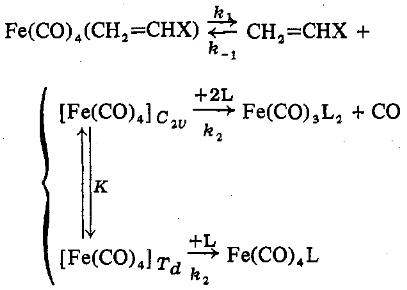
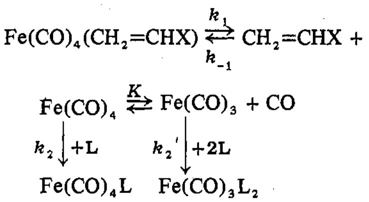
Two different reaction pathways of $Fe(CO)_4$ are indicated as follows.

(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



$$\mathrm{Fe(CO)_4(CH_2{=}CHX)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{CH_2{=}CHX} + \left\{\begin{array}{l} [\mathrm{Fe(CO)_4}]_{C_{2v}} \xrightarrow[k_2]{+2\mathrm{L}} \mathrm{Fe(CO)_3L_2} + \mathrm{CO} \\ \Updownarrow K \\ [\mathrm{Fe(CO)_4}]_{T_d} \xrightarrow[k_2]{+\mathrm{L}} \mathrm{Fe(CO)_4L} \end{array}\right. \qquad (4)$$

(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



$$\begin{array}{l} \mathrm{Fe(CO)_4(CH_2{=}CHX)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{CH_2{=}CHX} + \\ \mathrm{Fe(CO)_4} \overset{K}{\rightleftarrows} \mathrm{Fe(CO)_3} + \mathrm{CO} \\ k_2 \downarrow +\mathrm{L} \qquad k_2' \downarrow +2\mathrm{L} \\ \mathrm{Fe(CO)_4L} \qquad \mathrm{Fe(CO)_3L_2} \end{array} \qquad (5)$$

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 > $AsPh_3$ ≈ $SbPh_3$ > 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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(15) I. W. Stolz, G. R. Dobson, and R. K. Sheline, *J. Amer. Chem. Soc.*, **85**, 1013 (1963); J. Nasielski, P. Kirsh, and L. Wilputte-Steinert, *J. Organometal. Chem.*, **29**, 269 (1971); G. R. Dobson, M. F. A. El-Sayed, I. W. Stolz, and R. K. Sheline, *Inorg. Chem.*, **1**, 526 (1962).

(16) This mechanism was suggested by a reviewer.

(17) W. Reppe and W. Schweckendiek, *Justus Liebigs Ann. Chem.*, **560**, 104 (1968).

(18) S. Ahrland, J. Chatt, and M. R. Davies, *Quart. Rev., Chem. Soc.*, **12**, 265 (1958); G. R. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).

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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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(1) T. Kruck, *Angew. Chem., Int. Ed. Engl.*, **6**, 53 (1967).

(2) W. M. Douglas and J. K. Ruff, *J. Chem. Soc. A*, 3558 (1971).

did explode in these laboratories. The material is also light sensitive. Bis(tri-*n*-butyl)tin oxide, silver(I) oxide, and copper(I) oxide were obtained from commercial sources and used without further purification. The complex $BrPF_2Fe(CO)_4$ was prepared according to the literature.[2]

Preparation of μ-Oxo-bis(difluorophosphineiron tetracarbonyl). A. A solution of 5.71 g (18 mmol) of $BrPF_2Fe(CO)_4$ in 20 ml of THF was added dropwise to 4.07 g (18 mmol) of $AgMnO_4$ suspended in 200 ml of THF. After addition the reaction mixture was stirred for 1 hr and then filtered. The solvent was removed *in vacuo* and the residue was transferred to a molecular still. After removal of the excess $BrPF_2Fe(CO)_4$ by pumping on the residue for 2 hr under high vacuum, I was distilled by gentle warming. The yield varied between 30 and 40%.

