pendence exhibited by the dicyclohexyl, dimethyl, and piperidyl complexes is shown in Figure 7.

Unlike the iron(II) case,[11,12] it has not been shown definitely that the isomer shift of an iron(III) complex changes upon change from the low- to the high-spin state. For this reason, the lack of correlation between the susceptibility and isomer shift data cannot be employed as unequivocal evidence against the $^2T_{2g}$–$^6A_{1g}$ equilibrium hypothesis.

Conclusion

The problem of accounting for the unusual magnetic behavior of the tris(*N*,*N*-dialkyldithiocarbamate)iron(III) complexes must be reexamined. The Mössbauer spectra never show the presence of two doublets which would be expected if two spin states were in equilibrium. The isomer shift data show no indication of two states in equilibrium. The temperature dependence of the quadrupole splitting of these complexes falls short of that expected on the basis of a $^2T_{2g}$–$^6A_{1g}$ equilibrium. Perhaps the magnetic susceptibility and Mössbauer spectral data of these complexes could be better explained in terms of spin-mixed states.[26]

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CONTRIBUTION FROM THE RESEARCH AND PROCESS DEVELOPMENT DEPARTMENT,
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Reactions of Metal Carbonyl Derivatives. VIII.[1] Oxidation Reactions of Some Ditertiary Phosphine Derivatives of Bis(dicarbonyl-π-cyclopentadienyliron)[2]

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Treatment of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2$ [R = CH_2, C_2H_2, C_2H_4, C_3H_6, $N(C_2H_5)$] with limited quantities of iodine in benzene leads to the formation of the cations $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]^+$ which separate from solution as the triiodides. The corresponding tetraphenylboron derivatives are obtained by treating the above neutral compounds with iodine or bromine in benzene in the presence of $NaB(C_6H_5)_4$. Oxidation of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2$ to the cationic species is also readily effected by $AgClO_4$ and $AgSbF_6$. These cations which have magnetic moments corresponding to one unpaired electron per two iron atoms are reduced to the neutral parent compounds by reducing agents such as hydrazine and iodide ions. Reaction of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PCH_2P(C_6H_5)_2$ with excess iodine in dichloromethane affords $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PCH_2P(C_6H_5)_2]^+$ containing a bridging iodine as well as a bridging diphosphine ligand. In contrast the corresponding reaction involving $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ yields $[(\pi\text{-}C_5H_5)Fe(CO)_2L]^+$ [L is an adduct of $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$]. The neutral iodo derivative $\{(\pi\text{-}C_5H_5)Fe(CO)I\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ is shown to be also formed in the reaction of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ with iodine under the appropriate experimental conditions. Various physical and spectroscopic properties of $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]$(anion) and $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PCH_2P(C_6H_5)_2]$(anion) are discussed.

Introduction

Metal–metal bonds in organometallic complexes, being a source of electron density, readily participate in electrophilic reactions. For instance it has been reported that a metal–metal bond in $Os_3(CO)_{12}$ is readily cleaved as a result of protonic attack by H_2SO_4 to afford a cation, $[HOs_3(CO)_{12}]^+$, in which a hydridic group bridges two osmium atoms.[3] Electrophilic attack of halogens on metal–metal bonds in polynuclear carbonyl derivatives also results in the cleavage of these bonds. Thus $[Cr(CO)_5I]^-$,[4] $M(CO)_5X$ (M = Mn, Tc, Re; X = Cl, Br, I),[5–7] $\{Fe(CO)_3P(CH_3)_2X\}_2$ (X = Cl, Br, I),[8,9] $(\pi\text{-}C_5H_5)Mo(CO)_3I$,[10] $(\pi\text{-}C_5H_5)M'(CO)_2X$ (M′ = Fe, Ru, Os; X = Cl, Br, I),[11–16] and $(\pi\text{-}C_5H_5)M''(CO)I$ (M″ = Ni, Pt)[17,18] have been synthesized by treatment of $[Cr(CO)_5]_2^{2-}$, $\{M(CO)_5\}_2$, $\{Fe(CO)_3P(CH_3)_2\}_2$, $\{(\pi\text{-}C_5H_5)Mo(CO)_3\}_2$, $\{(\pi\text{-}C_5H_5)$-

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Table I

Colors, Conductivity, and Analytical and Molecular Weight Data

Compound	Color	Conductivity,[a] ohm^{-1} cm^2 mol^{-1}	Analyses, % C Calcd	C Found	H Calcd	H Found	Others Calcd	Others Found	Mol Wt Calcd	Mol Wt Found
$[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PCH_2P(C_6H_5)_2]B(C_6H_5)_4$[b]	Purple-brown	101	73.2	73.1	5.2	5.1	Fe, 11.2	11.0		
$[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PCH_2P(C_6H_5)_2]SbF_6$	Purple-brown	121	48.4	48.6	3.5	3.7	P, 6.8	6.5		
$[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2]B(C_6H_5)_4$	Brown	93	73.3	73.4	5.4	5.4	P, 6.1	5.9		
$[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2]SbF_6$[c]	Brown		49.5	46.3	3.7	3.7	P, 6.7	6.1		
$[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_3H_6P(C_6H_5)_2]B(C_6H_5)_4$[c]	Brown	89	73.5	72.0	5.5	5.4				
$[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2]SbF_6$	Purple	135	48.2	48.0	3.7	3.6	P, 6.5 N, 1.5	6.5 1.5		
$[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PCH_2P(C_6H_5)_2]B(C_6H_5)_4$	Yellow-brown	88	64.9	65.2	4.6	4.4	I, 11.3	11.7		
$[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PCH_2P(C_6H_5)_2]SbF_6$	Yellow-brown	138	42.5	42.1	3.1	3.1	I, 12.1	12.2		
$[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2]Cl_2$	Yellow	259	58.2	58.3	4.2	4.6	Cl, 8.7	8.9		
$[(\pi\text{-}C_5H_5)Fe(CO)(C_6H_5)_2PC_2H_2P(C_6H_5)_2]SbF_6$	Yellow	97	49.2	49.1	3.5	3.4	Fe, 7.2	6.9		
$[(\pi\text{-}C_5H_5)Fe(CO)(C_6H_5)_2PC_2H_4P(C_6H_5)_2]B(C_6H_5)_4$	Yellow	86	77.6	77.5	5.7	5.9	Fe, 6.4	6.3		
$[(\pi\text{-}C_5H_5)Fe(CO)(C_6H_5)_2PC_2H_4P(C_6H_5)_2]BF_4$	Yellow	99	60.6	61.0	4.6	5.1				
$(\pi\text{-}C_5H_5)Fe(CO)(C_6H_5)_2PCH_2P(C_6H_5)_2I$	Green	16	56.5	56.5	4.1	4.1	I, 19.2	18.4	660	676
$\{(\pi\text{-}C_5H_5)Fe(CO)I\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$	Green	14	48.0	48.4	3.6	3.3	I, 26.7	26.9		

