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Substitution Reaction Mechanism of (π-Monoolefin)iron Tetracarbonyl Complexes with Group V Ligands

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The substitution reactions of $Fe(CO)_4(CH_2{=}CHPh)$ with L ligands [L = PPh_3, $AsPh_3$, $SbPh_3$, pyridine (py)] are studied in toluene. The reaction with $AsPh_3$, $SbPh_3$, and py gives the monosubstituted complex $Fe(CO)_4L$. The reaction with PPh_3 forms simultaneously $Fe(CO)_4PPh_3$ and $Fe(CO)_3(Ph_3)_2$. On the basis of the kinetic results and of the factors influencing the $[Fe(CO)_4]/[Fe(CO)_3L_2]$ ratio, two possible reaction mechanisms are proposed. The influence of the ligand L on the reactivity of the intermediate $Fe(CO)_4$ is reported.

Introduction

In previous papers we have reported some reactions of olefinic complexes of the type $Fe(CO)_4(CH_2{=}CHX)$ (X = OEt, Cl, Br, Ph, *n*-Bu, CO_2Me, CN) with CO[1] and $SbPh_3$,[2] from the point of view of the effect of the ethylenic substituent on reaction rate and on the mass law retardation rate due to the ethylenic ligand. The results obtained allowed the reaction mechanism to be clarified and permitted determination of the reactivity of the intermediate $Fe(CO)_4$ with the various ethylenic ligands.[2] In addition, the linear dependence of the logarithm of the rate constants on the Hammett σ_P of the substituent X indicated that the stability of the iron–olefin bond is due prevailingly to π back-donation from the metal to the olefin.[2]

The present paper reports studies of the effect of several ligands L (L = PPh_3, $AsPh_3$, $SbPh_3$, py) on the rate of reaction with the intermediate $Fe(CO)_4$, with the intention of obtaining information on the nature of the intermediate and the mechanism of formation of the complexes $Fe(CO)_4L$ and $Fe(CO)_3L_2$, formed simultaneously by the PPh_3 ligand. The simultaneous formation of monosubstituted and disubstituted complexes, under experimental conditions such that formation of the disubstituted from monosubstituted complex by action of L[3] can be excluded, has also been observed in the photochemical reaction of $Fe(CO)_5$ with L[4] and also in thermal reactions of $Fe_2(CO)_9$[5] and $Fe_3(CO)_{12}$[6] with various ligands, but in no case were explanations given.

Clarification of the reaction mechanism for the former case might thus also throw light on the mechanism of those latter reactions.

Experimental Section

The complexes of $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, and π-monoolefiniron tetracarbonyl, $Fe(CO)_4(CH_2{=}CHX)$ (X = Cl, Br, OEt, Ph, *n*-Bu, CN) were prepared as in the literature.[1,2,7-11] $Fe(CO)_4L$ and $Fe(CO)_3L_2$ (L = PPh_3, $AsPh_3$, $SbPh_3$) were characterized *via* ir spectra and elemental analysis, after purification by literature methods.[12,13] $Fe(CO)_4py$ was characterized by ir spectra only, because of its instability.[14] Reaction of the olefinic complexes with *N,N'*-dimethylaniline did not give appreciable formation of substituted complex.

Rigorously dried and deoxygenated toluene was used as solvent. Kinetic runs were carried out in well-stoppered containers, from which aliquots were taken at intervals using a syringe. Analytical determinations were made on a Perkin-Elmer 257 ir spectrophotometer in 0.5-mm NaCl cells. Reactions were followed up to 60-70% completion. Values of the absorbance at infinite time, for both mono- and disubstituted complexes were measured experimentally at the end of the reaction. The concentrations of ligand L were at least 10 times greater than those of the $Fe(CO)_4(CH_2{=}CHX)$ complexes so that pseudo-first-order kinetics were followed. Concentrations of olefin, added so as to observe mass effect, were always in great excess with respect to those of the $Fe(CO)_4(CH_2{=}CHX)$ complexes so as to avoid variations in concentration due to the formation of the olefinic ligand during the reactions.