B. A 3.87-g (12.2-mmol) sample of $BrPF_2Fe(CO)_4$ and 4.34 g (7.3 mmol) of $[(n\text{-}C_4Hg)_3Sn]_2O$ were heated together at 50° for 2 hr and then at 90° for 0.5 hr. The mixture was transferred to a molecular still and pumped on under high vacuum for 0.5 hr at ambient temperature. A 1.12-g sample of I (37% yield) was obtained by distillation as described in part A.

C. A 3.71-g (11.7-mmol) sample of $BrPF_2Fe(CO)_4$ and 1.51 g (6.5 mmol) of Ag_2O were stirred together in 125 ml of benzene for 1 week. After filtration and work-up as described in part A, a 1.31-g sample of I was obtained (23% yield).

The use of Cu_2O instead of Ag_2O in the above reaction resulted in the isolation of I in 7% yield.

Anal.[3] Calcd for $C_8O_9P_2F_4Fe_2$: C, 19.59; F, 15.51; P, 12.65; O, 29.39; Fe, 22.86. Found: C, 19.67; F, 15.67; P, 12.67; O, 29.39; Fe, 23.12. Molecular weight: calcd, 490; found, 485 ± 6 (osmometry).[3]

Spectroscopic Measurements. Fluorine and phosphorus nmr spectra of I were obtained at 56.44 and 24.29 MHz, respectively, on a Varian DP-60 spectrometer[4] modified for field-frequency lock operation.[5] The lock signal for F spectra was internal $CFCl_3$; for P spectra the central peak in the spectrum of I was used. The power level at the locking fequency was kept low enough to avoid double-resonance effects. Chemical shifts (δ_F and δ_P) are referred to $CFCl_3$ (internal) or P_4O_6 (external) for F and P, respectively. Shifts to high frequency (downfield) of the reference are reported as positive. For 85% H_3PO_4 we found $\delta_P = -112.1$ ppm (lit.[6] 112.5 ppm). The mass spectrum of I was recorded on a Hitachi Perkin-Elmer RMU-6 spectrometer with ionizing voltage of 70 V and $\Delta M/M = 950$. The infrared spectrum of I (cyclohexane solution) was obtained with a Perkin-Elmer 621 spectrometer which was calibrated with indene. The accuracy and resolution are each estimated as 2 cm^{-1} in the critical carbonyl absorption region near 2000 cm^{-1}.

Results

The fluorine and phosphorus nmr spectra were completely compatible with the proposed formulation of the complex as a bis(iron tetracarbonyl) complex of μ-oxo-bis(difluorophosphine).

The spin system of $(CO)_4FePF_2OPF_2Fe(CO)_4$ may be characterized as $AA'XX'X''X'''$ by neglecting magnetic isotopes of small abundance. The analysis of the prototype system has been discussed in detail.[7-9] The fluorine spectrum essentially consists of a strong doublet with 1292.4-Hz spacing, with seven additional weak lines around each of the strong lines. The phosphorus spectrum is essentially a 1:2:1 triplet with 1292.4-Hz spacing, with nine additional lines around each outside line and 16 lines around the central line. Both spectra are centrosymmetric. The number of lines is only about half the number expected. The coupling constants for this molecule are such that some nondegenerate lines accidently fall at the same or nearly identical frequencies, thus reducing the apparent total; however, the nature of the spin system is not in doubt. Initial values of the coupling constants were obtained by following published procedures[7-9] and these values were refined by the use of the computer program UEAITR.[10] The values given in Table I are the result of fitting 18 lines. The rms error is 0.425 Hz and the maximum difference between calculated and observed line positions is 0.76 Hz. The errors in Table I are probable errors calculated by the program. The chemical shifts were not adjusted by the program. The geminal coupling constant, $^2J_{FF}$, could not be found. It was varied from ±5 to ±300 Hz without appreciable effect on the calculated spectrum. The information as to relative signs is as follows: We assume that $^1J_{PF}$ is negative.[11] Then $^3J_{PF}$ is positive. The two $^4J_{FF}$ (cis and trans) are each of the same sign, and this sign is opposite to that of $^2J_{PP}$, but the relation of these three signs to the sign of $^1J_{PF}$ has not been determined. The fact that the cis and trans couplings are nearly equal in sign and magnitude is a coincidence which carries no obvious structural implications.

