The Photolysis and Subsequent Reactions of Bis(triaryl phosphite) Complexes of Iron(0), *trans*-$[Fe(CO)_3\{P(OAr)_3\}_2]$

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On photolysis in solution, *trans*-$[Fe(CO)_3\{P(OAr)_3\}_2]$ complexes (Ar = Ph and *o*- and *p*-MeC_6H_4) lose CO to give red products. These cannot be isolated, but react *in situ* with various ligands, L (*e.g.* CO, phosphines, phosphites, isocyanides, CS_2, SO_2, tetracyanoethylene, and acetylenes) to give $[Fe(CO)_2\{P(OAr)_3\}_2(L)]$ derivatives, and with various compounds X–Y (*e.g.* H–H, D–D, H–Cl, and Cl–$SnCl_3$) to form $[Fe^{II}(CO)_2\{P(OAr)_3\}_2(X)(Y)]$ compounds. These reactions are often not simple and complicated mixtures of products may be obtained. Carbon tetrachloride and *N*-bromosuccinimide convert the red intermediate to a mixture of $[Fe(CO)_2\{P(OAr)_3\}_2(X)(Y)]$ and $[Fe(CO)_2\{P(OAr)_3\}_2X]$ (X = Y = Cl or Br). It is suggested that the latter contain *o*-metallated phosphite ligands and that the red intermediate compound is related to them and is best formulated as $[Fe\{P(OC_6H_3Z)(OAr)_2\}\{P(OAr)_3\}(CO)_2H]$ rather than $[Fe(CO)_2\{P(OAr)_3\}_2]$ (Z = H or Me).

It has been shown by Poliakoff and Turner [1] that the photolysis of matrix-isolated $[Fe(CO)_5]$ molecules at low temperatures results in CO loss. The $[Fe(CO)_4]$ fragments which remain are highly reactive. They show significant interactions with matrix atoms, *e.g.* Xe, or molecules, *e.g.* CH_4, which are not normally noted for their ligating properties. Such co-ordinatively unsaturated molecules have been postulated as the reactive intermediates in many substitution reactions of metal carbonyls, but are not normally observed.[2] However, metals having the d^8 electron configuration tend to form complexes in which they are four-co-ordinate, even though if they were five-co-ordinate the effective atomic number rule would be obeyed. This tendency increases (*a*) within a Group with increasing atomic number of the metal, and (*b*) in going from left to right across the Periodic Table. Thus it is least marked for iron(0), and most marked for platinum(II) where five-co-ordination is rarely observed.[3]

In this paper we describe the preparation and reactions of some complexes which in many respects act as derivatives of $[Fe^0(CO)_4]$. They are obtained by the continued irradiation of solutions of $[Fe_3(CO)_{12}]$ with excess of triaryl phosphite. The previously reported green $[Fe_3(CO)_{12-n}\{P(OAr)_3\}_n]$ [4] break down to yellow *trans*-$[Fe(CO)_3\{P(OAr)_3\}_2]$ which lose CO to give pink '$[Fe(CO)_2\{P(OAr)_3\}_2]$'. There is good evidence to suggest that these are not co-ordinatively unsaturated species.

EXPERIMENTAL

Triaryl phosphites,[5] triorganophosphines,[6] organoisocyanides,[7] $[Fe_3(CO)_{12}]$,[8] and $[Fe(CO)_3\{P(OAr)_3\}_2]$ (Ar = Ph, and *o*- and *p*-MeC_6H_4) [9] were prepared by previously published methods. Other chemicals were purchased.

All reactions were carried out in purified solvents under an atmosphere of nitrogen. They were monitored by i.r. spectroscopy.

The red intermediate compounds (1) were prepared by irradiating ice-cooled benzene solutions of $[Fe(CO)_3\{P(OAr)_3\}_2]$ (1 g in *ca.* 100 ml) with a Phillips HPR 125-W lamp. The reaction was complete within *ca.* 2 h. To these solutions was added an equimolar amount of a solid or liquid reagent [PR_3, $P(OR)_3$, RNC, amines, CH_2CHCN, $C_2(CN)_4$, PhC_2H, Ph_2C_2, CS_2, $SnCl_4$, CCl_4, or *N*-bromosuccinimide] whilst gaseous reagents (CO, C_2H_2, C_2H_4, SO_2, or HCl) were passed through them. The reactions were complete within 1—24 h. Reactions with hydrogen or deuterium were carried out under a static atmosphere of the gas in a sealed vessel for 4 d.