The reactions of $Fe(CO)_4(CH_2{=}CHPh)$ with PPh_3 in the presence of CO were carried in the apparatus of ref 1. The products were the mono- and disubstituted complexes. The formation of $Fe(CO)_5$ was not observed in order that the nucleophilicity of PPh_3 is much higher than CO.

Results

The kinetic study was carried out on the complex $Fe(CO)_4(CH_2{=}CHPh)$ which reacts with ligand L according to

$$\begin{aligned} Fe(CO)_4(CH_2{=}CHPh) + (2-\alpha)L \rightarrow \alpha Fe(CO)_4L + \\ (1-\alpha)Fe(CO)_3L_2 + CH_2{=}CHPh + (1-\alpha)CO \end{aligned} \qquad (1)$$

where α is the fraction of monosubstituted complex obtained during the reaction.

For L = $SbPh_3$ and py, $\alpha = 1$. Similarly for L = $AsPh_3$, $\alpha \simeq 1$, the amount of disubstituted product obtained during reaction being considered negligible. However, for L = PPh_3, α is very different from unity. The ratio $Fe(CO)_4PPh_3$:$Fe(CO)_3(PPh_3)_2$ is reported in the tables in terms of $\alpha/(1-\alpha)$ or α.

Rate constants are reported in Tables I-III, and other kinetic data, in Table IV. Table V reports variations in $\alpha/(1-\alpha)$ with the substituent X for the reaction between $Fe(CO)_4(CH_2{=}CHX)$ and L = PPh_3. Variations of $\alpha/(1-\alpha)$ with the nature and concentration of the L ligand, with the temperature, and with the CO partial pressure, for the reaction of the $Fe(CO)_4(CH_2{=}CHPh)$ complex with L ligand are reported in Table VI.

Discussion

(a) Reactions Giving Formation of Monosubstituted

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Table I. Pseudo-First-Order Rate Constants (k) for the Reaction $Fe(CO)_4(CH_2{=}CHPh) + py = Fe(CO)_4py + CH_2{=}CHPh$

T/°C	$10^2[L]$/ M	$10C_{CH_2=CHPh}$/ M	10^5k/ sec^{-1}
30.0	5.00	0	1.53
	5.00	0	1.45
40.0	11.1	0	7.54
	10.0	0	8.10
	4.39	0	7.85
	5.00	2.87	6.68
	5.00	5.14	5.54
	5.00	6.67	5.11
	5.00	7.86	4.58
	5.00	10.00	4.68
50.0	5.00	0	39.3
	5.00	0	35.1
	5.00	0.97	32.7
	5.00	2.34	27.9
	5.00	3.08	26.6
	5.00	5.20	22.1

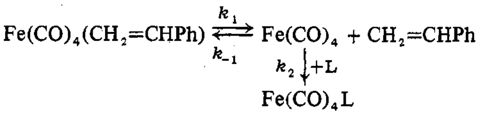
Table II. Pseudo-First-Order Rate Constants (k) for the Reaction $Fe(CO)_4(CH_2{=}CHPh) + AsPh_3 \rightarrow Fe(CO)_4AsPh_3 + CH_2{=}CHPh$

T/°C	$10^2[L]$/ M	$10C_{CH_2=CHPh}$/ M	10^5k/ sec^{-1}
30.0	5.00	0	1.43
	5.00	0.83	1.14
	5.00	1.09	1.10
	5.00	1.21	1.11
	5.00	2.50	0.97
	5.00	2.09	0.82
40.0	2.35	0	7.10
	5.67	0	6.96
	9.43	0	6.70
	19.50	0	6.90
	39.90	0	7.20
	60.90	0	7.30
	5.00	0	6.70
	5.00	1.45	5.63
	5.00	3.13	3.43
	5.00	4.85	2.75
45.0	5.00	0	16.0
	5.00	0.61	14.02
	5.00	1.20	11.5
	5.00	3.00	8.47
50.0	40.0	0	33.9
	49.0	0	35.6
	5.00	1.01	25.9
	5.00	2.09	19.7
	5.00	3.17	17.4
	5.00	5.11	12.9
	10.00	1.00	27.8
	3.21	1.00	21.8
	2.02	1.00	18.9
	1.57	1.00	16.6
	1.08	1.00	13.7

Complex Alone. This type of reaction is observed for the ligands $SbPh_3$, $AsPh_3$, and py.