The infrared spectrum of $OP_2F_4Fe_2(CO)_8$ shows six terminal carbonyl absorptions in the region 2105-1990 cm^{-1}. In neither the cyclohexane solution nor the thin film spectrum did the complex show any evidence of bridging carbonyl groups. The spectrum expected for the F_2POPF_2 portion of the molecule is similar to that of the uncomplexed PF_2-OPF_2.[12] In the coordinated ligand, the asymmetric POP stretch is lowered by 28 cm^{-1} and the symmetric POP stretch raised by 40 cm^{-1} relative to the free ligand. Furthermore, all three PF absorbances are raised by 14-23 cm^{-1} (assuming 1:1 assignment). These observations reflect the fact that coordination to the $Fe(CO)_4$ moieties decreases the electron density about the phosphorus atoms thus requiring more energy to effect a P-F or a symmetric P-O vibration. (See Table II.)

The mass spectrum (see Table III) of the new complex did not show the parent molecular ion at *m/e* 490. The highest observable peak, at *m/e* 462, corresponds to the species $OP_2F_4Fe_2(CO)_7^+$. The fragmentation pattern follows two pathways. The major one involves the loss of seven carbon monoxide groups to give the $OP_2F_4Fe_2^+$ framework. The $OP_2F_4Fe_2^+$ ion first loses an iron atom to form $OP_2F_4Fe^+$. This species then breaks up to form either PF_2^+ and OPF_2Fe^+ or OPF_2^+ and PF_2Fe^+ which subsequently break apart. There is only slight evidence that $OP_2F_4Fe^+$ loses an iron atom to give $OP_2F_4^+$ since a peak corresponding to this species is very weak. The second, and minor, fragmentation pattern results from asymmetrical cleavage of the OP_2F_4-$Fe_2(CO)_7^+$ ion into $Fe(CO)_4^+$ and $OP_2F_4Fe(CO)_3^+$. Each of these moieties then loses all the carbon monoxide groups and then fragments as previously mentioned.

Discussion

The synthesis of μ-oxo-bis(difluorophosphineiron tetracarbonyl) was conducted as part of a study on the reactions of coordinated fluorophosphine ligands. Centofanti and Parry[13] found that F_2POPF_2, upon reaction with diborane,

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[3] Meade Laboratories, Amherst, Mass.

[4] Certain commercial equipment is identified in this paper in order adequately to specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the equipment identified is necessarily the best available for the purpose.

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[7] R. M. Lynden-Bell, *Trans. Faraday Soc.*, 57, 888 (1961).

[8] R. M. Lynden-Bell, *Mol. Phys.*, 6, 601 (1963).

[9] R. W. Rudolph and R. A. Newmark, *J. Amer. Chem. Soc.*, 92, 1195 (1970).

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Table I. Nmr Parameters for Fluorophosphines and Their Adducts

	$(CO)_4FePF_2OPF_2$-$Fe(CO)_4$[a]	PF_2OPF_2[b]	PF_3[b]	$Fe(CO)_4$-PF_3[c]	$Ni(PF_3)_4$[d]	$PF_2OPF_2\cdot BH_3$[b]
δ_P,[e] ppm	−47.0	−1	−7		+25.6, +27[f]	−6.6 ($-PF_2$) −11.4 ($-PF_2\cdot BH_3$)
δ_F,[g] ppm	−3.94	−38.6	−36.2, −33.7[h]	−6.22	−16.7	−37.0 ($-PF_2$) −54.0 ($-PF_2\cdot BH_3$)
$^1J_{PF}$, Hz	−1297.69 ± 0.10	−1354	−1441[h]	−1329	*Ca.* −1320	−1386 ($-PF_2$) −1328 ($-PF_2\cdot BH_3$)
$^3J_{PF}$, Hz	+5.34 ± 0.13	+14				4
$^2J_{PP}$, Hz	∓51.54 ± 0.19	4				26.7
$^4J_{FF}$(cis or trans), Hz	±4.00 ± 0.17					
$^4J_{FF}$(trans or cis), Hz	±3.94 ± 0.19					