[a] $(1–10) \times 10^{-4}$ M solutions in acetone. [b] Measured in benzene. [c] Could not be obtained analytically pure; solvent occluded.

$M'(CO)_2\}_2$, and $\{(\pi\text{-}C_5H_5)M''(CO)\}_2$, respectively, with the appropriate halogens.

Detailed studies of the mechanism of halogenation of $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2$ and $\{(\pi\text{-}C_5H_5)Ru(CO)_2\}_2$ have revealed that bridged halogeno species of the type $[\{(\pi\text{-}C_5H_5)M(CO)_2\}_2X]^+$ (M = Fe, Ru; X = halogen) are initially formed in these reactions and that nucleophilic attack of halide ions on the latter yields $(\pi\text{-}C_5H_5)M(CO)_2X$.[19,20]

The reactions of metal carbonyl complexes with halogens which do not involve the oxidative addition of the latter are not well documented. An isolated example is the halogenation of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_4$ to yield $[(\pi\text{-}C_5H_5)Fe(CO)]_4{}^+$.[21,22]

A study of the reactions of the bridged derivatives $\{(\pi\text{-}C_6H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2$ [R = CH_2, C_2H_2, C_2H_4, C_3H_6, $N(C_2H_5)$] with halogens has now been made and the results thereof are reported here.

Experimental Section

The compounds $(\pi\text{-}C_5H_5)Fe(CO)_2X$ (X = Cl, I) and $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2$ [R = CH_2, C_2H_2, C_2H_4, C_3H_6, $N(C_2H_5)$] were synthesized by methods described previously.[13,23,24] All experiments were performed under a nitrogen atmosphere. The infrared, electronic absorption, nmr, and esr spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer, on a Beckmann DU-2 spectrophotometer, on Varian HA-100 and A-60A instruments, and on a Varian 4502 instrument, respectively. Magnetic susceptibilities were determined either by the Gouy method on a Newport Instruments Gouy balance or by means of a noncommercial vibrating-sample magnetometer. Conductivities were determined using a Metrohm E365B conductoscope (Table I). The molecular weights were measured using a Mechrolab vapor pressure osmometer. The elemental analyses were obtained by the Alfred Bernhardt Microanalytical Laboratory, Elbach-über-Engelskirchen, West Germany, by Messrs. K. P. Kunz and G. J. Roberts, National Chemical Research Laboratory, CSIR, Pretoria, and by Mrs. A. F. Beckett, Microanalytical Section, South African Iron and Steel Industrial Corporation Limited.

Preparation of the Compounds of the Type $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]$(anion). (i) $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]B(C_6H_5)_4$ **(R = CH_2, C_2H_4, C_3H_6).**—A solution of iodine (0.18 g, 0.7 mmol) in toluene (*ca.* 20 ml) was added dropwise to a stirred solution of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PCH_2P(C_6H_5)_2$ (0.48 g, 0.7 mmol) or $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (0.49 g, 0.7 mmol) or $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_3H_6P(C_6H_5)_2$ (0.50 g, 0.7 mmol) and $NaB(C_6H_5)_4$ (0.5 g, 1.5 mmol) in toluene (*ca.* 60 ml) and ethanol (*ca.* 5 ml) at 0°. The brown-purple product which separated from solution was crystallized from dichloromethane–petroleum ether (bp 40–60°); yield *ca.* 80%.

(ii) $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]SbF_6$ **[R = CH_2, C_2H_4, $N(C_2H_5)$].**—A solution of $AgSbF_6$ (0.24 g, 0.7 mmol) in benzene (*ca.* 50 ml) was added to a stirred solution of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PCH_2P(C_6H_5)_2$ (0.48 g, 0.7 mmol) or $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (0.49 g, 0.7 mmol) or $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$ (0.50 g, 0.7 mmol) in benzene (*ca.* 60 ml). The precipitate which separated from solution was extracted with dichloromethane and the solution filtered. The solvent was removed under reduced pressure to afford a brown-purple residue which was crystallized from dichloromethane–petroleum ether; yield *ca.* 80%.

Preparation of $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PCH_2P(C_6H_5)_2]$(anion) [anion = $B(C_6H_5)_4$, SbF_6] through Reaction of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PCH_2P(C_6H_5)_2$ with Excess Iodine in Dichloromethane.—A solution of iodine (0.36 g, 1.4 mmol) in dichloromethane (*ca.* 30 ml) was added dropwise to a stirred solution of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PCH_2P(C_6H_5)_2$ (0.48 g, 0.7 mmol) in dichloromethane (*ca.* 60 ml) and the resultant solution stirred for 25 hr. $NaB(C_6H_5)_4$ (0.5 g, 1.5 mmol) or $AgSbF_6$ (0.38 g, 1.1 mmol) in methanol (*ca.* 30 ml) was added and the solution was filtered where appropriate. The dichloromethane was removed under reduced pressure and the methanol solution stood at −5° for a short period. The compound which separated from solution was crystallized from dichloromethane–petroleum ether; yield *ca.* 55%.