The kinetic data of Tables I and II show that the experimental rate constants (k) are dependent on both L and olefinic ligand concentrations. Figure 1 shows the linear plots of $1/k$ *vs.* [styrene] at constant ligand L concentration; Figure 2 shows the linear plot of $1/k$ *vs.* $1/[AsPh_3]$ at constant concentration of styrene. The intercepts of Figure 1 and Figure 2 correspond to the $1/k$ value determined experimentally in the absence of excess styrene.

These results indicate that the mechanism 2, suggested previously for the reaction of these complexes with CO[1] and $SbPh_3$,[2] is also valid for the above ligands.



$$\begin{array}{ccc} Fe(CO)_4(CH_2{=}CHPh) & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & Fe(CO)_4 + CH_2{=}CHPh \\ & & k_2 \downarrow +L \\ & & Fe(CO)_4L \end{array} \qquad (2)$$

Table III. Pseudo-First-Order Rate Constants of Complex Disappearance (k_c), of $Fe(CO)_4PPh_3$ Appearance (k_m), and of $Fe(CO)_3(Ph_3)_2$ Appearance (k_d) for the Reaction $Fe(CO)_4(CH_2{=}CHPh) + (2-\alpha)PPh_3 \rightarrow \alpha Fe(CO)_4PPh_3 + (1-\alpha)Fe(CO)_3(PPh_3)_2 + CH_2{=}CHPh + (1-\alpha)CO$

T/°C	$10^2\times$ [L]/ M	$10\times$ $C_{CH_2=CHPh}$/ M	$10^5\times$ k_c/ sec^{-1}	10^5k_m/ sec^{-1}	10^5k_d/ sec^{-1}
29.5	0.92	0	1.15	1.22	1.20
	4.02	0	1.30	1.20	1.25
	8.18	0	1.22	1.18	1.24
	24.23	0	1.14	1.18	1.20
40.0	10	0	6.85	7.15	7.60
	10	0	6.75	6.90	7.50
	10	0.98	6.00	6.30	6.70
	10	1.93	5.62	5.55	6.05
	10	2.99	5.16	5.02	5.50
	10	4.01	4.72	4.60	4.93
	10	5.11	4.27	4.18	4.46
	1.02	0	6.70	6.60	6.80
50.0	10	0	35.3	34.6	33.7
	10	0.95	31.1	29.4	31.3
	10	2.04	27.4	26.3	28.7
	20	2.02	31.4	30.2	30.1
	30	2.04	32.6	32.1	31.5
	50	2.03	33.6	33.5	33.1
	10	3.04	24.6	22.8	26.0
	10	4.18	22.0	21.4	24.4
	10	5.15	20.8	20.8	23.2

Table IV. Rate Constants at Various Temperatures and Activation Parameters for Reaction 1

L	T/ °C	10^5k_1/ sec^{-1}	tan ϕ[a]/M^{-1} sec	k_2/k_{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$ (313.2°K)/ eu
PPh_3	40	6.80	1.66×10^4	8.9	32.7 ± 0.5	$+26 \pm 2$
	50	34.6	3.80×10^3	7.7		
$AsPh_3$	30	1.43	2.2×10^5	6.37	30.4 ± 0.5	$+21 \pm 2$
	40	7.34	4.33×10^4	6.22		
	45	19.05	1.92×10^4	6.49		
	50	33.32	9.26×10^3	6.30		
$SbPh_3$[b]	40	8.00	4.00×10^4	6.25	29.5 ± 0.5	$+16 \pm 2$
	50	34.60	9.33×10^3	6.10		
py	30	1.53				
	40	8.26	1.15×10^4	21.1	29.6 ± 0.5	$+17 \pm 2$
	50	37.00	3.5×10^3	20.0		
CO[c]	40	3.70	2.80×10^6	1.48	29.0 ± 0.5	$+13 \pm 2$
	50	16.0	0.50×10^6	2.17		