[a] This work. See text for discussion of error limits. [b] L. Centofanti and R. W. Parry, *Inorg. Chem.*, 7, 1005 (1968). [c] F. Ogilvie, R. J. Clark, and J. G. Verkade, *ibid.*, 8, 1904 (1969). [d] G. S. Reddy and R. Schmutzler, *ibid.*, 6, 823 (1967). [e] Literature values have been adjusted to a P_4O_6 reference. Shifts are given to high frequency (low field) of external P_4O_6. [f] R. J. Clark and E. O. Brimm, *Inorg. Chem.*, 4, 651 (1965). [g] Literature values of chemical shifts have been adjusted where necessary to a $CFCl_3$ reference, using δ_F + 78.45 ppm for CF_3COOH: J. W. Emsley, J. Feeney, and L. K. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Oxford, 1966, p 873. Positive shifts to high frequency of reference. [h] J. F. Nixon, *J. Chem. Soc. A*, 1136 (1967).

Table II. Infrared Spectrum of $O[PF_2(CO)_4]_2$ (cm^{-1})

Freq	Assignment	Freq	Assignment
2105 w	ν_{CO}	948 m	Asym P–O–P
2099 w		886 m	ν_{PF}
2094 m		871 sh	
2027 s		856 sh	
2011 s		722 vw	Sym P–O–P
1990 s			

Table III

m/e	% intens	Ion	m/e	% intens	Ion
462	91	$OP_2F_4Fe_2(CO)_7$	172	37	
434	39	$OP_2F_7Fe_2(CO)_6$	169	8	$OPF_2Fe(CO)$
406	43	$OP_2F_4Fe_2(CO)_5$	168	23	$Fe(CO)_4$, $Fe_2(CO)_2$
378	43	$OP_2F_4Fe_2(CO)_4$	159	7	$Fe(CO)_3F$
350	100	$OP_2F_4Fe_2(CO)_3$	154	2	F_2POPF_2
322	100	$OP_2F_4Fe_2(CO)_2$	153	4	$PF_2Fe(CO)$
308	4	$Fe_2(CO)_7$	150	11	OPFFe(CO)
294	52	$OP_2F_4Fe_2(CO)$	141	27	OPF_2Fe
280	3	$Fe_2(CO)_6$	140	20	$Fe(CO)_3$, $Fe_2(CO)$
266		$OP_2F_4Fe_2$	137	7	
264	14		135	9	
262	22		131	42	$Fe(CO)_2F$
238	13	$OP_2F_4Fe(CO)$	129	6	
235	7		125	17	PF_2F3
234	8		122	18	OPFFe
228	7		112	91	$Fe(CO)_2$, Fe_2
225	22	$OPF_2Fe(CO)_3$	106	12	PF Fe
224		$Fe_2(CO)_4$	104	10	
240	22	OP_2F_4Fe	87	3	FeP
200	20	$POPF_2Fe$	85	5	OPF_2
199	5		84	91	Fe(CO)
197	39	$OPF_2Fe(CO)_2$	75	30	FeF
196	25	$Fe(CO)_5$, $Fe_2(CO)_3$	69	10	
191	3		68	5	
190	4		56	91	Fe
181	8	$PF_2Fe(CO)_2$, POPFFe	47	8	PO

formed only the monoadduct $F_2POPF_2\cdot BH_3$. Attempts to prepare the diadduct were unsuccessful. This behavior was rationalized on the basis that electron drift away from the uncoordinated $-PF_2$ group to the coordinated $-PF_2$ group would reduce the base strength of the uncoordinated phosphorus to the point where adduct formation with BH_3 was not possible. Similarly, it was found that P_2F_4 would coordinate only one BH_3 group, forming $F_2PPF_2\cdot BH_3$.[14] In this case the reduced base strength of the uncoordinated phosphorus atom was again attributed to electron transfer. Attempts to couple $(CO)_4FePF_2Br$ by reaction with mercury and other metals to form $(CO)_4FePF_2PF_2Fe(CO)_4$ were unsuccessful.[15]

