Reduction-Oxidation Properties of Organotransition-metal Complexes. Part 8.[1] Formation and Reactivity of the Radical Cations $[Fe(CO)_3L_2]^+$, and the Mechanism of the Oxidative Elimination Reaction of $[Fe(CO)_3L_2]$ with Halogens

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Cyclic-voltammetric studies in CH_2Cl_2 show that $[Fe(CO)_3L_2]$ [1; L = PPh_3, $AsPh_3$, $PMePh_2$, $P(NMe_2)_3$, or $P(OPh)_3$; L_2 = $Ph_2PCH_2CH_2PPh_2$ (dppe) or $Ph_2PCH_2PPh_2$ (dppm)] undergoes one-electron oxidation to the radical cation $[Fe(CO)_3L_2]^+$ (2) which may be chemically generated from (1) using silver(I) salts or $[N(C_6H_4Br\text{-}p)_3][PF_6]$. The complex (2; L = PPh_3) reacts with halogens to give diamagnetic $[FeX(CO)_3(PPh_3)_2][PF_6]$ (3) which yields $[FeX_2(CO)_{4-n}(PPh_3)_n]$ (4; X = I, n = 1; X = Br, n = 1 and 2; X = Cl, n = 2) with X^-. Halide ions react directly with (2; L = PPh_3) to give mixtures of (1; L = PPh_3) and (4) *via* the paramagnetic intermediate $[FeX(CO)_3(PPh_3)_2]$ (5). A mechanism is proposed for the oxidative elimination reaction of (1) with halogens; the reactions of (2), and i.r. stopped-flow kinetic studies, implicate (2) and (5) as redox-active intermediates.

THE one-electron transfer reactions of $[V(CO)_6]$,[2] $[Cr(CO)_6]$,[3] and many Group 5B donor, isocyanide, and carbene complexes of $[M(CO)_6]$ (M = Cr, Mo, or W) [4] and $[M(CO)_6]^+$ (M = Mn or Re) [5] have been extensively studied by chemical and electrochemical methods. Of particular interest has been the work on the effects of geometrical isomerism on the redox behaviour of $[M(CO)_2(L\text{-}L)_2]^z$ [L–L = $Ph_2P(CH_2)_nPPh_2$, n = 1—3, M = Cr, Mo, or W, z = 0; M = Mn, z = 1],[6] $[M(CO)_4(\text{carbene})_2]$ (M = Mo or W, carbene = 2,4-dimethyl-1,2,4-triazolin-3-ylidene, *etc.*),[7] $[Mn(CO)_{6-n}(CNMe)_n]^+$ (n = 3 or 4),[8] and $[MX(CO)_3L_2]$ (M = Mn or Re, X = Cl or Br, L = Group 5B donor).[9,10] Apart from the oxidation of $[Fe(CO)_5]$ to $[Fe(CO)_5]^+$ in trifluoroacetic acid [11] the redox chemistry of the iron carbonyls and their Lewis-base derivatives had been neglected until recently. However, reports of the one-electron oxidation and/or reduction of $[Fe_3(CO)_{12-n}L_n]$ (n = 0;[12] n = 1—3, L = phosphine or phosphite [13]), and of the formation of $[Fe(CO)_3(\text{carbene})_2]^+$, $[Fe(CO)_2L(\text{carbene})_2]^+$, and $[Fe(CO)_2L_2(\text{carbene})]^+$ (carbene = $=\overline{\text{CN(Me)CH}_2\text{CH}_2\text{N}}\text{Me}$, L = phosphine or phosphite) from neutral precursors [14] closely followed our preliminary report of the work detailed herein.[15] We now describe chemical and electrochemical studies of the oxidation of $[Fe(CO)_3L_2]$ [1; L = PPh_3, $AsPh_3$, $PMePh_2$, $P(NMe_2)_3$, or $P(OPh)_3$; L_2 = dppe ($Ph_2PCH_2CH_2PPh_2$) or dppm ($Ph_2PCH_2PPh_2$)] to $[Fe(CO)_3L_2]^+$ (2), the reactions of $[Fe(CO)_3(PPh_3)_2][PF_6]$ with halogens and with halide ions, and preliminary i.r. stopped-flow kinetic studies of the reaction of (1; L = PPh_3) with iodine in $CHCl_3$. These studies have led us to propose a mechanism, involving one-electron transfer, for the oxidative elimination reaction between (1) and halogens.

RESULTS AND DISCUSSION

Electrochemical Studies.—Cyclic-voltammetric studies in CH_2Cl_2 show that (1) undergoes one-electron oxidation to (2) at the platinum electrode. In most cases the process is reversible (Table 1) with values of $(i_p)_{ox}/(i_p)_{red}$ close to unity; that $[Fe(CO)_3(PPh_3)_2][PF_6]$ (see below) undergoes one-electron reduction at a potential identical to that of the oxidation of (1; L = PPh_3) is a further indication of the full reversibility of the electron-transfer reaction $(1) \rightleftharpoons (2) + e^-$ when L = PPh_3. For (1; L = $PMePh_2$) the value of $(i_p)_{ox}/(i_p)_{red}$ (1.3 at a scan rate of 200 mV s^{-1}) implies incomplete reversibility, and the absence of any reduction wave on the return sweep of the cyclic voltammogram of (1; L = $AsPh_3$) suggests rapid chemical reaction of (2; L = $AsPh_3$) once formed. The e.s.r. and i.r. carbonyl spectra of (2; L = $AsPh_3$) have, however, been detected (see below).

