi\text{-}C_5H_5Fe(CO)_2X$ (X = halogen) from the reaction mixture.[29]

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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER, BRITISH COLUMBIA, CANADA

Five-Coordinate Iron Carbonyl Complexes with Fluorocarbon-Bridged Ligands

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The fluorocarbon-bridged di(tertiary phosphines) ffos and $f_6$fos react with iron pentacarbonyl to yield the compounds ffosFe(CO)$_3$, ffosFe(CO)$_4$, and $f_6$fosFe(CO)$_3$. A related di(tertiary arsine) gives ffarsFe(CO)$_4$ and ffarsFe$_2$(CO)$_8$. The Fe(CO)$_3$ compounds have C$_{2v}$ symmetry and the structures are probably based on a distorted trigonal bipyramid with equatorial–equatorial substitution. The ligands act, respectively, as monodentate and bridging groups in the Fe(CO)$_4$ and Fe$_2$(CO)$_8$ compounds. The Mössbauer spectra of these and related compounds show little variation in isomer shift. However it seems that the Mössbauer quadrupole splittings can be used to distinguish between *cis*- and *trans*-disubstituted derivatives of a trigonal-bipyramidal iron(0) complex. Other spectroscopic data for these compounds are given. In particular the carbonyl infrared spectra show some interesting features.

Tertiary phosphine and arsine derivatives of iron pentacarbonyl of the sorts $R_3EFe(CO)_4$ and $(R_3E)_2Fe(CO)_3$ are well known and have been obtained by a variety of methods.[1] It has been shown[1c] that the triphenylphosphine derivatives have the trigonal-bipyramidal structure of the parent carbonyl with monosubstitution occurring in an apical position (C$_{3v}$ symmetry with three CO stretching bands) and disubstitution in both apical positions (D$_{3h}$ symmetry with one CO stretching band). Chelating di(tertiary phosphines and arsines) also react with iron carbonyl compounds to yield complexes such as diarsFe(CO)$_3$,

diphosFe(CO)$_3$, and diphosFe$_2$(CO)$_8$[1d,1e,2] (diphos = 1,2-bis(diphenylphosphino)ethane and diars = 1,2-bis(dimethylarsino)benzene). The Fe$_2$(CO)$_8$ derivative is a bridged compound. Nothing appears to have been written about the structures of the chelate complexes, although if a trigonal-bipyramidal structure is assumed, it is apparent that the ligand could be coordinated in either an equatorial–equatorial or apical–equatorial manner (Figure 1).

The present paper describes the preparation and possible structures of some new five-coordinate iron carbonyl complexes of the novel fluorocarbon-bridged ligands $D\overline{C=CD(CF_2)_n CF_2}$: ffos, $n = 1$, D $= (C_6H_5)_2P$; $f_6$fos, $n = 2$, D $= (C_6H_5)_2P$; ffars, $n = 1$,

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