[a] Values deduced from the disappearance of the olefinic complex. [b] Values from ref 2. [c] Values from ref 1.

Table V. $\alpha/(1-\alpha)$ and α for the Reaction[a] $Fe(CO)_4(CH_2{=}CHX) + (2-\alpha)PPh_3 \rightarrow \alpha Fe(CO)_4PPh_3 + (1-\alpha)Fe(CO)_3(PPh_3)_2 + CH_2{=}CHX + (1-\alpha)CO$ ($C_{PPh_3} = 10^{-1}$ M)

X	T/°C	$\alpha/(1-\alpha)$	α
OEt	40.0	2.72	0.73
n-Bu	40.0	2.69	0.73
Ph	40.0	2.67	0.73
Cl	40.0	2.50	0.72
Br	40.0	2.84	0.74
CN	70.0	2.55	0.72

[a] The reaction of $Fe_2(CO)_9$ with PPh_3 gives at 50° $\alpha/(1-\alpha) = 3.60$ and $\alpha = 0.780$; the reaction of $Fe_3(CO)_{12}$ with PPh_3 gives at 40° $\alpha/(1-\alpha) = 0.75$ and $\alpha = 0.43$.

Applying the stationary-state approximation to the intermediate $Fe(CO)_4$, the kinetic expression

$$v = \frac{k_1k_2[L]}{k_{-1}[\text{styrene}] + k_2[L]}[C] = k[C] \qquad (3)$$

is obtained, in which [L], [C], and [styrene] are the concentrations of the entering ligand, olefinic complex, and added

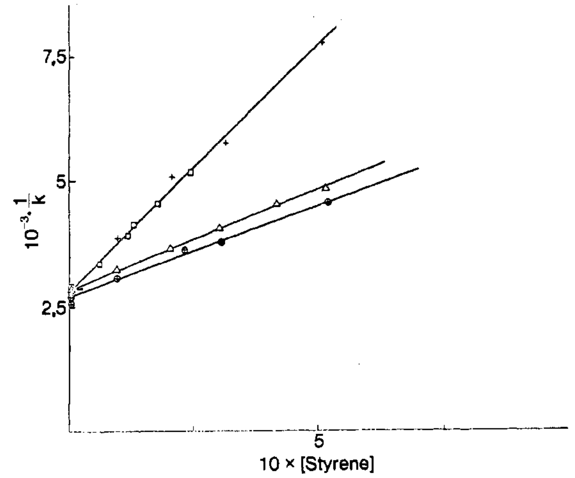


Figure 1. Plots of $1/k$ *vs.* [styrene] for the reaction of $Fe(CO)_4(CH_2{=}CHPh)$ with L ligand: L = PPh_3 (△), py (⊕), $SbPh_3$ (□), $AsPh_3$ (+); data at 50°.

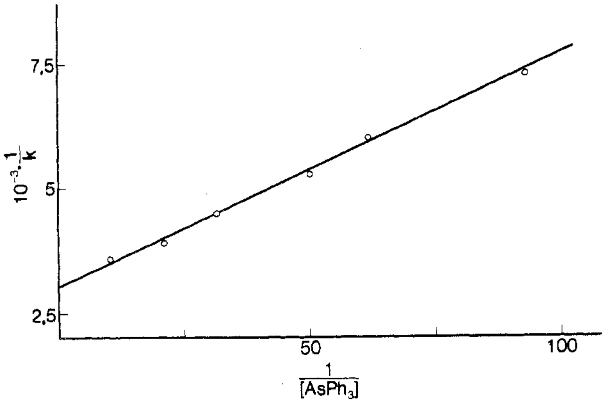


Figure 2. Plot of $1/k$ *vs.* $1/[AsPh_3]$ for the reaction of $Fe(CO)_4(CH_2{=}CHPh)$ with $AsPh_3$ ligand; data at 50°.

excess olefin, respectively. Rate constant symbols refer to reaction 2.