TABLE 1

Infrared and electrochemical [a] data for $[Fe(CO)_3L_2]^z$

L	Z	$\nu(CO)$ [b] / cm^{-1}	E_p [c] / V	$(E_p)_{ox} - (E_p)_{red}$ [d] / mV	$(i_p)_{ox}/(i_p)_{red}$ [d]
PPh_3	0	1 885	0.33	155	0.98
PPh_3	1	1 999	0.33	170	1.00
$AsPh_3$	0	1 876	0.39 [e]		
$PMePh_2$	0	1 878	0.28 [f]	150	1.30
$P(NMe_2)_3$	0	1 865	0.14	170	0.97
$P(OPh)_3$	0	1 923	0.69	170	0.95
½ dppm	0	1 981vs, 1 907s, 1 896vs	0.16	160	1.03
½ dppe	0	1 985vs, 1 913s, 1 889vs	0.12	150	0.98

[a] For the reversible one-electron oxidation of $[Ni\{S_2C_2(CN)_2\}_2]^{2-}$: $(E_p)_{ox} - (E_p)_{red}$ = 160 mV. [b] In CH_2Cl_2. [c] Relative to a calomel electrode (1 mol dm^{-3} in LiCl). [d] Values for scan rate of 100 mV s^{-1}. [e] $(E_p)_{ox}$ value only, no reverse peak was detected. [f] $[(E_p)_{ox} + (E_p)_{red}]/2$ value given although process is not fully chemically reversible.

There is a marked dependence of E_p on the nature of L in that an increase in the basicity of the ligand results in a shift of E_p to more negative potential. E_p also appears to depend on geometry in that $[Fe(CO)_3(\text{dppe})]$, with *cis*-phosphorus donor atoms, is more readily oxidised than *trans*-$[Fe(CO)_3(PMePh_2)_2]$ (the donor abilities of the ligands are likely to be very similar).

Synthetic Studies.—The potentials recorded in Table 1 suggest that chemical oxidation of (1) to (2) should be readily accomplished. Diazonium salts, which we have used as mild one-electron oxidants,[16] and the nitrosonium ion, a more powerful oxidising agent, undergo carbonyl substitution reactions with (1) to give $[Fe(CO)_2ZL_2]^+$ (Z = NO[17] or $N_2C_6H_4R$;[18] R = H, *p*-F, *m*-F, *etc.*, L = phosphine, phosphite, or arsine). We have, therefore, used either silver(I) salts or the ammonio-cation, $[N(C_6H_4Br\text{-}p)_3]^+$ to form (2) from (1). The readily isolable salt $[N(C_6H_4Br\text{-}p)_3][SbCl_6]$[19] is somewhat limited in use as a simple, one-electron oxidant in that the anion is redox active,[20] and also a source of nucleophilic chloride ions. Although the hexafluorophosphate salt is less stable in the solid state it may be generated in CH_2Cl_2 solution from $[N(C_6H_4Br\text{-}p)_3]$ and $Ag[PF_6]$ and, after filtration to remove metallic silver, used *in situ*. Thus (1) and $[N(C_6H_4Br\text{-}p)_3][PF_6]$ in CH_2Cl_2 readily afford deep green solutions of (2). For (2; $L = PPh_3$) the complex is isolable as green crystals of $[Fe(CO)_3(PPh_3)_2][PF_6]\cdot 0.5CH_2Cl_2$; the formulation as a solvate was confirmed by elemental analysis (C, H, and Cl). Although no other examples of (2) could be isolated, their formation was verified by e.s.r. spectroscopy (see below) and, for the complexes of unidentate ligands, L, by the i.r. carbonyl spectrum (Table 2). The reaction between (1) and silver(I) salts is somewhat more complicated in that the i.r. spectra of the reaction mixtures show the presence of other carbonyl-containing products. For example, although a solution of (2; $L = PPh_3$) is eventually formed when $Ag[PF_6]$ is added to (1; $L = PPh_3$) in CH_2Cl_2, the i.r. spectrum shows the initial formation of a species with ν(CO) at 1 925s and 1 897vs cm^{-1}. The decay of this spectrum is accompanied by the increase in intensity of that due to (2; $L = PPh_3$), and the deposition of metallic silver. For more basic phosphines the intermediate [*e.g.* $L = PMePh_2$, ν(CO) at 1 925s and 1 901vs cm^{-1}] is more long-lived. However, its isolation from the reactions between (1) and silver(I) ions in acetone, CH_2Cl_2, tetrahydrofuran (thf), or toluene has proved impossible.

TABLE 2

Infrared and e.s.r. data[a] for $[Fe(CO)_3L_2]^+$ (2)

L	$\langle g \rangle_{av.}$	$\langle A_P \rangle$/G[b]	$\tilde{\nu}$(CO)/cm^{-1}
PPh_3	2.050	18.5	1 999
$AsPh_3$	2.054	17.6[c]	1 992
$PMePh_2$	2.052	18.8	1 993
$P(OPh)_3$	2.053	25.0	2 029
½ dppm	2.048	22.6	*d*
½ dppe	2.045	20.4	*d*

[a] In CH_2Cl_2 at 25 °C. [b] Three lines with relative intensities 1 : 2 : 1 unless stated otherwise. [c] $\langle A_{As} \rangle$ Seven-line spectrum. [d] Not measured.