Reaction of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ with Excess Iodine.—A solution of iodine (0.71 g, 2.8 mmol) in dichloromethane (*ca.* 30 ml) was added dropwise to a stirred solution of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (0.49 g, 0.7 mmol) in dichloromethane (*ca.* 60 ml) and the resultant solution stirred for 10 min. $NaB(C_6H_5)_4$ (0.5 g, 1.5 mmol) in methanol (*ca.* 20 ml) and benzene (*ca.* 30 ml) was added. The dichloromethane was slowly removed under reduced pressure. The yellow compound which separated from solution was washed with benzene and crystallized from dichloromethane–petroleum ether. Satisfactory analyses for the final product could not be obtained but it was identified as a derivative of the type $[(\pi\text{-}C_5H_5)Fe(CO)_2(\text{ligand})]B(C_6H_5)_4$ (ligand is an adduct of $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$) by means of infrared spectroscopy (see Discussion).

Reaction of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2$ (R = CH_2, C_2H_4) with Excess $AgClO_4$.—A solution of $AgClO_4$ (0.8 g, 3.4

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mmol) in acetone (*ca.* 30 ml) was added to a solution of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PCH_2P(C_6H_5)_2$ (0.48 g, 0.7 mmol) or $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (0.49 g, 0.7 mmol) in dichloromethane (*ca.* 50 ml) and the resultant solution was stirred for 5 hr. The solution was concentrated to a small volume and benzene was slowly added. The compound which separated from solution was crystallized from dichloromethane–petroleum ether. Satisfactory analyses could not be obtained for both products but they were identified as derivatives of the type $[(\pi\text{-}C_5H_5)Fe(CO)_2(\text{ligand})]B(C_6H_5)_4$ (ligand is an adduct of $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ ($n = 1, 2$)) by means of infrared spectroscopy (see Discussion).

Reaction of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_2P(C_6H_5)_2$ with Excess $AgSbF_6$. Preparation of $[(\pi\text{-}C_5H_5)Fe(CO)(C_6H_5)_2PC_2H_2P(C_6H_5)_2]SbF_6$.—A solution of $AgSbF_6$ (0.5 g, 1.4 mmol) in acetone (*ca.* 30 ml) was added to a solution of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_2P(C_6H_5)_2$ (0.49 g, 0.7 mmol) in acetone (*ca.* 50 ml) and the resultant solution was irradiated with ultraviolet light for 5 hr. The solution was filtered and the solvent removed under reduced pressure. The residue was extracted with dichloromethane and the solution filtered. The solution was concentrated to a small volume and methanol added. The yellow crystalline compound which separated was recrystallized from dichloromethane–methanol; yield *ca.* 60%.

$[(\pi\text{-}C_5H_5)Fe(CO)(C_6H_5)_2PC_2H_2P(C_6H_5)_2]SbF_6$ is more conveniently synthesized from $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ by a method analogous to that employed in the synthesis of $[(\pi\text{-}C_5H_5)Fe(CO)(C_6H_5)_2PC_2H_4P(C_6H_5)_2]B(C_6H_5)_4$ from $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$, however.

Reaction of Iodine with $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ in Benzene under Reflux. Preparation of $\{(\pi\text{-}C_5H_5)Fe(CO)I\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$.—A solution of iodine (0.21 g, 0.8 mmol) in benzene (*ca.* 20 ml) was added dropwise to a stirred solution of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (0.49 g, 0.7 mmol) in benzene (*ca.* 60 ml) under reflux. The resultant solution was refluxed for a further 30 min. The solution was filtered and the benzene removed under reduced pressure. The green residue was crystallized from dichloromethane–petroleum ether; yield *ca.* 55%.

Preparation of $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2]Cl_2$.—A solution of $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ (0.4 g, 1.9 mmol) in benzene (*ca.* 30 ml) was added to a benzene solution (*ca.* 50 ml) of $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (0.4 g, 1.0 mmol) and the resultant mixture allowed to stand at room temperature for 15 hr. The yellow crystalline compound which separated from solution was washed with benzene and dried thoroughly; yield *ca.* 75%.

Preparation of $[(\pi\text{-}C_5H_5)Fe(CO)(C_6H_5)_2PC_2H_4P(C_6H_5)_2]$(anion) [anion = BF_4, $B(C_6H_5)_4$].—A solution of $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ (0.5 g, 2.3 mmol) and $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (1.2 g, 3.0 mmol) in tetrahydrofuran (*ca.* 100 ml) was irradiated with ultraviolet light for 5 hr. $NaB(C_6H_5)_4$ (0.9 g, 2.6 mmol) in ethanol (*ca.* 40 ml) or $NaBF_4$ (0.3 g, 2.7 mmol) in water (*ca.* 15 ml) was added. The tetrahydrofuran was slowly removed under reduced pressure. The yellow product which separated from solution was crystallized from dichloromethane–petroleum ether; yield *ca.* 75%.

Preparation of $(\pi\text{-}C_5H_5)Fe(CO)(C_6H_5)_2PCH_2P(C_6H_5)_2I$.—A solution of $(\pi\text{-}C_5H_5)Fe(CO)_2I$ (0.3 g, 1.0 mmol) and $(C_6H_5)_2PCH_2P(C_6H_5)_2$ (0.5 g, 1.3 mmol) in benzene (*ca.* 60 ml) was refluxed for 8 hr. The solution was filtered and the solvent removed under reduced pressure. Purification of the product was achieved by crystallization from dichloromethane–petroleum ether; yield *ca.* 60%.

Preparation of $\{(\pi\text{-}C_5H_5)Fe(CO)I\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ from $(\pi\text{-}C_5H_5)Fe(CO)_2I$.—A solution of $(\pi\text{-}C_5H_5)Fe(CO)_2I$ (0.3 g, 1.0 mmol) and $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (0.5 g, 1.3 mmol) in benzene (*ca.* 60 ml) was refluxed for 8 hr. The solution was filtered and the solvent removed under reduced pressure. Purification of the product was achieved by crystallization from dichloromethane–petroleum ether; yield *ca.* 65%.