When the reactions were complete, the solutions were filtered and the solvents removed at reduced pressure. The residues were purified by recrystallization (generally from toluene–hexane), or by column chromatography followed by recrystallization.

The compounds isolated, their yields, melting points, analyses, and i.r. spectra (recorded on a Perkin-Elmer 337 i.r. spectrometer, see ref. 7 for details) are reported in the Table; a Perkin-Elmer R 12 spectrometer was used to record n.m.r. spectra, with $SiMe_4$ as internal reference.

RESULTS AND DISCUSSION

The u.v. irradiation of solutions of *trans*-$[Fe(CO)_3\{P(OAr)_3\}_2]$ (Ar = Ph, *p*-MeC_6H_4, or *o*-MeC_6H_4) results in a colour change from yellow to pink with the evolution of carbon monoxide. The reactions were complete within 2 h, and, if carried out at 0 °C, were clean. Removal of the solvent gave very air-sensitive red oils (1) which could not be analysed. Consequently their solutions were used directly for a variety of reactions involving either ligand addition or oxidative addition. Although monitoring these by i.r. spectroscopy suggested that they were often high-yield processes, only very small amounts of pure products were obtained in many instances (Table). Sometimes this could be attributed to side-reactions, but usually it was because chromatography had to be used for product isolation and purification, and much decomposition took place on the column. A further problem was that apparently pure products failed to crystallize, and the liquids were susceptible to oxidation. In all instances these final products were yellow to orange in colour unless it is stated otherwise.

If carbon monoxide is bubbled through a solution of (1), the initial *trans*-$[Fe(CO)_3\{P(OAr)_3\}_2]$ complex is obtained in high yields in a reaction which requires *ca.* 9 h for completion. There is a limited tendency to form $[Fe(CO)_4\{P(OAr)_3\}]$. The reactions of (1) with tertiary phosphines and phosphite ligands, L, are similarly slow and clean at room temperature or in