We have recently isolated, and fully characterised, 1 : 2 adducts of silver(I) salts with $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]$[21] and $[Mn(CN)(PPh_3)(NO)(\eta\text{-}C_5H_5)]$,[22] for example $[Ag\{Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)\}_2][PF_6]$, and related species such as $[Ag\{M(CO)_3(\eta\text{-}C_5H_5)\}_2]^-$ (M = Cr, Mo, or W) have been studied by others.[23] The formulation of the initial products of the reactions between (1) and silver(I) salts as $[Ag\{Fe(CO)_3L_2\}_2]^+$, containing octahedral *mer*-tricarbonyliron units linked by iron–silver bonds, would be in agreement with the observation of a silver-metal deposit on decomposition to (2), and with the i.r. carbonyl spectrum. The Lewis-base nature of (1) has previously been demonstrated by the formation of a metal–metal bonded adduct with $AlCl_3$.[24]

Although the electrochemical study (see above) showed the one-electron oxidation of (1; $L = AsPh_3$) to be chemically irreversible, the reaction with $Ag[PF_6]$ in CH_2Cl_2 does involve initial formation of (2; $L = AsPh_3$), detected by e.s.r. (see below) and i.r. spectroscopy (Table 2). The initially formed deep green solution becomes paler rapidly, however, and after several minutes $[Fe(CO)_4(AsPh_3)]$ can be isolated from the yellow solution. The formation of the tetracarbonyl suggests disproportionation of (2; $L = AsPh_3$).

E.S.R. Studies.—The room-temperature *X*-band e.s.r. spectrum of $[Fe(CO)_3(PPh_3)_2][PF_6]$ in CH_2Cl_2 solution (Table 2) consists of three lines (1 : 2 : 1 relative intensity) [Figure 1(*a*)] due to the coupling of the free electron to two equivalent phosphorus nuclei (^{31}P, $I = \frac{1}{2}$). Together with the observation of only one carbonyl band in the i.r. spectrum the e.s.r. data establish that the cation is trigonal-bipyramidal *trans*-$[Fe(CO)_3(PPh_3)_2]^+$, and that no major structural change accompanies oxidation of (1; $L = PPh_3$). The frozen-solution *X*-band e.s.r. spectrum (in CH_2Cl_2) of $[Fe(CO)_3(PPh_3)_2][PF_6]$ is ill defined, but the *Q*-band spectrum [Figure 1(*b*)] of a powdered sample

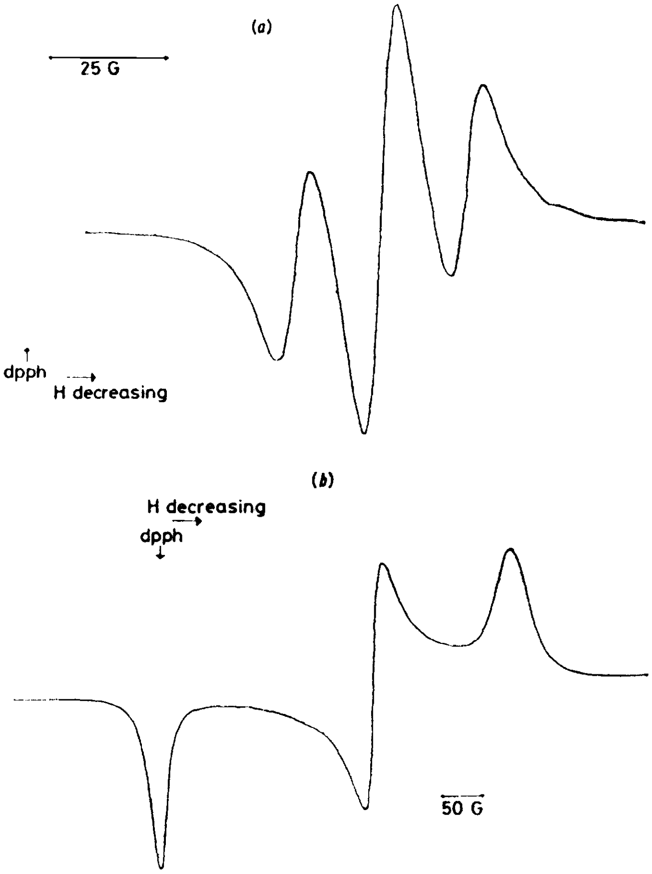

FIGURE 1 (*a*) Room-temperature *X*-band e.s.r. spectrum of $[Fe(CO)_3(PPh_3)_2][PF_6]$ in CH_2Cl_2; (*b*) *Q*-band e.s.r. spectrum of solid $[Fe(CO)_3(PPh_3)_2][PF_6]$. 1 G = 10^{-4} T of the salt shows, as expected for a trigonal-bipyramidal structure, three g values ($g_1 = 2.089$, $g_2 = 2.055$, and $g_3 = 2.004$) with $\langle g_{av.} \rangle = 2.049$, in excellent agreement with that found in solution.

The addition of silver(I) salts or [N(C_6H_4Br-*p*)$_3$][PF_6] to [1; L = $PMePh_2$ or $P(OPh)_3$] in CH_2Cl_2 results in the formation of solutions displaying e.s.r. spectra similar to that of (2; L = PPh_3) (Table 2), confirming formation of [2; L = $PMePh_2$ or $P(OPh)_3$]. The initial deep green solution formed from (1; L = $AsPh_3$) and Ag[PF_6] in CH_2Cl_2 shows a seven-line spectrum (Table 2),* as expected for (2; L = $AsPh_3$), with coupling of the free electron to two equivalent arsenic nuclei (^{75}As, $I = \frac{3}{2}$).

Whereas mixtures of (1; L_2 = dppe or dppm) and silver(I) salts in CH_2Cl_2 also exhibit three-line e.s.r. spectra, similar to those of [2; L = PPh_3, $PMePh_2$, or $P(OPh)_3$], the structure of (2; L_2 = dppe or dppm) cannot be deduced. The presence of other carbonyl-containing species in the reaction mixture precludes assignment of the carbonyl spectrum of (2; L_2 = dppe or dppm). Thus, whereas [1; L = PPh_3, $PMePh_2$, or $P(OPh)_3$] retain their basic structure on oxidation the same cannot be said for (1; L_2 = dppe or dppm).