Results

By analogy with the halogenation reactions of $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2$[11–13,19] discussed above, the reactions of bis-substituted derivatives of the type $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2$ (I) with iodine are expected to yield, as products, the neutral compounds $\{(\pi\text{-}C_5H_5)Fe(CO)I\}_2(C_6H_5)_2PRP(C_6H_5)_2$ (V) and possibly to involve the ionic species $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PRP(C_6H_5)_2]^+$ (III) as intermediates. The compound $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ was found to react with iodine in benzene to form a brown ionic product which separated from solution as a triiodide. Difficulty was experienced in characterizing this derivative however. The corresponding tetraphenylborate was obtained by performing the above reaction in the presence of sodium tetraphenylborate. This compound was characterized as the paramagnetic, halogen-free derivative $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2]B(C_6H_5)_4$ (II) and not $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PC_2H_4P(C_6H_5)_2]B(C_6H_5)_4$ (III) as expected. The neutral derivatives $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2$ ($R = CH_2$, C_3H_6) were similarly treated with iodine in benzene in the presence of $NaB(C_6H_5)_4$ and analogous paramagnetic products, *viz.*, $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]B(C_6H_5)_4$, were isolated.

It was further established that oxidation of the bis-substituted derivatives of the type $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2$ (I) to the corresponding paramagnetic species is also readily effected by salts of silver(I). Thus treatment of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2$ [$R = CH_2$, C_2H_2, C_2H_4, $N(C_2H_5)$] with an equimolar amount of $AgSbF_6$ or $AgClO_4$ in benzene readily afforded $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]$(anion) (II) (anion = ClO_4, SbF_6).

The reactions of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2$ (I) [$R = CH_2$, C_2H_2, C_2H_4, $N(C_2H_5)$] with iodine in dichloromethane were monitored by means of infrared spectroscopy and it was established that they are extremely rapid and that the formation of the cationic species $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]^+$ (II) is complete after the addition of 1 mol of iodine to 2 mol of the parent complex. It was further apparent from these latter studies that apart from $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_2P(C_6H_5)_2]$(anion), the paramagnetic derivatives are thermodynamically stable in solution and that their isolation from the iodination reactions performed in benzene was not necessarily a result of their enforced precipitation from solution.

The ionic compounds $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]B(C_6H_5)_4$ (II) [$R = CH_2$, C_2H_4, C_3H_6, $N(C_2H_5)$] were readily reduced to the neutral complexes $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2$ (I) by strong reducing agents such as hydrazine in solution. Slow reduction was also effected by mild reducing agents such as I^-. It is thus apparent that the equilibrium

$$2\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2 + I_2 \rightleftharpoons 2[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]^+ + 2I^-$$

is established in solution.

$\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PCH_2P(C_6H_5)_2$ (I) was found to react with excess iodine in dichloromethane to afford a cationic species whose infrared spectrum contained a single C–O stretching band at *ca.* 1980 cm^{-1}. This cation was isolated as the tetraphenylborate and hexafluoroantimonate salts and characterized as $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PCH_2P(C_6H_5)_2]^+$ (III) containing both a bridging iodine and a bridging ditertiary phosphine ligand. A second product was also observed to be formed in very low yield in this reaction but it could not be separated from the major product.

It was identified as a compound of the type $[(\pi\text{-}C_5H_5)Fe(CO)_2(\text{ligand})](\text{anion})$ (IV) by means of infrared spectroscopy [ν(C–O) 2060 (s) and 2019 cm^{-1} (s), measured in dichloromethane] (see Discussion). Similar products to those above were formed in the reaction of $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PCH_2P(C_6H_5)_2]ClO_4$ (II) with excess iodine in dichloromethane. Although the yield of the compound of the type $[(\pi\text{-}C_5H_5)Fe(CO)_2(\text{ligand})](\text{anion})$ in this latter reaction was approximately half that of the product $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PCH_2P(C_6H_5)_2](\text{anion})$, it could still not be isolated pure. The compound $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PCH_2P(C_6H_5)_2](\text{anion})$ (III) may be regarded as a bis-substituted derivative of $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2I](\text{anion})$. However, whereas the latter reacts extremely readily with iodide ions in solution to yield $(\pi\text{-}C_5H_5)Fe(CO)_2I$,[19] the former proved to be inert toward this nucleophile in solution.

The reaction of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (I) with excess iodine in dichloromethane also afforded two products, the relative yield of which depended on the molar ratio of the two reactants. For instance the two compounds were formed in approximately equimolar amounts, as determined by infrared analysis, in the reaction employing a parent dimer to iodine molar ratio of 1:2 whereas the yield of the one was negligible in the reaction employing a tenfold excess of iodine. The major product in this latter reaction was readily isolated in crystalline form as the tetraphenylborate salt which was identified as a compound of the type $[(\pi\text{-}C_5H_5)Fe(CO)_2(\text{ligand})]B(C_6H_5)_4$ (IV) by means of infrared analysis [ν(C–O) 2055 (s) and 2013 cm^{-1} (s), measured in dichloromethane]. The second product in the above reactions was characterized as the neutral iodo derivative $\{(\pi\text{-}C_5H_5)Fe(CO)I\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (V). Significantly the yield of this compound was increased by performing the iodination in the presence of iodide ions and, further, was obtained in highest yield by dropwise addition of iodine in benzene to a benzene solution of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ under reflux. Similar compounds to the two discussed above were formed in the reactions of $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2]ClO_4$ (II) with excess iodine in dichloromethane.