From (3)

$$\frac{1}{k}=\frac{k_{-1}[\text{styrene}]}{k_1k_2[\text{L}]}+\frac{1}{k_1}$$

This equation answers for the linearity of Figures 1 and 2 and for the equality of $1/k$, determined in absence of excess styrene, and $1/k_1$, determined from the intercept of Figures 1 and 2.

From the slopes of Figure 1 (tan ϕ of Table IV), k_2/k_{-1} values are obtained. A plot of log (k_2/k_{-1}) *vs.* $1/T$ gives a straight line parallel to the abscissa, indicating that the activation enthalpies of the reaction between $Fe(CO)_4$ and L and of that between $Fe(CO)_4$ and styrene are equal.

(b) Reactions Giving a Mixture of Monosubstituted and Disubstituted Products. The most significant experimental facts concerning the reaction with L = PPh_3, throwing light on the reaction mechanism, are as follows.

(1) In the absence of excess styrene, the rate of disappearance of the olefinic complex is first order with respect to the complex and zero order with respect to ligand L.

The rates of appearance of the mono- and disubstituted complexes are zero order with respect to ligand L, if the latter is present in concentrations at least 20 times those of the complex. The rate constants deduced from the appearance of the mono- and disubstituted complexes correspond, within experimental error, to those deduced from the disappearance of the ethylenic complex (Table III).

Table VI. Values of $\alpha/(1-\alpha)$ and α with Different Ligands L, at Various Concentrations of L and at Various Temperatures, for the Reaction $Fe(CO)_4(CH_2{=}CHPh) + (2-\alpha)L \rightarrow \alpha Fe(CO)_4L + (1-\alpha)Fe(CO)_3L_2 + CH_2{=}CHPh + (1-\alpha)CO$

L	T/°C	P_{CO}/atm	[L]/M	$\alpha/(1-\alpha)$	α
py	40	0	10^{-1}	∞	1
$SbPh_3$	40	0	10^{-1}	∞	1
$AsPh_3$	40	0	10^{-1}	25.4	0.97
PPh_3	40	0	10^{-1}	2.55	0.72
PPh_3	30	0	10^{-1}	2.60	0.72
PPh_3	50	0	10^{-1}	2.47	0.71
PPh_3	60	0	10^{-1}	2.48	0.71
PPh_3	70	0	10^{-1}	2.49	0.71
PPh_3	60	0	10^{-2}	2.72	0.73
PPh_3	60	0	1	2.80	0.74
PPh_3	50	0	5×10^{-2}	2.60	0.72
PPh_3	50	1	5×10^{-2}	2.90	0.74

(2) The mass effect observed for the disappearance of the ethylenic complex is also observed for the appearance of the mono- and disubstituted complexes.

In all cases the concentration of olefinic ligand added in excess is at least 20 times that of the complex (Table III).

(3) The ratio $\alpha/(1-\alpha)$ is, within experimental errors, independent of the nature of substituent X of the olefinic ligand in the $Fe(CO)_4(CH_2{=}CHX)$ complexes and corresponds roughly to that observed for the reaction between $Fe_2(CO)_9$ and PPh_3 (Table V).

(4) The ratio $\alpha/(1-\alpha)$ is dependent on the nature of entering ligand L, but not on its concentration (Table VI).

(5) The ratio $\alpha/(1-\alpha)$ is independent of the temperature in the range 30-70° (Table VI).