Yields, melting points, analyses, and i.r. spectra for some reaction products

Compound[a]	Yield (%)[b]	M.p. (°C)[c]	Analysis Found (calc.) (%)			I.r. spectra[d]	
			C	H	Others	ν(CO)	Other
$[Fe(CO)_2\{P(OMe)_3\}\{P(OC_6H_4Me\text{-}p)_3\}_2]$	36	128—129	59.7 (60.1)	5.7 (5.4)		1 887 (10), 1 951 (2.9)	
$[Fe(CO)_2(PPh_3)\{P(OPh)_3\}_2]$	7	156—159	67.8 (67.6)	4.7 (4.5)		1 881 (10), 1 942 (2.8)	
$[Fe(CO)_2(CNMe)\{P(OC_6H_4Me\text{-}p)_3\}_2]$	2	139 (decomp.)	64.6 (64.5)	5.2 (5.2)	N 1.6 (1.6)	1 889 (10),[e] 1 939 (7.7)[e]	ν(CN) 2 118 (1.6)[e]
$[Fe(CO)_2(tcne)\{P(OPh)_3\}_2]$	10	146 (decomp.)	61.2 (61.5)	3.3 (3.5)	N 6.7 (6.5)	2 026 (10),[f] 2 079 (0.5)[f]	ν(CN) 2 223 (0.6)[f]
$[Fe(CO)_2(tcne)\{P(OC_6H_4Me\text{-}p)_3\}_2]$	18	129—131	63.2 (63.0)	4.5 (4.4)	N 6.9 (6.6)	2 025 (10),[f] 2 080 (0.5)[f]	ν(CN) 2 223 (1.0)[f]
$[Fe(CO)_2(Ph_2C_2)\{P(OPh)_3\}_2]$	30	105 (decomp.)	68.4 (68.6)	4.3 (4.4)		1 915 (10),[f] 1 981 (7.8)[f]	ν(CC) 1 827 (1.3)[f]
$[Fe(CO)_2(PhC_2H)\{P(OPh)_3\}_2]$	2	87—89	66.3 (66.4)	4.8 (4.2)		1 949 (10),[f] 1 980 (6.8)[f]	
$[Fe_2(CO)_4(PhC_2H)\{P(OPh)_3\}_4]$	4	161—163	64.6 (64.5)	4.9 (4.2)		1 921 (2.0), 1 929 (sh)	1 950 (4.7) 1 978 (7.0), 2 010 (10)
$[Fe(CO)_2(SO_2)\{P(OPh)_3\}_2]$	54	130—134	57.1 (57.4)	3.6 (3.8)	S 3.6 (3.8)	1 954 (10), 2 010 (6.5)	$\nu(SO_2)$ 1 085(s), 1 245(s)
$[Fe(CO)_2(CS_2)\{P(OPh)_3\}_2]$	22	69	58.2 (58.0)	3.5 (3.8)	S 9.1 (7.9)	1 963 (10), 2 022 (9.4)	$\nu(CS_2)$ 1 152
$[Fe(CO)_2(CS_2)\{P(OC_6H_4Me\text{-}o)_3\}_2]$	18	83—85	60.6 (60.5)	5.0 (4.7)	S 7.4 (7.2)	1 962 (10), 2 020 (9.2)	$\nu(CS_2)$ 1 160
$[Fe(CO)_2\{P(OPh)_3\}_2(SnCl_3)Cl]$	22	110 (decomp.)	46.2 (46.0)	3.2 (3.4)	Cl 14.3 (14.4)	2 020 (10), 2 073 (10)	
$[Fe(CO)_2\{P(OC_6H_4Me\text{-}p)_3\}_2(SnCl_3)Cl]$	32	113 (decomp.)	49.0 (49.0)	3.9 (3.9)	Cl 12.8 (13.2)	2 017 (10), 2 070 (9.3)	
$[Fe(CO)_2\{P(OPh)_3\}_2(H)Cl]$	49	136 (decomp.)	59.6 (59.5)	4.0 (4.0)	Cl 4.0 (4.6)	1 995 (10), 2 052 (7.1)	
$[Fe(CO)_2\{P(OPh)_3\}_2H_2]$		81—82	61.9 (62.2)	4.6 (4.4)		1 988 (10),[g] 2 030 (9.7)[g]	ν(FeH) 1 928 (0.5)[g]
$[Fe(CO)_2\{P(OPh)_3\}_2D_2]$		86—87	61.4 (61.9)	4.6 (4.1)		1 977 (10),[g] 2 029 (8.1)[g]	
$[Fe(CO)_2\{P(OPh)_3\}_2Cl_2]$			57.0 (57.0)	3.9 (3.7)	Cl 9.6 (8.9)	2 019 (9.3), 2 065 (10)	
$[Fe(CO)_2\{P(OC_6H_4Me\text{-}o)_3\}_2Cl_2]$	11	90—92	58.0 (58.5)	5.0 (4.5)	Cl 8.4 (8.1)	2 019 (7.4), 2 060 (10)	
$[Fe(CO)_2\{P(OPh)_3\}_2Cl]$			58.9 (59.5)	3.9 (3.8)	Cl 4.7 (4.6)	2 026 (10,br), 2 065 (8.9)	802,[h] 1 102[h]
$[Fe(CO)_2\{P(OC_6H_4Me\text{-}o)_3\}_2Cl]$			62.0 (62.2)	4.9 (4.6)	Cl 4.2 (4.2)	2 014 (8.8), 2 059 (10)	
$[Fe(CO)_2\{P(OPh)_3\}_2Br]$			56.9 (56.4)	3.5 (3.6)	Br 10.5 (9.9)	2 010	802,[h] 1 102[h]
trans-$[Fe(CO)_2\{P(OC_6H_4Me\text{-}o)_3\}_2Br]$			58.9 (59.0)	4.9 (4.6)	Br 9.4 (9.0)	2 003	1 060[h]
cis-$[Fe(CO)_2\{P(OC_6H_4Me\text{-}o)_3\}_2Br]$			58.4 (59.0)	4.5 (4.6)		2 016 (8.8), 2 057 (10)	1 060[h]