As mentioned previously the reaction of 2 mol of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_2P(C_6H_5)_2$ (I) with 1 mol of iodine in dichloromethane affords $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_2P(C_6H_5)_2]^+$ (II). Salts of this cation could not be isolated however owing to the rapid decomposition of this species in solution to a product whose infrared spectrum is consistent with it being of the type $[(\pi\text{-}C_5H_5)Fe(CO)_2(\text{ligand})](\text{anion})$ (IV) [ν(C–O) 2061 (s) and 2020 cm^{-1} (s), measured in dichloromethane]. A derivative with a single C–O stretching band at 1986 cm^{-1} and possibly of the type $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PC_2H_2P(C_6H_5)_2](\text{anion})$ (III) was formed on treatment of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_2P(C_6H_5)_2$ with excess iodine in dichloromethane. The simultaneous formation of the mononuclear compound previously discussed, as a result of the decomposition of the paramagnetic species initially formed, prevented the isolation of the bridged derivative however.

In contrast to the cations $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]^+$ (II) (R = CH_2, C_2H_2, C_2H_4), $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2]^+$ was found to be somewhat unreactive toward iodine. For instance it was observed that $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2]^+$ is still the major product in the reaction of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$ with a tenfold excess of iodine in dichloromethane even after a reaction period of 24 hr; the low yield of the second product in this reaction prevented its isolation.

The reactions of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2$ (I) [R = CH_2, C_2H_4, $N(C_2H_5)$] with excess silver perchlorate and hexafluoroantimonate in dichloromethane–acetone afforded products of the type $[(\pi\text{-}C_5H_5)Fe(CO)_2(\text{ligand})](\text{anion})$ (IV) (anion = ClO_4, SbF_6). Although crystalline derivatives were isolated from the reactions involving $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2$ (R = CH_2, C_2H_4), satisfactory analyses could not be obtained. A similar type of compound was formed in the corresponding reaction involving $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_2P(C_6H_5)_2$. However this product slowly reverted to $[(\pi\text{-}C_5H_5)Fe(CO)(C_6H_5)_2PC_2H_2P(C_6H_5)_2](\text{anion})$ in solution; the rate of this conversion was considerably increased by irradiating the solution with ultraviolet light.

The reactions of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2$ (I) [R = CH_2, C_2H_2, C_2H_4, $N(C_2H_5)$] with bromine afforded products similar to the corresponding reactions involving iodine. In all reactions more than one product was formed however and this prevented their isolation.

To assist in the characterization of some of the products isolated in this study, the reactions of $(\pi\text{-}C_5H_5)Fe(CO)_2X$ (X = Cl, I) with several of the above ditertiary phosphines were studied. Treatment of $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ with $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ in benzene effected the displacement of the chloro group and afforded a yellow crystalline derivative characterized as $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2]Cl_2$.[25] Carbonyl replacement in $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ was effected by irradiating a tetrahydrofuran or acetone solution of $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ and $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ with ultraviolet light. The cationic species so formed was precipitated as the tetraphenylborate and tetrafluoroborate salts and characterized as $[(\pi\text{-}C_5H_5)Fe(CO)(C_6H_5)_2PC_2H_4P(C_6H_5)_2]^+$. Neutral products were obtained from the reactions of $(\pi\text{-}C_5H_5)Fe(CO)_2I$ with ditertiary phosphines. For instance the reaction of this iodo compound with $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ in a molar ratio of 2:1 in refluxing benzene gave $\{(\pi\text{-}C_5H_5)Fe(CO)I\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (V). In contrast, the corresponding reaction involving $(C_6H_5)_2PCH_2P(C_6H_5)_2$ afforded $(\pi\text{-}C_5H_5)Fe(CO)(C_6H_5)_2PCH_2P(C_6H_5)_2I$ and unreacted $(\pi\text{-}C_5H_5)Fe(CO)_2I$.

Discussion

The compounds $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2](\text{anion})$ (II) [anion = $B(C_6H_5)_4$, R = CH_2, C_2H_4, C_3H_6; anion = SbF_6, R = CH_2, C_2H_4, $N(C_2H_5)$] were characterized by elemental analysis as were all other derivatives synthesized in this study unless otherwise stated. The magnetic susceptibilities of the complexes $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]SbF_6$ [R = CH_2, C_2H_4, $N(C_2H_5)$], measured at room

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TABLE II

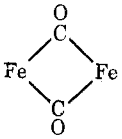
MAGNETIC AND INFRARED, NMR, VISIBLE, AND ESR SPECTRAL DATA

Compound	C–O str freq,[a,b] cm^{-1}	C_5H_5 proton resonances,[c,d] ppm	Visible spectral data[a]		Esr data[e]	Magnetic data[f]	
			λ_{max}, mμ	ε	g_1, g_2, g_3 (±0.01)	χ^{RT}_m, cm^3/mol	μ_{eff}, BM
$[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PCH_2P(C_6H_5)_2]B(C_6H_5)_4$	1826 m, 1772 s	vb	524	1932			
$[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PCH_2P(C_6H_6)_2]SbF_6$	1831 m, 1772 s	vb			2.00, 2.09	1126×10^{-6}	*Ca.* 2.0
$[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_2P(C_6H_5)_2]SbF_6$	*Ca.* 1860 ms, 1795 s						
$[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2]B(C_6H_5)_4$	*Ca.* 1835 m, 1780 s	vb	507	1131			
$[\{(\pi\text{-}C_5H_6)Fe(CO)\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2]SbF_6$	*Ca.* 1830 m, 1773 s	vb			2.00, 2.08, 2.28	1160×10^{-6}	*Ca.* 2.0
$[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_3H_6P(C_6H_5)_2]B(C_6H_5)_4$	1835 m, 1763 s	vb					
$[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2]SbF_6$	1798	vb	533	2056[g]	2.00, 2.09	987×10^{-6}	*Ca.* 1.9
$[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PCH_2P(C_6H_5)_2]B(C_6H_5)_4$	1984	5.67 b; 5.77 b[h]					
$[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PCH_2P(C_6H_5)_2]SbF_6$	1984	5.26 d, J_{PH} = 1.2 Hz 5.37 d, J_{PH} = 1.2 Hz[i]					
$[\{(\pi\text{-}C_5H_6)Fe(CO)_2\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2]Cl_2$	2053 s, 2008 s						
$[(\pi\text{-}C_5H_5)Fe(CO)(C_6H_5)_2PC_2H_2P(C_6H_5)_2]SbF_6$	1992	4.91 t, J_{PH} = 1.5 Hz[i]					
$[(\pi\text{-}C_5H_5)Fe(CO)(C_6H_5)_2PC_2H_4P(C_6H_5)_2]B(C_6H_5)_4$	1981	4.93 t, J_{PH} = 1.3 Hz[i]					
$[(\pi\text{-}C_5H_5)Fe(CO)(C_6H_5)_2PC_2H_4P(C_6H_5)_2]BF_4$	1980	5.12 b[h]					
$(\pi\text{-}C_5H_5)Fe(CO)(C_6H_5)_2PCH_2P(C_6H_5)_2I$	1950	5.62 d, J_{PH} = 1.5 Hz[h]					
$\{(\pi\text{-}C_5H_5)Fe(CO)I\}_2(C_6H_6)_2PC_2H_4P(C_6H_5)_2$	1948	5.66 b[h]					