The complexes [Fe(CO)$_3L_2$] [L_2 = $Ph_2PCH_2PPh_2$,[25] $Me_2PCH_2CH_2PMe_2$,[26] $Me_2PCF_2CH_2PMe_2$, $Ph_2P(CH_2)_3$-PPh_2, or *o*-phenylenebis(dimethylarsine)[27]] are stereochemically non-rigid to −70 °C (in the case of the arsenic ligand to −140 °C). It was of interest, therefore, to determine by e.s.r. methods whether (2; L_2 = dppe or dppm) might also be fluxional and whether a 'frozen' structure with inequivalent phosphorus atoms could be detected.

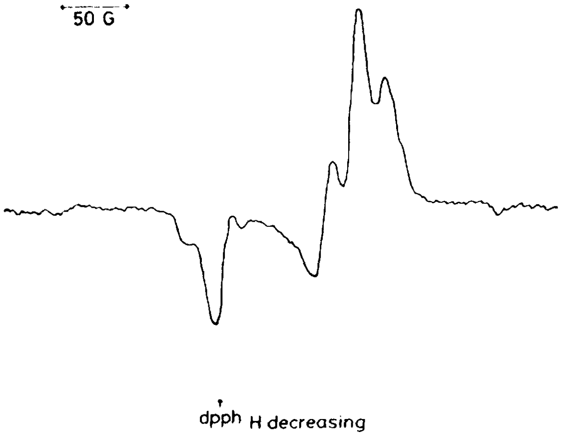

FIGURE 2 *X*-Band e.s.r. spectrum of [Fe(CO)$_3$(dppe)]$^+$ in frozen CH_2Cl_2 at −140 °C. 1 G = 10^{-4} T

On cooling a CH_2Cl_2 solution containing (2; L = dppe) no change in the *X*-band e.s.r. spectrum occurred, apart from line-broadening, until the freezing point; at −140 °C the spectrum shown in Figure 2 was obtained [the behaviour of (2; L_2 = dppm) is similar but the spectra are less well resolved]. In contrast to the *Q*-band e.s.r. spectrum [Figure 1(*b*)] of solid (2; L = PPh_3), only two g values ($g_1 = 2.006$ and $g_2 = 2.063$) are resolved, the average of which [$g_{av.} = (g_1 + 2g_2)/3 = 2.044$] is in agreement with that found in solution. Each absorption shows hyperfine coupling to two phosphorus nuclei which, however, is not sufficiently well resolved to distinguish between either the presence of equivalent phosphorus atoms or of inequivalent phosphorus atoms with similar hyperfine coupling constants. This ambiguity, together with our inability to measure the *Q*-band e.s.r. spectrum, has precluded further comments on the stereochemical non-rigidity of (2; L_2 = dppe or dppm).

The Reactivity of (2), *and Comments on the Oxidative Elimination Reactions of* (1) *with Halogens.*—Connor and Riley,[28] have recently shown that the oxidative-addition reaction between *cis*-[Mo(CO)$_2$(dmpe)$_2$] (dmpe = Me_2-$PCH_2CH_2PMe_2$) and alkyl halides, RX, involves the formation of *trans*-[Mo(CO)$_2$(dmpe)$_2$]$^+$ and '[RX]$^-$.' Both the metal-centred radical and the radical R$^\bullet$ (R = CPh_3), formed by dissociation of [RX]$^-$, were detected by e.s.r. methods.

Electron transfer is unlikely to occur as the initial step in all oxidative-addition or -elimination reactions but might be expected when the addendum can function as an oxidant and the substrate can undergo one-electron oxidation. We have shown that (2) can be formed from (1), and it is clear that, of the halogens, even iodine is strong enough to oxidise (1) [it will, for example, react with ferrocene ($E_p = 0.38$ V) to give the ferricinium ion]. We have therefore investigated the reactions of (2) with halogens and with halide ions, and have carried out preliminary stopped-flow i.r. kinetic studies on the reaction between (1; L = PPh_3) and iodine, to determine whether the formation of (2) is involved in the oxidative elimination reactions between (1) and halogens.[29]

Addition of halogens, X_2, to [Fe(CO)$_3$(PPh_3)$_2$][PF_6] in CH_2Cl_2 (1 : 1 ratio of Fe : X) instantly affords yellow or orange solutions from which crystalline salts, [FeX(CO)$_3$-(PPh_3)$_2$][PF_6] (3; X = Cl, Br, or I), can be isolated. Subsequent reaction with the appropriate halide, in equimolar quantities, then gives [FeX_2(CO)$_{4-n}L_n$] (4; X = I, $n = 1$; X = Br, $n = 1$ and 2; X = Cl, $n = 2$).

In each case the i.r. carbonyl spectrum of (3) in CH_2Cl_2 shows three bands [X = I, $\tilde{\nu}$(CO) = 2 114w, 2 063vs, and 2 041m; X = Br, $\tilde{\nu}$(CO) = 2 107w, 2 056vs, and 2 041m; X = Cl, $\tilde{\nu}$(CO) = 2 096w, 2 047vs, and 2 034m cm^{-1}] with relative intensities very similar to those of (4; X = I, L = PPh_3, $n = 1$) [$\tilde{\nu}$(CO) = 2 087w, 2 040vs, and 2 028m (sh) cm^{-1}]. It has been assumed previously that [FeI_2(CO)$_3$L] (L = phosphine or phosphite) has a *fac*-tricarbonyl structure, and, for example, the interpretation of the Mössbauer spectra of these complexes has been based on this assumption.[30] The ^{31}P n.m.r. spectra of (3) (X = Cl, −35.16 p.p.m.; X = Br, −35.10 p.p.m., relative to 85% aqueous H_3PO_4) in CD_2Cl_2 show only one singlet resonance (apart from that due to the [PF_6]$^-$ anion) clearly showing that

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* The reaction of (1; L = $AsPh_3$) in CH_2Cl_2 with a suspension of Ag[PF_6] results in the steady-state generation of (2; L = $AsPh_3$). Thus an e.s.r. spectrum can be detected even though cyclic voltammetry suggests (2; L = $AsPh_3$) to be unstable.