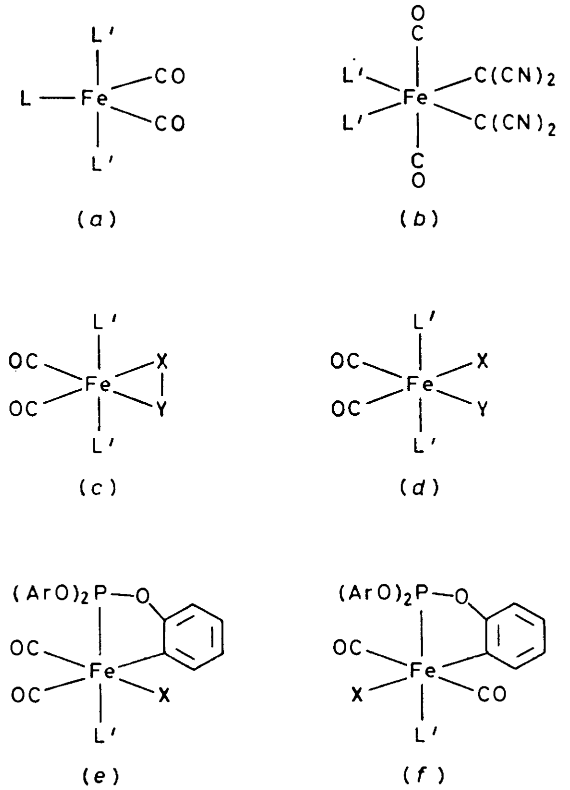
[a] tcne = Tetracyanoethylene. [b] Not recorded if below 1%. [c] Determined in sealed tubes; decomp., melted with decomposition. [d] Peak positions with relative peak heights in parentheses with ν(CO) region in CS_2 solution and the others in the solid state unless stated otherwise. [e] Tetrahydrofuran solution. [f] Chloroform solution. [g] Hexane solution. [h] *o*-Metallation bands; br = broad, sh = shoulder.

refluxing benzene. Numerous complexes of the general type $[Fe(CO)_2(L)\{P(OAr)_3\}_2]$ were obtained, but only those listed the Table could be crystallized. Their i.r. spectra in the 1 700—2 100 cm^{-1} region were as anticipated for this class of compound having the structure shown in the Figure (*a*) (*cf.* $[Fe(CO)_2(PPh_3)_3]$ in ref. 10); however, they do not define which phosphorus ligands occupy the axial positions.

The i.r. spectra of the reaction mixtures obtained from (1) and isocyanides, pyridines, or amines were very complicated. The only characterizable product was $[Fe(CO)_2(CNMe)\{P(OC_6H_4Me\text{-}p)_3\}_2]$.

Both ethylene and acrylonitrile gave single products with (1) but these were unstable and could not be isolated. Tetracyanoethylene (tcne), on the other hand, gave a blue solution from which was crystallized yellow $[Fe(CO)_2(tcne)\{P(OAr)_3\}_2]$ when Ar = Ph or *p*-MeC_6H_4, but when Ar = *o*-MeC_6H_4 a complex inseparable mixture was formed. The single strong absorption band and another much weaker one at higher frequencies due to the ν(CO) vibrations of these products suggests that the $Fe(CO)_2$ moiety has a *trans* arrangement in a quasi-octahedral complex [Figure (*b*)]. Although the bulky phosphite ligands normally prefer to be mutually *trans*, here they are *cis* due to the strong π-acceptor ability of the tcne ligand. Similar behaviour has been observed in $[IrBr(CO)(tcne)(PPh_3)_2]$,[11] and $[IrCl(CO)(tcne)(AsPh_3)_2]$.[12]

