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Preliminary communication

THE ELECTROCHEMISTRY OF ORGANOTRANSITION-METAL COMPLEXES

III*. FORMATION AND REACTIVITY OF THE RADICAL CATIONS $[trans\text{-}Fe(CO)_3(PR_3)_2]^+$ AND $[Fe(CO)_3(Ph_2PCH_2CH_2PPh_2)]^+$

NEIL G. CONNELLY** and KAREN R. SOMERS
Department of Inorganic Chemistry, The University of Bristol, Bristol BS8 1TS (Great Britain)

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Summary

$[Fe(CO)_3L_2]$ (L = PPh_3, PPh_2Me, $P(OPh)_3$ or $P(NMe_2)_3$; L_2 = $Ph_2PCH_2CH_2PPh_2$) undergo reversible one-electron oxidations to give the radical cations $[Fe(CO)_3L_2]^+$ which have been studied by IR and ESR spectroscopy.

Although the reversible one-electron oxidations of $[Cr(CO)_6]$ [2], $[M(CO)_{6-n}L_n]$ (M = Cr, Mo, or W; *n* = 1,2, or 4; L = carbene, isocyanide, phosphine, etc.) [3], and $[M(CO)_2\{Ph_2P(CH_2)_nPPh_2\}_2]$ (M = Cr, Mo, or W; *n* = 1 [4] or 2 [5]) have been studied either chemically or electrochemically and the chemical oxidation of $[Mn(CO)_2(dppe)_2]^+$ (dppe = $Ph_2PCH_2CH_2PPh_2$) to the corresponding dication has been carried out [6] no similar studies have been made on other Lewis base derivatives of mononuclear carbonyls. We have now found that $[Fe(CO)_3L_2]$ complexes are reversibly oxidised to the radical cations $[Fe(CO)_3L_2]^+$.

Cyclic voltammetric studies in CH_2Cl_2 show that $[trans\text{-}Fe(CO)_3L_2]$ (L = PPh_3, PPh_2Me, $P(OPh)_3$ or $P(NMe_2)_3$) (I) and $[Fe(CO)_3(dppe)]$ (II) each undergo a reversible one-electron oxidation corresponding to the formation of $[Fe(CO)_3L_2]^+$ (III) and $[Fe(CO)_3(dppe)]^+$ (IV) respectively. For I the oxidation potential, E_p, (Table 1) depends on L such that E_p is lowered as the donor ability of L is increased. In addition there is a linear correlation between E_p and $\nu(CO)$ for I, as has been found for other series of carbonyl containing species [7,8].

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*For part II see ref. 1.

**Author to whom correspondence should be addressed.

TABLE 1

INFRARED, ELECTROCHEMICAL, AND ESR DATA FOR $[Fe(CO)_3L_n]^z$ [a]

L	n	z	ν(CO) (cm^{-1})	E_p(volts) [b]	$\langle g_{ave} \rangle$	$\langle A_p \rangle$ (Gauss)
$P(OPh)_3$	2	0	1923	0.68	—	—
	2	1	2029	—	2.053	25.0
PPh_3	2	0	1885	0.34	—	—
	2	1	1999	—	2.051	19.2
PPh_2Me	2	0	1878	0.28	—	—
	2	1	1993	—	2.052	18.8
$P(NMe_2)_3$	2	0	1865	0.14	—	—
dppe	1	0	1985(vs) 1913(s) 1889(vs)	0.11	—	—
	1	1	—	—	2.050	20.6

[a] All measurements in CH_2Cl_2. [b] Versus SCE (1 M in LiCl).

The magnitudes of E_p for I and II suggest that chemical oxidation to III and IV should be possible. Although $[NO]^+$ and $[N_2R]^+$ (R = aryl), which may function as one-electron oxidants [8], afford the substitution products $[Fe(CO)_2L_2N]^+$ (N = NO [9] or N_2R [10]), and iodine is oxidatively added to I to give $[Fe(CO)_3LI_2]$ [11], $Ag[PF_6]$ reacts with I or II to give deep green solutions containing III and IV respectively. With I (L = PPh_3) the monocation III (L = PPh_3) is the exclusive product. Its IR spectrum (Table 1) in the carbonyl region shows only one band, shifted to higher wavenumber by approximately 100 cm^{-1} from the value for I, and its ESR spectrum shows three lines, of relative intensities 1:2:1, consistent with the presence of a radical cation containing two equivalent phosphine ligands. The spectra suggest that the overall D_{3h} symmetry of the neutral complex is retained on oxidation. Addition of $Ag[PF_6]$ to CH_2Cl_2 solutions of the other monodentate phosphine derivatives and of II not only gives III or IV (Table 1) but also other carbonyl containing products the presence of which has prevented unequivocal assignment of the IR spectrum of IV. Although these products have not yet been fully characterised prolonged reaction between I and $Ag[PF_6]$ results in a solution with an IR spectrum very similar to that of $[Fe(CO)_3(PPh_3)I_2]$ [12] (e.g. for L = PPh_2Me, ν(CO) 2116 w, 2069 vs, and 2049 s). We therefore propose that $[Fe(CO)_3LCl_2]$ (V) is formed, by the reaction of III with CH_2Cl_2.

The formation of V from I via III suggests that oxidative addition of I_2 to $[Fe(CO)_3L_2]$ may also occur via the formation of $[Fe(CO)_3L_2]^+$, which subsequently reacts with I^-. We have therefore studied the reactions of III (L = PPh_3) with X^- (X = Cl or I) in 1:1 ratios in CH_2Cl_2 and found that I (L = PPh_3) is rapidly regenerated in both cases. With iodide ion equal quantities of I and $[Fe(CO)_3(PPh_3)I_2]$ are formed suggesting that III oxidises iodide to iodine which is then oxidatively added to I via a pathway not involving a reversible electron-transfer reaction. However, although the oxidation of iodide to iodine by III is feasible, the formation of I in the reaction of III with chloride ion cannot occur by a similar route since III cannot be a better oxidising agent than chlorine. Further studies are therefore in hand concerning the mechanism of the reaction between halide ions and III, and also on the possible occurrence of reversible electron-transfer reactions during the oxidative addition of halogens to [$Fe(CO)_3L_2$].

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