(3) are *mer*-tricarbonyls with *trans* phosphine ligands. The close similarity between the spectra of (3) and $[FeI_2(CO)_3L]$ therefore reveals that the latter are also *mer*-tricarbonyls. It should be noted that $[MnBr(CO)_3(PPh_3)_2]$, which again has an i.r. carbonyl spectrum with relative intensities extremely similar to those of $[FeI_2(CO)_3L]$, has also been shown to have a *mer*-tricarbonyl-*trans*-bis(phosphine) structure.[10]

The reaction of halide ions with (2; L = PPh_3) in a 1 : 1 ratio in CH_2Cl_2 rapidly yields (1; L = PPh_3) and (4). Although the formation of (1; L = PPh_3) would seem to imply oxidation of halide to halogen by (2) this is clearly impossible; the presence of (4) in the reaction mixture points to a more complex reaction which e.s.r. studies have helped to clarify. Thus, the addition of solid $[N(PPh_3)_2]Cl$, $[PPh_4]Br$, or $[NBu^n_4]I$ to CH_2Cl_2 solutions of (2; L = PPh_3) in the cavity of an e.s.r. spectrometer resulted in the detection of spectra with parameters shown in Table 3. Although the spectra rapidly decayed in CH_2Cl_2, and were difficult to reproduce, a more stable spectrum (X = Cl) was obtained in toluene. Addition of the dry, deoxygenated solvent to a solid mixture of $[N(PPh_3)_2]Cl$ and $[Fe(CO)_3(PPh_3)_2][PF_6]$ (neither component is soluble in toluene) resulted in the slow formation of a yellow solution and observation of the e.s.r. spectrum shown in Figure 3(*a*). The three-line signal, with $\langle g_{av.} \rangle$ and $\langle A_p \rangle$ values similar to those in CH_2Cl_2, is superimposed on the solid-state spectrum [Figure 3(*b*)] of unchanged $[Fe(CO)_3(PPh_3)_2][PF_6]$, and in the absence of $[N(PPh_3)_2]Cl$ is not detectable. After complete dissolution of the reactants, and evaporation to dryness of the reaction mixture, the i.r. carbonyl spectrum in CH_2Cl_2 again showed the formation of (1; L = PPh_3) and $[FeCl_2(CO)_2(PPh_3)_2]$; the reactions in toluene and CH_2Cl_2 are, therefore, very similar.

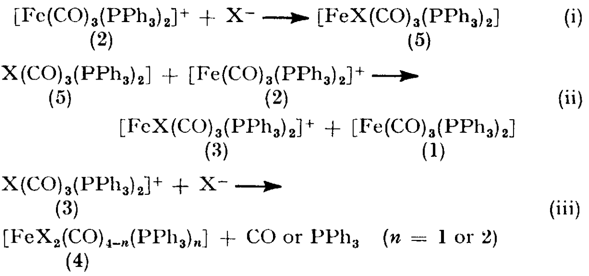
TABLE 3

E.s.r. data for $[FeX(CO)_3(PPh_3)_2]$ (5)

X	$\langle g \rangle_{av.}$	$\langle A_p \rangle$/G [a]
Cl	2.049	24.7 [b]
Cl	2.044	24.2 [c]
Br	2.057	23.7 [c]
I	2.075	24.0 [c]

[a] Three lines with relative intensity 1 : 2 : 1. [b] Generated by mixing solid samples of $[Fe(CO)_3(PPh_3)_2][PF_6]$ and $[N(PPh_3)_2]Cl$ in toluene. [c] Generated by adding solid halide to a CH_2Cl_2 solution of $[Fe(CO)_3(PPh_3)_2][PF_6]$.

The observation of e.s.r. spectra with $\langle g_{av.} \rangle$ dependent on X, and the nature of the final products suggest that (2; L = PPh_3) and X^- yield a paramagnetic, 19-electron intermediate, $[FeX(CO)_3(PPh_3)_2]$ (5), which subsequently reacts to give (1) and (4). Although the disproportionation of (5) would give rise to equimolar quantities of (1) and (4), *i.e.* $2[FeX(CO)_3(PPh_3)_2] \longrightarrow [Fe(CO)_3(PPh_3)_2] + [FeX_2(CO)_{4-n}(PPh_3)_n] + CO$ or PPh_3 (n = 1 or 2), such a reaction does not occur. Addition of halide ion to (2; L = PPh_3) (1 : 2 ratio) leads to the immediate, and total, conversion of (2) into (1), (3), and small amounts of (4). If, on formation of (5), disproportionation had occurred, the products of the 1 : 2 reaction would have been unchanged (2), (1), and (4) in a 2 : 1 : 1 ratio. The reaction of (2) with halide ion therefore occurs * as shown in Scheme 1. That small amounts of (4) are formed in the reaction between X^- and (2) (1 : 2 ratio) is due to competition between reactions (i) and (iii) (Scheme 1).



$$\underset{(2)}{[Fe(CO)_3(PPh_3)_2]^+} + X^- \longrightarrow \underset{(5)}{[FeX(CO)_3(PPh_3)_2]} \qquad \text{(i)}$$

$$\underset{(5)}{[FeX(CO)_3(PPh_3)_2]} + \underset{(2)}{[Fe(CO)_3(PPh_3)_2]^+} \longrightarrow \underset{(3)}{[FeX(CO)_3(PPh_3)_2]^+} + \underset{(1)}{[Fe(CO)_3(PPh_3)_2]} \qquad \text{(ii)}$$

$$\underset{(3)}{[FeX(CO)_3(PPh_3)_2]^+} + X^- \longrightarrow \underset{(4)}{[FeX_2(CO)_{4-n}(PPh_3)_n]} + CO \text{ or } PPh_3 \quad (n = 1 \text{ or } 2) \qquad \text{(iii)}$$

SCHEME 1

Complex (2) reacts both with halogens and with halide ion, eventually to produce (4) the final product in the oxidative elimination reaction between (1) and halogens. We have, therefore, carried out preliminary stopped-flow i.r. kinetic studies on the reaction between (1; L = PPh_3) and iodine in $CHCl_3$ in an attempt to determine whether initial formation of (2) does occur, and to differentiate between the subsequent possible pathways involving iodide ions or iodine.