[a] Measured in CH_2Cl_2. [b] Abbreviations: s, strong; ms, medium strong; m, medium. [c] τ scale (TMS reference). [d] Abbreviations: v, very; d, doublet; t, triplet; b, broad. [e] Measured in solid state at 77°K. [f] Measured in solid state at room temperature. [g] Values for tetraphenylborate. [h] Measured in $CDCl_3$. [i] Measured in CD_3COCD_3.

temperature, are recorded in Table II and correspond to magnetic moments of *ca.* 2.0, 2.0, and 1.9 BM, respectively, after the necessary diamagnetic corrections have been made. The *g* values obtained from the esr spectra of $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]SbF_6$ [R = CH_2, C_2H_4, $N(C_2H_5)$], measured as polycrystalline samples, are also reported in Table II.

The infrared spectra of $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]$(anion) [R = CH_2, C_2H_2, C_2H_4, C_3H_6, $N(C_2H_5)$; anion = $B(C_6H_5)_4$; SbF_6] in the C–O stretching region are summarized in Table II and contain peaks corresponding to bridging carbonyl groups only. The structure represented in Figure 1 is thus proposed for the cations of these derivatives and is analogous to that previously proposed for the neutral complexes of the type $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2$ (I).[24] Two infrared-active carbonyl stretching modes are predicted for $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2$ and $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2$ [R = CH_2, C_2H_2, C_2H_4, C_3H_6, $N(C_2H_5)$] but it is further expected that the A_1 mode will be of zero intensity for structures containing a planar



group. The appearance of a single bridging carbonyl stretching peak in the solution infrared spectra of these compounds has been previously noted and interpreted in terms of the FeC(O)FeC(O) group adopting a planar or near-planar configuration.[24,26,27] The presence of a single bridging carbonyl stretching mode in the spectrum of $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2]SbF_6$ is thus not inconsistent with the bridging carbonyl groups in this compound also adopting a planar configuration. Two bridging carbonyl stretching peaks are observed in the spectra of $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]$(anion) [R = CH_2, C_2H_2, C_2H_4, C_3H_6; anion = $B(C_6H_5)_4$, SbF_6], however. It is thus apparent that these compounds adopt a configuration in solution in which the carbonyl groups deviate considerably from planarity. It is not unreasonable to assume that the ratio of the intensities of the A_1 and B_1 modes is a measure of the bending of the FeC(O)FeC(O) ring about the Fe–Fe axis. On this basis the infrared data for $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]$(anion) are consistent with an increase in the deviation of the bridging carbonyl groups from planarity along the series R = $N(C_2H_5)$ < R = C_2H_4 < R = CH_2 ∼ R = C_3H_6 < R = C_2H_2. Significantly this series parallels a corresponding series relating to the relative rates of oxidation of these derivatives by iodine and Ag(I).

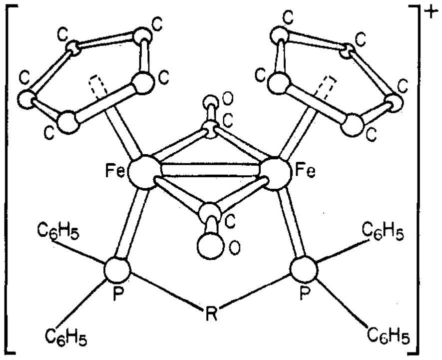


Figure 1.—Proposed structure for the cations $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]^+$ [R = CH_2, C_2H_2, C_2H_4, C_3H_6, $N(C_2H_5)$] showing the stereochemistry of the iron atoms only.

Both the magnetic moments and the *g* values of $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]SbF_6$ [R = CH_2, C_2H_4, and $N(C_2H_5)$] are consistent with these compounds containing one unpaired electron per two iron atoms. Although the possibility of the unpaired electron in the above paramagnetic species being delocalized over the FeC(O)FeC(O) ring cannot be eliminated on the above physical and spectroscopic data, it is suggested, on the basis of the known electrophilic properties of metal–metal bonds in organometallic derivatives, that the one-electron oxidation of compounds of the type $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2$ to give $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]^+$ involves the loss of an electron from the metal–metal bond in the neutral species and the forma-

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(27) R. D. Fischer, A. Vogler, and K. Noack, *J. Organometal. Chem.*, **7**, 135 (1967).