(6) The disubstituted product cannot be obtained by reaction of the monosubstituted complex with L, because the ratio $\alpha/(1-\alpha)$ does not vary appreciably for a time much greater that the reaction time, in the temperature range studied (30-70°). On the other hand, the reaction

$$Fe(CO)_4PPh_3 + PPh_3 \rightarrow Fe(CO)_3(PPh_3)_2 + CO$$

has previously been studied[3] and the mechanism found to be dissociative with very low rate constants at 130°. This may explain why the above reaction does not take place at the temperature at which the kinetics were followed.

(7) The effect of CO at atmospheric pressure is small (Table VI).

The above results indicate the following conclusions.

(a) The first stage of reaction cannot influence the ratio $\alpha/(1-\alpha)$, since this ratio is independent of the nature of substituent X in the $Fe(CO)_4(CH_2{=}CHX)$ complexes.

(b) The first stage must be dissociative in type since the rate constant with [styrene] = 0 is zero order with respect to entering ligand and first order with respect to complex (see also the activation parameters in Table IV).

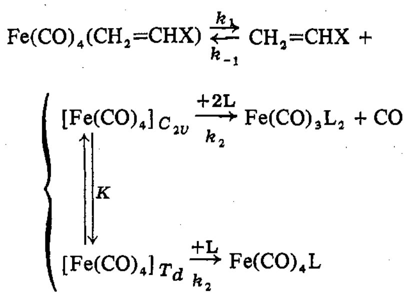
(c) The stages following the first dissociative one must be much faster than this since the rate constants deduced from the appearance both of the monosubstituted and of the disubstituted one are the same and equal to that deduced from the disappearance of the olefinic complex.

It follows from the above that the first stage of reaction may be identical with the dissociative stage of reaction 2.

The formation of mono- and disubstituted complexes may thus be attributed to different reaction possibilities of the $Fe(CO)_4$ group, the reaction intermediate. Since this intermediate is the same whatever the starting olefin complex, the nondependence of $\alpha/(1-\alpha)$ on the type of substituent X is understandable.

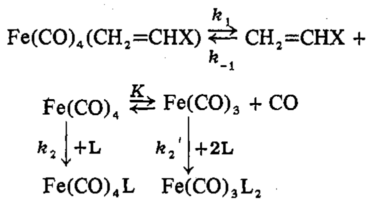
Two different reaction pathways of $Fe(CO)_4$ are indicated as follows.

(1) An isomerization to the T_d structure of $Fe(CO)_4$ (C_{2v}), obtained by dissociation of the metal-olefin bond. If the C_{2v} and T_d structures have different reactivity, as found for the octahedral complexes $M(CO)_6$,[15] the formation of monosubstituted and disubstituted complexes should occur following



$$Fe(CO)_4(CH_2{=}CHX) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_2{=}CHX +$$
$$\begin{tikzcd} {[Fe(CO)_4]_{C_{2v}}} \arrow[r, "+2L", "k_2"'] \arrow[d, shift left, "K"] & Fe(CO)_3L_2 + CO \\ {[Fe(CO)_4]_{T_d}} \arrow[r, "+L", "k_2"'] \arrow[u, shift left] & Fe(CO)_4L \end{tikzcd} \qquad (4)$$

(2) There is a further dissociation of $Fe(CO)_4$ to $Fe(CO)_3$,[16] that, reacting with L ligand, forms the disubstituted complexes according to



$$Fe(CO)_4(CH_2{=}CHX) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_2{=}CHX +$$
$$\begin{tikzcd} Fe(CO)_4 \arrow[r, shift left, "K"] \arrow[d, "+L", "k_2"'] & Fe(CO)_3 + CO \arrow[l, shift left] \arrow[d, "+2L", "k_2'"'] \\ Fe(CO)_4L & Fe(CO)_3L_2 \end{tikzcd} \qquad (5)$$

The small effect of CO pressure does not allow us to distinguish between the above mechanisms; experimental data at high CO pressure are necessary.