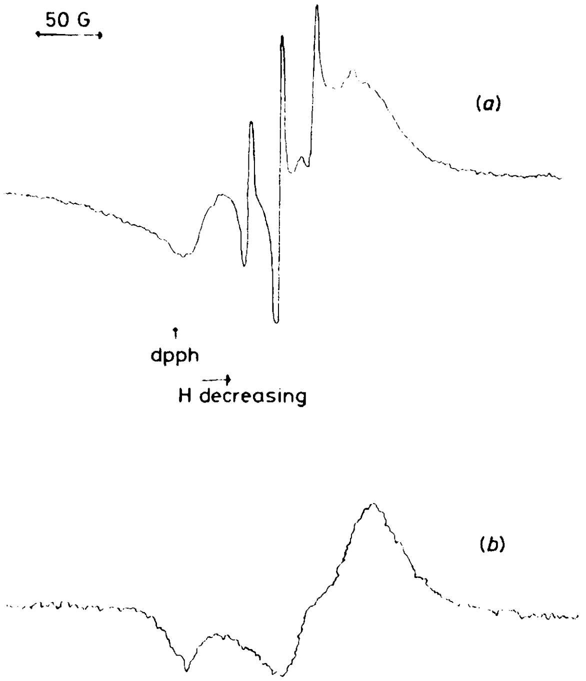


FIGURE 3 E.s.r. spectrum of $[Fe(CO)_3(PPh_3)_2][PF_6]$ in toluene (*a*) in the presence of, and (*b*) in the absence of, $[N(PPh_3)_2]Cl$. 1 G = 10^{-4} T

Equimolar quantities (1.02×10^{-3} mol dm^{-3}) of (1; L = PPh_3) and iodine were allowed to react at 0 °C in $CHCl_3$ in an i.r. stopped-flow system [31] and the kinetics measured as a function of wavelength between 2 120

* The instability of (3) in solution thwarted attempts to verify, by cyclic voltammetry, that the redox process $(3) + e^- \rightleftharpoons (5)$ can occur.

and 1 870 $\mathrm{cm^{-1}}$. The spectra for the first 350 ms of the reaction were generated by computer interpolation from the data (Figure 4). The most important, and extremely unusual, observation is that a sharp initial decrease in the concentration of (1; L = $\mathrm{PPh_3}$) is followed by its slow increase. In addition an intermediate with the correct i.r. carbonyl spectrum for $[\mathrm{FeI(CO)_3(PPh_3)_2}]^+$ is formed.

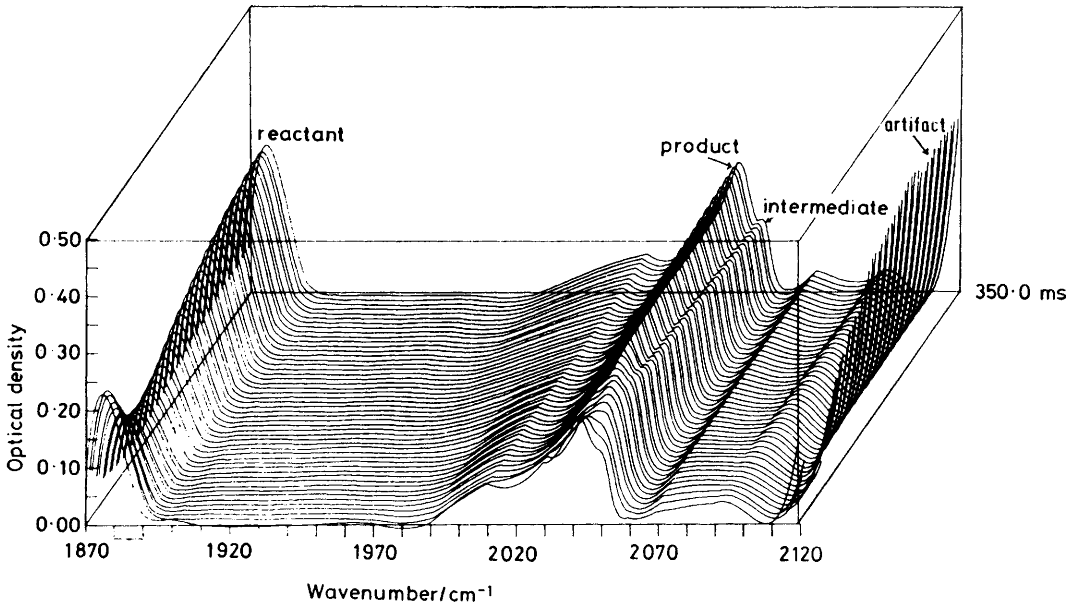


FIGURE 4 Computer-interpolated i.r. spectra for the first 350 ms of the reaction between $[\mathrm{Fe(CO)_3(PPh_3)_2}]$ and $\mathrm{I_2}$ at 0 °C in $\mathrm{CHCl_3}$. The initial concentration of each reactant was 1.02×10^{-3} mol $\mathrm{dm^{-3}}$