Although indirectly related to the work reported herein, it was found by Charlton and Cavell[16] that SPF_2I would react with mercury to form SPF_2SPF_2. Although their data indicated that

$$F_2\overset{\overset{S}{\|}}{P}-\overset{\overset{S}{\|}}{P}F_2$$

was not formed, they did indicate that halofluorophosphines in which the lone pair is coordinated will react with an appropriate reagent, eliminating the nonfluorine halogen followed by coupling though in this case a material of different structure was obtained. It is well known that such coupling can occur in normal phosphines. For example, P_2F_4 is prepared by the reaction of PF_2I with mercury. Thus, it seemed reasonable that precoordination of PF_2Br to $Fe(CO)_4$ would not preclude the formation of the μ-oxo-bis(difluorophosphineiron tetracarbonyl) derivative reported herein.

A detailed study of the nmr spectrum of $O[PF_2Fe(CO)_4]_2$ was undertaken. It is of interest to compare the results of this study with the parent fluoride, PF_2OPF_2, and also with related metal carbonyl-fluorophosphine complexes. The published values for selected compounds are given in Table I which is intended to be representative rather than exhaustive. The nmr parameters of PF_3 and PF_2OPF_2 are rather similar, so that a comparison of their complexes should be of interest. The compound $Ni(PF_3)_4$ shows a strong downfield shift of both F and P resonances similar to but somewhat smaller in magnitude than observed here for $(CO)_4FePF_2OPF_2Fe(CO)_4$ (the entire series $Ni(CO)_{4-n}(PF_3)_n$, n = 1-4, has been reported to show little variation in either P or F chemical shift[17]). The F shift reported for $Fe(CO)_4PF_3$ is somewhat closer to the value reported here. A decrease of 50–100 Hz in $|^1J_{PF}|$ is similarly recorded for all of these molecules upon complexation. That these changes intimately involve the transition metal, rather than being due merely to an increase in the coordination number of phosphorus, is demonstrated by the data for $PF_2OPF_2\cdot BH_3$ in which both P and F nmr signals are shifted upfield upon coordination, while $|^1J_{PF}|$ has increased. Simple donation of electrons by the phosphorus might be expected to reduce the diamagnetic shielding and thus lower the resonance field in complexes with BX_3, while back-bonding from a metal in

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[15] W. M. Douglas and J. K. Ruff, unpublished results.

[16] T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, 8, 2436 (1969).

[17] R. J. Clark and E. O. Brimm, *Inorg. Chem.*, 4, 651 (1965).

a complex with a transition metal containing ligand might be expected to raise the resonance field. This is in fact the exact opposite of the observed effect which must have a less simple explanation. The adduct $PF_2OPF_2 \cdot BH_3$ is consistent with the general observation that four-coordinate phosphorus has its resonance further upfield than three-coordinate.[18] The results for the metal carbonyl-fluorophosphine adducts suggest that more loosely bound electrons are present ($d\pi$-$d\pi$ bonding) which would cause an increase in the paramagnetic contribution to the shielding.[18] This is in agreement with the deep color of the adduct which also argues for easily excited electrons.