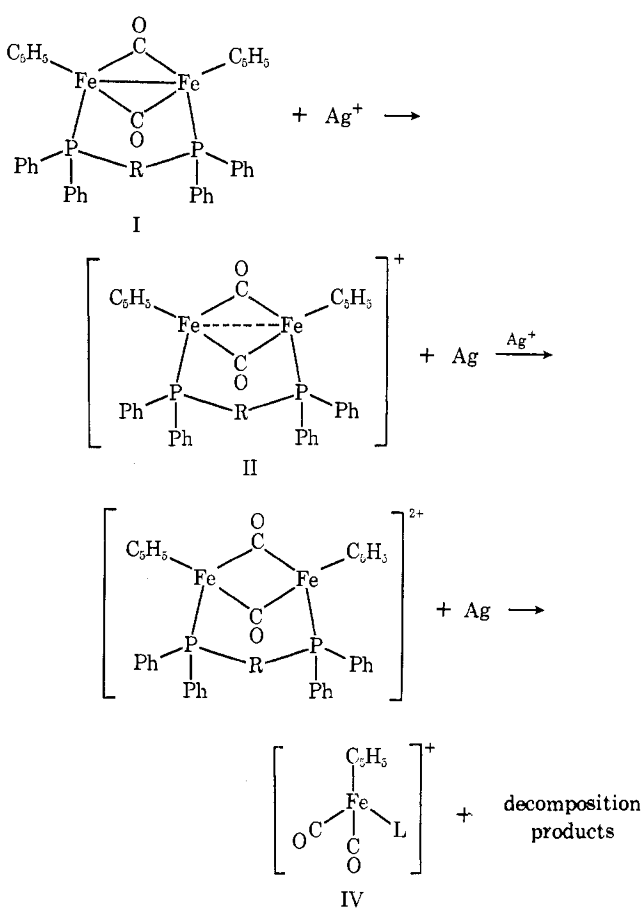
tion of ionic products containing a *one-electron metal–metal bond*.[28,29]

Two cyclopentadienyl proton resonances are observed in the nmr spectra of the bridged iodo derivatives, $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PCH_2P(C_6H_5)_2]$(anion) [anion = $B(C_6H_5)_4$, SbF_6]. The relative intensities of these peaks were found to vary with the anion and with the solvent employed. For instance, the peaks are of approximate equal intensity in the spectrum of $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PCH_2P(C_6H_5)_2]SbF_6$ measured in $CDCl_3$ whereas the peak to lower field is at least 3 times more intense than that to higher field in the corresponding spectrum recorded in CD_3COCD_3. Further the low-field peak in the spectrum of $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PCH_2P(C_6H_5)_2]B(C_6H_5)_4$ measured in $CDCl_3$ is very weak compared with that to high field. It is thus proposed that the compounds $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PCH_2P(C_6H_5)_2]$(anion) occur as a mixture of isomers in solution. The infrared spectra of the derivatives $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PCH_2P(C_6H_5)_2]$(anion) [anion = $B(C_6H_5)_4$, SbF_6, BF_4, I_3] in solution contain a single terminal C–O stretching peak. This peak is asymmetric, however, suggesting the superimposition of two bands.

As mentioned previously satisfactory analyses could not be obtained for the crystalline tetraphenylborate derivative isolated from the reaction of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ with excess iodine in dichloromethane and for the crystalline perchlorate derivatives isolated from the reactions of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2$ ($R = CH_2$, C_2H_4) with excess $AgClO_4$ in dichloromethane–acetone. The presence of a π-cyclopentadienyl group in these compounds was established from the nmr and ir data while the ionic nature of the species was indicated from conductivity measurements. The frequencies of the two C–O stretching bands observed in the infrared spectra of these products were found to correspond with those for $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2]Cl_2$. However, the solubility of these complexes in acetone and dichloromethane is considerably greater than that of $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2]Cl_2$ indicating that these compounds are not of the type $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2(C_6H_5)_2PRP(C_6H_5)_2]$(anion)$_2$. It is thus proposed that these compounds are of the type $[(\pi\text{-}C_5H_5)Fe(CO)_2$(ligand)](anion) (IV) with the ditertiary phosphine ligand (ligand) acting as monodentate. The ratios of the intensities of the phenyl and cyclopentadienyl resonances in the nmr spectra of these derivatives are consistent with this proposal. The inability to obtain reproducible analytical results for these compounds may be attributed to partial addition of iodine, silver ions, etc., to the unbonded phosphorus atom in $[(\pi\text{-}C_5H_5)Fe(CO)_2$(ligand)](anion).

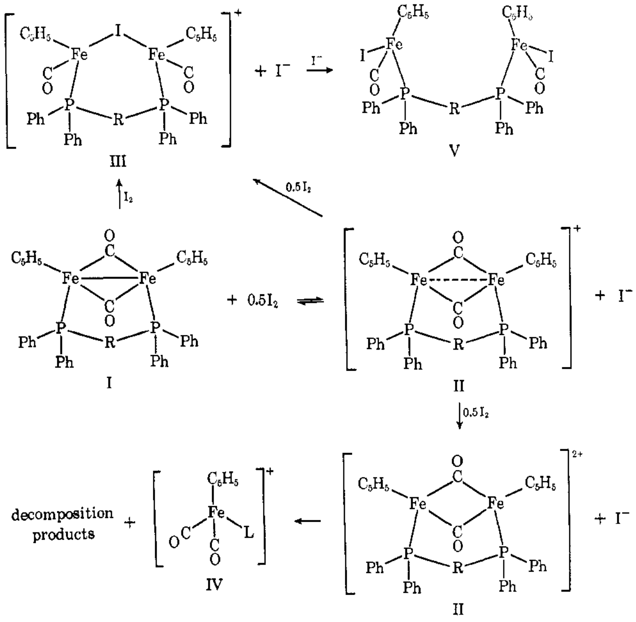
The mechanism proposed for the oxidation of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2$ (I) to $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]^+$ (II) and $[(\pi\text{-}C_5H_5)Fe(CO)_2L]^+$ (IV) [$R = CH_2$, C_2H_2, C_2H_4, C_3H_6, $N(C_2H_5)$; L = ditertiary phosphine adduct] by $AgSbF_6$ or $AgClO_4$ is outlined in Scheme I. Consistent with this proposal is the observation that treatment of $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]$(anion) with excess $AgClO_4$ in dichloromethane results in the deposition of silver.