The single product from a slow reaction of (1) with diphenylacetylene is $[Fe(CO)_2(PhC_2Ph)\{P(OPh)_3\}_2]$. Its molecular structure is probably similar to that of $[Fe(CO)_4\{C_2(CO_2H)_2\}]$,[13] with the axial CO groups replaced by the bulky phosphite ligands. A relatively weak absorption band in its i.r. spectrum at 1 827 cm^{-1} is assigned to the ν(C=C) vibration. Its frequency and those of the two ν(CO) vibrations of the molecule, and the OC–Fe–CO angle θ of *ca.* 100° indicated by the relative intensities of the latter pair,[14] suggest that the iron–acetylene bonding lies between two extremes. These are, on the one hand, that of the metal–olefin type with co-ordination to trigonal bipyramidal Fe^0 [Figure (*a*), L = PhC$_2$Ph] for which ν(C=C) = 2 000—2 030 cm^{-1},[2b] ν(CO) = *ca.* 1 890 and 1 940 cm^{-1} (Table), and θ = *ca.* 120°. On the other hand there is the metallocyclopropene type co-ordinated to pseudo-octahedral Fe^{II} [Figure (*c*), X–Y = PhC=CPh] for which ν(C=C) is *ca.* 1 750—1 770 cm^{-1},[2b] ν(CO) = *ca.* 1 990 and 2 030 cm^{-1} (*cf.* $[Fe(CO)_2\{P(OPh)_3\}_2H_2]$ in the Table), and θ = *ca.* 90°.



(*a*) (*b*) (*c*) (*d*) (*e*) (*f*)

The proposed structures of various $[Fe(CO)_2(L)(L')_2]$, $[Fe(CO)_2(X{-}Y)(L')_2]$, and $[Fe(CO)_2(L')_2(X)(Y)]$ complexes described in the text [L′ = $P(OAr)_3$]

A number of products are formed in the reaction of (1) with phenylacetylene. Two were isolated using chromatography, both in low yields. They have the empirical formulae $[Fe(CO)_2(PhC_2H)\{P(OPh)_3\}_2]$ and $[Fe_2(CO)_n(PhC_2H)\{P(OPh)_3\}_3]$ (n = *ca.* 4). Their i.r. spectra do not show absorption bands due to ν(C=C) vibrations and are not similar to that of $[Fe(CO)_2(Ph_2C_2)\{P(OPh)_3\}_2]$ even though the two $[Fe(CO)_2(\text{acetylene})\{P(OPh)_3\}_2]$ complexes react with CS$_2$ to give $[Fe(CO)_2(CS_2)\{P(OPh)_3\}_2]$ {*cf.* $[Pt(PhC_2H)(PPh_3)_2]$ and CS$_2$ which form $[Pt(CS_2)(PPh_3)_2]$ (ref. 15)} and must contain an $Fe(CO)_2\{P(OPh_3)_3\}_2$-type of moiety. The very low yields of both phenylacetylene complexes precluded further characterization. Acetylene itself gave a very complicated reaction with (1), but no products could be isolated.

If sulphur dioxide is passed through a benzene solution of (1) for 1 h $[Fe(CO)_2(SO_2)\{P(OPh)_3\}]$ is formed. Its i.r. spectrum suggests that, like $[Fe(CO)_2(SO_2)(PEt_3)_2]$, it has an S-bonded SO$_2$ ligand.[16]

Although carbon disulphide does not react with $[Fe(CO)_3\{P(OAr)_3\}_2]$ even after many hours at 70 °C, compounds (1) are very rapidly converted to $[Fe(CO)_2(CS_2)\{P(OAr)_3\}_2]$. Compounds of this type have been prepared previously from a phosphorus(III) ligand, CS$_2$, and $[Fe_2(CO)_9]$ [17] or $[Fe(CO)_3(\text{benzylideneacetone})]$.[18] They have a *trans* arrangement of the phosphite ligands with a planar $(OC)_2Fe(CS_2)$ moiety [Figure (*c*), with X–Y = S–CS].[18]