On the basis of the kinetic data, and the chemistry of (2; L = $\mathrm{PPh_3}$), we have proposed a mechanism, shown in Scheme 2, for the reaction between iodine and (1). The mechanism is probably somewhat over-simplified in that other steps may be envisaged {*e.g.* $[\mathrm{Fe(CO)_3L_2I}] + \mathrm{I^\bullet} \longrightarrow [\mathrm{Fe(CO)_3L_2I}]^+ + \mathrm{I^-}$} but in essence is correct.

$$\underset{(1)}{[\mathrm{Fe(CO)_3L_2}]} + \mathrm{I_2} \longrightarrow \underset{(2)}{[\mathrm{Fe(CO)_3L_2}]^+} + \mathrm{I^\bullet} + \mathrm{I^-} \tag{iv}$$

$$\underset{(1)}{[\mathrm{Fe(CO)_3L_2}]} + \mathrm{I^\bullet} \longrightarrow \underset{(2)}{[\mathrm{Fe(CO)_3L_2}]^+} + \mathrm{I^-} \tag{v}$$

$$\underset{(2)}{[\mathrm{Fe(CO)_3L_2}]^+} + \mathrm{I^-} \rightleftharpoons \underset{(5)}{[\mathrm{Fe(CO)_3L_2I}]} \tag{vi}$$

$$\underset{(2)}{[\mathrm{Fe(CO)_3L_2}]^+} + \underset{(5)}{[\mathrm{Fe(CO)_3L_2I}]} \longrightarrow \underset{(1)}{[\mathrm{Fe(CO)_3L_2}]} + \underset{(3)}{[\mathrm{Fe(CO)_3L_2I}]^+} \tag{vii}$$

$$\underset{(3)}{[\mathrm{Fe(CO)_3L_2I}]^+} + \mathrm{I^-} \longrightarrow \underset{(4)}{[\mathrm{Fe(CO)_3LI_2}]} + \mathrm{L} \tag{viii}$$

$$\underset{(3)}{[\mathrm{Fe(CO)_3L_2I}]^+} + \mathrm{I^-} \longrightarrow \underset{(4)}{[\mathrm{Fe(CO)_2L_2I_2}]} + \mathrm{CO} \tag{ix}$$

SCHEME 2

Further support for the proposed mechanism comes from the observation that $[\mathrm{Fe(CO)_3(carbene)_2}]^+$ can be isolated from the reaction between $[\mathrm{Fe(CO)_3(carbene)_2}]$ [carbene = $=\overline{\mathrm{CN(Me)CH_2CH_2N}}\mathrm{Me}$] and a deficiency of iodine.[14] The initial reactions (iv)—(vi) are extremely fast and the final product $[\mathrm{FeI_2(CO)_3(PPh_3)}]$ is formed even in the time of mixing of the reactants. Reaction (vii) is clearly substantiated by chemical studies (see above) and by the kinetic data which show regeneration of (1) and formation of (3). That the concentration of (3) decreases after initial formation is due to reaction (viii) which, again, is chemically confirmed. Step (ix) is not important for the reaction between (1; L = $\mathrm{PPh_3}$) and $\mathrm{I_2}$ but may be dominant for other ligands, L, and particularly for other halogens, for which the mechanism is obviously also applicable. For example (1; L = $\mathrm{PPh_3}$) and chlorine afford, as the final product, $[\mathrm{FeCl_2(CO)_2(PPh_3)_2}]$.

At relative concentrations of iodine to (1; L = $\mathrm{PPh_3}$) greater than 1 : 1 the kinetics become immeasurably fast and the yield of $[\mathrm{FeI_2(CO)_3(PPh_3)}]$ is drastically reduced. Reactions also occur over a wide time scale; under the conditions for which the spectra in Figure 4 were generated the reactant peak finally decreases in intensity over a period of tens of seconds to give mostly $[\mathrm{FeI_2(CO)_3(PPh_3)}]$. Rate data and further kinetic spectra will be presented at a later date.

Conclusion.—Electrochemical and chemical studies suggest that one-electron transfer is an integral part of the oxidative elimination reaction between $[\mathrm{Fe(CO)_3L_2}]$ and halogens. Similarities between the reactions of $[\mathrm{Fe(CO)_3(PPh_3)_2}]^+$ with halide ions, and certain of those detected in i.r. stopped-flow kinetic studies of the reaction between $[\mathrm{Fe(CO)_3(PPh_3)_2}]$ and iodine, further substantiate the suggestion. It is noteworthy that the reaction between $[\mathrm{Fe(CO)_3(PPh_3)_2}]$ and tetracyanoethylene (tcne) to give $[\mathrm{Fe(CO)_2(tcne)(PPh_3)_2}]$, formally an oxidative elimination reaction related to that with the halogens, involves formation of [tcne]$^-$, detected by e.s.r. spectroscopy.[32]

EXPERIMENTAL

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. The complexes, $[Fe(CO)_3L_2]$ [L = $AsPh_3$, PPh_3, $PMePh_2$, $P(NMe_2)_3$, or $P(OPh)_3$; L_2 = dppm or dppe],[33] and $N(C_6H_4Br$-*p*$)_3$ [34] were prepared by published procedures; silver(I) salts were purchased from Fluorochem Ltd., Glossop, Derbyshire. Infrared spectra were recorded on Perkin-Elmer PE 257, PE 457, or PE 580 spectrophotometers and calibrated against the absorption band of polystyrene at 1 601 cm^{-1}. Phosphorus-31 n.m.r. spectra were obtained on a JEOL PFT 100 spectrometer and calibrated against 85% aqueous H_3PO_4 as external reference. *X*-Band and *Q*-band e.s.r. spectra were recorded on a Varian Associates 4502/15 instrument and were calibrated against a solid sample of the diphenylpicrylhydrazyl (dpph) radical. Electrochemical studies were made using a Beckman Electroscan 30. Cyclic voltammetry was carried out using platinum wire auxiliary and working electrodes and a calomel electrode (1 mol dm^{-3} in LiCl) as reference. Solutions were 10^{-3} mol dm^{-3} in complex and 0.05 mol dm^{-3} in $[NEt_4][ClO_4]$ as supporting electrolyte. Criteria for reversibility are based on the assumption that data for the complex under study should be similar to that found for the reversible one-electron oxidation of $[Ni\{S_2C_2(CN)_2\}_2]^{2-}$.