The infrared spectrum of $(CO)_4FePF_2OPF_2Fe(CO)_4$ in the carbonyl stretching region is like that of $(CO)_4FePF_2X$ (X = Br, SCN, Cl) but unlike that of $(CO)_4Fe\,PF_2NR_2$ in showing more absorptions than expected for either axially substituted or equatorially substituted iron alone.[2] Coupling of carbonyl stretching vibrations *via* the PF_2OPF_2 ligand would be expected to cause only a small splitting of the separate bands. The presence of six absorptions may be regarded as evidence for the existence of both axially and equatorially substituted iron. Since the two ends of the molecule are expected to have little influence on each other, an approximately statistical distribution of axial-axial, axial-equatorial, and equatorial-equatorial isomers is presumed to be present in the absence of a complete assignment of the infrared spectrum. This result is not inconsistent with the nmr finding of a single isomer.[19]

It is of interest to note that the mass spectrum of this complex did not exhibit a parent molecular ion. The highest observable peak at m/e 462 corresponded to the species $OP_2F_4Fe_2(CO)_7^+$. The appearance of this species in the spectrometer suggests that under the conditions employed, the parent species loses one carbon monoxide ligand and structurally rearranges to a diiron enneacarbonyl derivative in which two of the bridging carbonyl groups are replaced by the F_2POPF_2 ligand. In fact, weak peaks do occur for the species $Fe_2(CO)_x$ (x = 7.6, 4-0) and for PF_2OPF_2. Attempts to prepare the species $OP_2F_4Fe_2(CO)_7$ either from $Fe_2(CO)_9$ and F_2POPF_2 or from $OP_2F_4Fe_2(CO)_8$ by thermal or photochemical means were unsuccessful.

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Registry No. $BrPF_2Fe(CO)_4$, 42886-00-0; I, 42886-01-1.

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[19] E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, **20**, 245 (1966).

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Kinetic Studies of Phosphine and Phosphite Exchange Reactions of Substituted Iron Tricarbonyl Carbene Complexes. A Competitive Study of Lewis Bases for the Intermediate $[Fe(CO)_3C(OC_2H_5)CH_3]$

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Kinetic and mechanistic studies of phosphorus ligand exchange reactions of *trans*-$(C_6H_5)_3PFe(CO)_3C(OC_2H_5)R$ (R = CH_3 and C_6H_5) with L′ (L′ = $P(n\text{-}C_4H_9)_3$, $P(OC_6H_5)_3$, and $P(C_6H_{11})_3$) to form *trans*-$L'Fe(CO)_3C(OC_2H_5)R$ compounds are reported. The rates of these substitution reactions are independent of the nature and concentration of the incoming ligands (L′) and proceed according to the rate expression: rate = $k_1[(C_6H_5)_3PFe(CO)_3C(OC_2H_5)R]$. These reaction rates are dependent upon the nature of the carbene ligand with $C(OC_2H_5)C_6H_5$ labilizing the *trans*-phosphine ligand more strongly than $C(OC_2H_5)CH_3$. Competitive reactions for the intermediate $[Fe(CO)_3C(OC_2H_5)CH_3]$ have been investigated for a number of ligands. The $[Fe(CO)_3C(OC_2H_5)CH_3]$ intermediate reacts with various phosphorus ligands at different rates and shows a preference for more nucleophilic reagents. Equilibrium constant measurements for the reaction $(C_6H_5)_3PFe(CO)_3C(OC_2H_5)CH_3 + L' \rightleftharpoons L'Fe(CO)_3C(OC_2H_5)CH_3 + P(C_6H_5)_3$ are also reported.

Introduction

There are numerous reports in the literature of kinetic and mechanistic studies of carbon monoxide substitution by Lewis bases in transition metal carbonyl complexes.[2] The less numerous studies involving replacement of metal-bound Lewis bases in substituted metal carbonyl complexes include the following: (1) rather detailed kinetic and mechanistic investigations of amine displacement from amine substituted group VIb metal carbonyl derivatives;[3-6] (2) carbon monoxide replacement of L (phosphines and phosphites) in $(phen)Cr(CO)_3L$ complexes;[7] (3) reactions of $(DTH)M(CO)_4$ (M = Cr and Mo; DTH = 2,5-dithiahexane) with phosphites to yield *cis*- and *trans*-$(phosphite)_2M(CO)_4$ complexes;[8] (4) kinetic studies of the substitution with α,α'-bipyridyl for phosphines and phosphites (L) in the carbonyl derivatives of

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