The reactive red intermediate compound (1) also undergo oxidative–addition reactions to give complexes of Fe^{II}. These generally have higher ν(CO) frequencies than the ligand-addition derivatives of Fe^0 described above. Thus with SnCl$_4$, (1) forms only $[Fe(CO)_2\{P(OC_6H_4Z)_3\}_2(SnCl_3)Cl]$ (Z = H or *p*-Me). A similar reaction appears to occur when Z = *o*-Me, but only $[Fe(CO)_2\{P(OC_6H_4Me\text{-}o)_3\}_2Cl_2]$ could be isolated. It is possible that steric effects decrease the stability of the SnCl$_3$ derivative by encouraging the loss of SnCl$_2$. In contrast the thermal reaction of SnCl$_4$ with $[Fe(CO)_3(PPh_3)_2]$ results in loss of triphenylphosphine and formation of $[Fe(CO)_3(PPh_3)(SnCl_3)Cl]$,[19] whilst with $[Fe(CO)_3\{P(OPh)_3\}_2]$ the reaction is complicated, although small amounts of $[Fe(CO)_2\{P(OPh)_3\}_2(SnCl_3)Cl]$ may be isolated.

Within 1 h, dry HCl gas converts (1) to the rather unstable $[Fe(CO)_2\{P(OPh)_3\}_2(H)Cl]$. The i.r. spectrum of this compound is similar to that of the other $[Fe^{II}(CO)_2\{P(OAr)_3\}_2(X)(Y)]$ derivatives which we have prepared. We suggest that all have the structure shown in the Figure (*d*), having a *cis*-Fe(CO)$_2$ moiety with a OC–Fe–CO angle of *ca.* 90°. This arrangement is confirmed for $[Fe(CO)_2\{P(OPh)_3\}_2(H)Cl]$ where the ^{1}H n.m.r. spectrum shows a hydrogen atom bound directly to iron (9.95 p.p.m. upfield from SiMe$_4$) and split into a 1 : 2 : 1 triplet (J_{PH} 63 Hz) by the two equivalent axial phosphite ligands. The H–Cl addition is *cis*.

The arrangement is also confirmed by the spectra of $[Fe(CO)_2\{P(OPh)_3\}_2H_2]$, the white product obtained by the slow reaction of (1) with dihydrogen. In this compound the FeH$_2$ moiety gives rise in the ^{1}H n.m.r. spectrum to an upfield 1 : 2 : 1 triplet at 10.95 p.p.m. with J_{PH} 63 Hz, and also to ν(Fe–H) at 1 928 cm^{-1} in the i.r. spectra. Both these features are absent from the spectra of $[Fe(CO)_2\{P(OPh)_3\}_2D_2]$. We have not been able to detect ν(Fe–D), but have observed that the absorption band due to the asymmetric C–O stretch at 1 977 cm^{-1} in the i.r. spectrum of $[Fe(CO)_2\{P(OPh)_3\}_2D_2]$ (Table) is shifted to 1 988 cm^{-1} for $[Fe(CO)_2\{P(OPh)_3\}_2H_2]$. This is due to coupling of ν(CO) and ν(FeH) modes of the same symmetry, which is more important for the hydride than the deuteride. Neither of these compounds, nor $[Fe(CO)_2\{P(OPh)_3\}_2(H)Cl]$, react with carbon disulphide at room temperature.

The reactions of (1) with carbon tetrachloride give $[Fe(CO)_2\{P(OAr)_3\}_2Cl_2]$ as the principal product; *N*-bromosuccinimide forms $[Fe(CO)_2\{P(OAr)_3\}_2Br_2]$. In all instances two other complexes having the empirical formulae $[Fe(CO)_2\{P(OAr)_3\}_2X]$ ($X = Cl$ or Br) are formed in very low and variable yields. In one the two CO groups are *cis*, and give rise to two ν(CO) absorption bands of comparable intensities. The other shows only one ν(CO) band and is either a monocarbonyl or, more likely, a *trans*-dicarbonyl. The compounds isolated are listed in the Table.