The kinetic spectra were generated by recording kinetics at the wavenumbers 1 870, 1 880, 1 890, 1 900, 1 910, 1 930, 1 950, 1 970, 1 990, 2 010, 2 030, 2 040, 2 045, 2 047, 2 049, 2 052, 2 055, 2 060, 2 070, 2 090, 2 100, 2 105, 2 110, and 2 120 cm^{-1} on a Datalab DL 905 transient recorder; for these wavenumbers the first 350 ms of the reaction were studied. The data were stored on a cassette tape then transferred to the University main computer for processing by a suite of Algol W programs. These programs use the NAG library algorithm EO1 AAF [35] to interpolate points in wavelength and time between the recorded data for the computer plot to be generated. Care has to be taken to provide enough data, particularly at the edges of the spectral region, to prevent generation of artifacts such as that shown at 2 120 cm^{-1} in Figure 4. Solutions for the stopped-flow study were prepared and used under an atmosphere of dry nitrogen. Chloroform was washed with water, to remove ethanol, dried over P_2O_5, distilled from P_2O_5, and used immediately. Reaction solutions were shielded from light.

Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

Tricarbonylbis(triphenylphosphine)iron Hexafluorophosphate Hemidichloromethane, $[Fe(CO)_3(PPh_3)_2][PF_6]\cdot0.5CH_2Cl_2$.—Tri(*p*-bromophenyl)amine (0.145 g, 0.3 mmol) and $Ag[PF_6]$ (0.084 g, 0.33 mmol) were stirred in CH_2Cl_2 (10 cm^3) for 4 min. The resultant deep blue solution, containing $[N(C_6H_4Br$-*p*$)_3][PF_6]$, was filtered through Kieselguhr to remove metallic silver, and added to a stirred solution of $[Fe(CO)_3(PPh_3)_2]$ (0.20 g, 0.3 mmol) in CH_2Cl_2 (10 cm^3). After 1 min the deep green solution was filtered, hexane (10 cm^3) was added, and the volume of the mixture reduced to give deep green crystals of the product, yield 0.20 g (78%) (Found: C, 55.7; H, 3.6; Cl, 4.3. $C_{39.5}H_{31}ClF_6FeO_3P_3$ requires C, 55.7; H, 3.6; Cl, 4.2%).

The *complex* is soluble in polar solvents such as $CHCl_3$, CH_2Cl_2, and acetone to give air-sensitive green solutions. The solid complex decomposes in air in hours and is best stored *in vacuo*.

Tricarbonyliodobis(triphenylphosphine)iron Hexafluorophosphate–Dichloromethane (1/1), $[FeI(CO)_3(PPh_3)_2][PF_6]\cdot CH_2Cl_2$.—To solid $[Fe(CO)_3(PPh_3)_2][PF_6]\cdot0.5CH_2Cl_2$ (0.10 g, 0.12 mmol), was added I_2 (0.017 g, 0.067 mmol) in CH_2Cl_2 (10 cm^3). After stirring for 2 min hexane (30 cm^3) was added to give orange crystals of the *product*. Yield 0.08 g (70%) (Found: C, 47.1; H, 3.0. $C_{40}H_{32}Cl_2F_6FeIO_3P_3$ requires C, 47.0; H, 3.1%); $\nu(PF_6)$ at 835 cm^{-1} (Nujol).

The *complex* is soluble in polar solvents to give orange solutions which darken even under nitrogen. The solid complex is air-sensitive and decomposes under nitrogen in several days. Orange crystalline $[FeBr(CO)_3(PPh_3)_2][PF_6]$ (yield 83%) (Found: C, 52.5; H, 3.5. $C_{39}H_{30}BrF_6FeO_3P_3$ requires C, 52.6; H, 3.4%) and pale yellow crystalline $[FeCl(CO)_3(PPh_3)_2][PF_6]$ (yield 96%) (Found: C, 55.2; H, 3.9. $C_{39}H_{30}ClF_6FeO_3P_3$ requires C, 55.4; H, 3.6%) may be prepared similarly by dropwise addition of CH_2Cl_2 solutions of the halogen to $[Fe(CO)_3(PPh_3)_2][PF_6]\cdot0.5CH_2Cl_2$ in CH_2Cl_2. The solid complexes are more stable than the iodo-complex, but rapidly decompose in solution.

The Reaction of $[Fe(CO)_3(AsPh_3)_2]$ *with* $Ag[PF_6]$.—To a stirred solution of $[Fe(CO)_3(AsPh_3)_2]$ (0.20 g, 0.27 mmol) in CH_2Cl_2 (10 cm^3) was added solid $Ag[PF_6]$ (0.068 g, 0.27 mmol). Silver metal was deposited and a deep green solution which rapidly became yellow was formed. On filtration, evaporation of the filtrate to dryness, and recrystallisation from hexane, yellow crystals of $[Fe(CO)_4(AsPh_3)]$ were isolated. Yield 0.02 g {15% based on $[Fe(CO)_3(AsPh_3)_2]$}.

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