SCHEME I



The above mechanism is also incorporated into that proposed for the iodination of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2$ (I) to the various products discussed earlier in the text (Scheme II). This scheme is

SCHEME II



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[28] Subsequent to our preliminary communication suggesting this type of bond in compounds of the type $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]$(anion),[2] a communication reporting a one-electron metal–metal bond in $[(\pi\text{-}C_5H_5)Fe(CO)SCH_3]_2{}^+$ has been published.[29]

[29] N. G. Connelly and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 7472 (1970).

based on the following observations and considerations. (i) The reaction of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2$ (I) with iodine in dichloromethane in a molar ratio 2:1 gives solely $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]^+$ (II). (ii) Treatment of $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]^+$ (II) with a large excess of iodide ions regenerates the neutral complex $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2$ (I). (iii) The reaction of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PCH_2P(C_6H_5)_2$ (I) with a tenfold excess of iodine in dichloromethane affords solely $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PCH_2P(C_6H_5)_2]^+$ (III) based on infrared evidence, whereas the corresponding reaction involving $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PCH_2P(C_6H_5)_2]$(anion) (II) gives $[(\pi\text{-}C_5H_5)Fe(CO)_2L]$(anion) (IV) [L = adduct of $(C_6H_5)_2PCH_2P(C_6H_5)_2$] as well as $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PCH_2P(C_6H_5)_2]$(anion) (III) in approximate relative yields 1:2. (iv) The reaction of $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2$ with iodine to afford $(\pi\text{-}C_5H_5)Fe(CO)_2I$ has previously been shown to involve the bridged iodo species $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2I]^+$ as an intermediate, and nucleophilic attack of iodide ions on the latter yields $(\pi\text{-}C_5H_5)Fe(CO)_2I$.[19] (v) The yield of $\{(\pi\text{-}C_5H_5)Fe(CO)I\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (V) is increased by iodinating $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (I) in the presence of excess iodide ions and is decreased by increasing the iodine:parent dimer molar ratio.

The inability of $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PCH_2P(C_6H_5)_2]^+$ (III) to react with iodide ions to form $\{(\pi\text{-}C_5H_5)Fe(CO)I\}_2(C_6H_5)_2PCH_2P(C_6H_5)_2$ (V) is attributed to its stability toward rearrangement. This contrasts with the apparently high reactivity of $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PC_2H_4P(C_6H_5)_2]^+$ (III). It should be noted that the reactions of monosubstituted derivatives of $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2$ with iodine have also been shown to afford products of the type $[(\pi\text{-}C_5H_5)Fe(CO)_2L]$(anion) resulting from asymmetric cleavage of the parent.[30]

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(30) R. J. Haines and A. L. du Preez, *Inorg. Chem.*, **8**, 1459 (1969).

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Organometallic Chemistry of the Transition Metals. XXVI. The Carbonylation of Ruthenium Diolefin Complexes[1]

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The atmospheric pressure carbonylation of the ruthenium diolefin complexes $[(\text{diene})RuCl_2]_n$ (diene = norbornadiene or bidentate benzene) under various conditions is described. Atmospheric pressure carbonylation of $[(\text{diene})RuCl_2]_n$ derivatives in the absence of an added reducing agent gives the ruthenium carbonyl chloride $[Ru(CO)_3Cl_2]_2$. This carbonyl chloride undergoes a reversible reaction with ethanol to give $[(C_2H_5OH)Ru(CO)_2Cl_2]_n$. Atmospheric pressure carbonylation of $[(\text{diene})RuCl_2]_n$ derivatives in the presence of added hydrazine gives a mixture of the ruthenium(II) ammines $[Ru(NH_3)_5L]Cl_2$ (L = CO and N_2). Atmospheric pressure carbonylation of $[(\text{diene})RuCl_2]_n$ derivatives in the presence of added hydrazine and triphenylphosphine gives not only the ruthenium(II) ammines $[Ru(NH_3)_5L]Cl_2$ (L = CO and N_2) but also the ruthenium(0) complex *trans*-$[(C_6H_5)_3P]_2Ru(CO)_3$. Atmospheric pressure carbonylation of $[(\text{diene})RuCl_2]_n$ derivatives in the presence of zinc gives variable yields of $Ru_3(CO)_{12}$; side reactions in these carbonylations lead to other products such as the norbornadiene complex $C_7H_8Ru(CO)_2(OH)_2$ and tetrametallic ruthenium carbonyl hydrides such as $H_4Ru_4(CO)_{12}$. Atmospheric pressure carbonylation of the bidentate benzene complex $[C_6H_6RuCl_2]_n$ in ethanolic lithium acetate in the presence of zinc gives a ~50% yield of the tetrametallic ruthenium carbonyl hydride $H_2Ru_4(CO)_{13}$. Atmospheric pressure carbonylation of $[Ru(CO)_3Cl_2]_2$ in methanol in the presence of zinc gives $Ru_3(CO)_{12}$.

Introduction

Within the last several years dodecacarbonyltriruthenium, $Ru_3(CO)_{12}$, has become an important starting material for the preparation of numerous ruthenium complexes, particularly those containing carbonyl groups.[3] All known preparations of $Ru_3(CO)_{12}$ from common ruthenium compounds such as the hydrated chloride require elevated pressures. Thus, the generally preferred method for preparing $Ru_3(CO)_{12}$ by reductive carbonylation of hydrated ruthenium chloride with zinc in methanol solution is reported[4] to require at least 5–10 atm carbon monoxide pressure. One further disadvantage of this latter method for preparing $Ru_3(CO)_{12}$ is the apparent tendency for the zinc reducing agent, particularly if too finely divided, to reduce the ruthenium trichloride to unreactive ruthe-

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(1) (a) Part XXV: R. B. King and A. Efraty, *J. Organometal. Chem.*, **27**, 409 (1971). (b) This work was presented at the Second North American Meeting of the Catalysis Society, Houston, Texas, Feb 1971.

(2) Postdoctoral research associate, 1968–1969, 1970–1971.

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