Both mechanisms 4 and 5, if the stages after the first one are very fast, explain all the kinetic results obtained (mass law retardation effect, first-order reaction rate, identical rate constants for appearance and disappearance). Moreover, these mechanism explain why a mixture of $Fe(CO)_4L$ and $Fe(CO)_3L_2$ complexes is also obtained in the photochemical[4] and thermal[17] reactions of $Fe(CO)_5$ with L and in the thermal reactions of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$[6] with L. For each of these reactions, the reaction intermediate may be $Fe(CO)_4$, as shown in the reactions 4 and 5.

(c) Effect of Substituent L on the k_2/k_{-1} Ratio. The values of k_2/k_{-1} collected in Table IV give an indication of the nucleophilicity of the various ligands compared to that of styrene, in the reaction with $Fe(CO)_4$. Inserting the value obtained previously for CO[1] and $SbPh_3$[2] the reactivity order obtained is py $>$ PPh_3 $>$ $AsPh_3$ $\approx$ $SbPh_3$ $>$ CO.

This order is that expected for the reactivity of a "hard" center with "hard" ligand[18] for which the basicity is the factor determining the rate of reaction. This is in agreement with the order previously found for the reactivity of the olefinic ligands with the $Fe(CO)_4$ group.[2]

Acknowledgment. The author is indebted to Professor U. Mazzucato for helpful criticism.

Registry No. $Fe(CO)_4(CH_2{=}CHPh)$, 12193-57-6; py, 110-86-1; $AsPh_3$, 603-32-7; $SbPh_3$, 603-36-1; PPh_3, 603-35-0; $Fe(CO)_4(CH_2{=}CHOEt)$, 33409-79-9; $Fe(CO)_4(CH_2{=}CHBu)$, 38722-52-0; $Fe(CO)_4(CH_2{=}CHCl)$, 12192-44-8; $Fe(CO)_4(CH_2{=}CHBr)$, 33479-79-7; $Fe(CO)_4(CH_2{=}CHCN)$, 12317-43-0; $Fe_2(CO)_9$, 15321-51-4; $Fe_3(CO)_{12}$, 17685-52-8.

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Reactions of Coordinated Ligands. II. μ-Oxo-bis(difluorophosphineiron tetracarbonyl)

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Reaction of $Fe(CO)_4PF_2Br$ with potential sources of the oxide ion (*e.g.*, Ag_2O, Cu_2O, etc.) yielded the new complex compound, $Fe(CO)_4PF_2OPF_2Fe(CO)_4$. A more convenient preparation of this material involved the use of $AgMnO_4$ instead of the metal oxides. The ^{31}P and ^{19}F nmr parameters for the complex were obtained by analysis of the spectra as a AA'XX'X''X''' spin system.

The use of fluorophosphine derivatives as ligands for low-valent transition metals has been widely explored.[1] One useful phosphine ligand has been found to be F_2PBr since after coordination further reaction of the phosphorus-bromine bond can occur. Thus, starting with $Fe(CO)_4PF_2Br$, a series of simple complexes of the type $Fe(CO)_4PF_2X$ can be readily prepared.[2] Further investigation of reactions of coordinated difluorobromophosphine has led to the isolation of μ-oxo-bis(difluorophosphineiron tetracarbonyl), $Fe(CO)_4PF_2OPF_2Fe(CO)_4$ (I).

Experimental Section

Since the starting materials $BrPF_2Fe(CO)_4$ and I are sensitive to oxygen and moisture, all handling of materials was carried out either under vacuum or in a nitrogen atmosphere.

Materials. Silver permanganate was prepared from $KMnO_4$ and $AgNO_3$ in water. *Caution! $AgMnO_4$ should be handled with care.* The material is safe while wet but potentially explosive when dry. It is routinely stored in black plastic bottles in quantities of 1–2 g. The bottles are kept well separated from one another. One such vial

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