There are features in the i.r. and ^1H n.m.r. spectra of the monohalide complexes which suggest that they are *o*-metallated derivatives of Fe^{II}; two possible isomers are illustrated in the Figure 1[(*e*) and (*f*)] ($X =$ Cl or Br). These diagnostic features are absorption bands at *ca.* 800, 950, and/or 1 100 cm^{-1} which are not present in the i.r. spectra of, *e.g.*, $[Fe(CO)_3\{P(OPh)_3\}]$ or $[Fe(CO)_2\{P(OPh)_3\}_2Cl_2]$. Also, the n.m.r. spectra of these last two compounds are much simpler than those of the monohalides, which also show diagnostic resonances at *ca.* 7.9—8.2 p.p.m. downfield from $SiMe_4$, and at lower fields than the resonances due to the remainder of the aromatic protons (6.5—7.3 p.p.m.) (*cf.* ref. 20).

The Structure of (1).—The i.r. spectra of (1) show two principal absorption bands and a shoulder in the ν(CO) region. Typical frequencies and relative intensities are, for $[Fe(CO)_3\{P(OPh)_3\}_2]$ in CS_2 solution, ν(CO) = 1 926 cm^{-1}, and for (1) in hexane ν(CO) = 1 987 (7.5), 1 997 (3.8, sh), and 2 030 (10) cm^{-1}. The spectra of (1) are virtually independent of solvent, *e.g.* in acetone the corresponding peaks are at 1 984, 1 993, and 2 030 cm^{-1}.

Although compounds (1) often act as though they were co-ordinatively unsaturated, the i.r. spectral data are not consistent with an $Fe(CO)_2\{P(OAr)_3\}_2$ formulation. Not only would this structure show solvent-dependent i.r. spectra, but also the loss of a CO ligand in going from $[Fe(CO)_3\{P(OAr)_3\}_2]$ to $[Fe(CO)_2\{P(OAr)_3\}_2]$ would be expected to result in a decline in ν(CO) frequencies rather than the observed increase. However, the observed ν(CO) frequencies, though not in the region associated with $[Fe^0(CO)_2(L)\{P(OAr)_3\}_2]$ complexes, are consistent with an octahedral Fe^{II} derivative, *cf.* $[Fe(CO)_2\{P(OPh)_3\}_2H_2]$ (Table). Consequently we suggest that *o*-metallation of the phosphite ligand has occurred, and that compounds (1) are best formulated as, *e.g.*, $[Fe(CO)_2\{P(O{\cdot}C_6H_4\text{-}o)(OPh)_2\}\{P(OPh)_3\}H]$. Two isomers are shown in the Figure [(*e*) and (*f*)] ($X = H$), but others are possible. At least two are necessary to explain the observed i.r. spectrum. Although we have obtained rather poor ^1H n.m.r. spectra of some of the compounds (1) in benzene solution, we have not been able to detect the resonance of a hydrogen bound directly to iron. However, this may be due to the molecules being fluxional, with each of the twelve (or six) *ortho*-C–H bonds being able to take part in the *o*-metallation process *via* a co-ordinatively unsaturated, short-lived $[Fe(CO)_2\{P(OAr)_3\}_2]$ intermediate. Reversible *o*-metallation behaviour of this type has been proposed by Parshall *et al.*[21] to account for the ligand–metal hydrogen transfer in $[Co\{P(OPh)_3\}_4H]$.

This formulation of (1) is consistent with the specificity of their formation from $[Fe(CO)_3(L)_2]$ when $L = P(OAr)_3$, but not when $L = PPh_3$, $P(OPh)(O_2C_2H_4)$, $P(OMe)_3$, or $P(OEt)_3$, which give $[Fe(CO)_4(L)]$ on irradiation. It has been shown that *o*-metallation is facilitated by more bulky ligands and by their ability to form five-membered metallocyclic rings.[22] The second of these requirements is fulfilled only by $L = P(OPh)(O_2C_2H_4)$, which is not sufficiently bulky, and by $P(OAr)_3$, which are.

The formation of the monohalide complexes such as $[Fe(CO)_2\{P(OC_6H_4)(OPh)_2\}\{P(OPh_3)_3\}X]$ ($X = Cl$ or Br) is readily explained. It is well known that both CCl_4 and *N*-bromosuccinimide are able to convert an M–H moiety to M–Cl or M–Br.[23] Their reaction with (1) would be expected to result in at least a limited amount of a similar reaction.

[8/1832 *Received*, 19*th October*, 1978]

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