The Radical Cation $[Fe(CO)_3(PPh_3)_2]^+$: Novel Source of Iron(II) Carbonyl Complexes

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Summary The iron(I) complex $[Fe(CO)_3(PPh_3)_2]^+$ undergoes novel radical–radical coupling and redox reactions, with paramagnetic (NO, NO_2, *etc.*) and diamagnetic ($[S_2\overset{-}{C}\overset{+}{N}R_2]^-$, $S_2\overset{-}{C}\overset{+}{P}R_3$, *etc.*) ligands, respectively, to give iron(II) carbonyl derivatives such as $[Fe(NO_2)(CO)_3(PPh_3)_2]^+$ and $[Fe(CO)_2(PPh_3)_2(S_2CPPh_3)]^{2+}$.

Whereas many mononuclear metal carbonyl derivatives are known[1] to undergo one-electron transfer reactions the chemistry of the products is virtually unexplored. We now report that the paramagnetic, formally Fe^I, complex $[Fe(CO)_3(PPh_3)_2][PF_6]$ (**1**)[2] is the precursor to a range of novel Fe^{II} carbonyls which cannot be prepared directly from $[Fe(CO)_3(PPh_3)_2]$ (**2**).

$[Fe(CO)_3(PPh_3)_2][PF_6]$ (**1**)

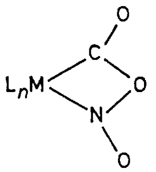
$[Fe(CO)_3(PPh_3)_2]$ (**2**)

$[Fe(CO)_2(NO)(PPh_3)_2][PF_6]$ (**3**)

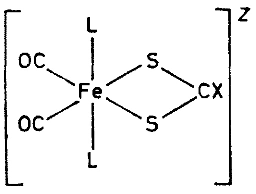
$[Fe(NO_2)(CO)_3(PPh_3)_2][PF_6]$ (**4**)

In CH_2Cl_2, NO gas and (**1**) undergo radical–radical coupling to give quantitative yields of $[Fe(CO)_2(NO)(PPh_3)_2][PF_6]$[3] {**3**; ^{31}P n.m.r. $[(CD_3)_2CO]$, δ 58·98 p.p.m.,† singlet}. A similar reaction with NO_2 affords yellow crystals of *mer,trans*-$[Fe(NO_2)(CO)_3(PPh_3)_2][PF_6]$ {**4**; 70%, $\nu(CO)(CH_2Cl_2)$ 2 113(wk) and 2 053(br.s) cm^{-1}; $\nu(NO_2)$ (Nujol) 1 410(med) cm^{-1}; ^{31}P n.m.r. $[(CD_3)_2CO]$, δ 38·52 p.p.m., singlet] which on heating under reflux in acetone yields (**3**). Oxygen transfer from co-ordinated NO_2 to CO, to give CO_2 and a nitrosyl ligand, is thought[4] to occur *via* intermediates such as (**5**). In refluxing CH_2Cl_2 (**4**) is slowly converted into (**3**) *via* a species, as yet inseparable from (**4**) or (**3**), with carbonyl $[\nu(CO)(CH_2Cl_2)$ 2 065(s) and 2 025(s) $cm^{-1}]$ and ^{31}P n.m.r. [δ 50·36 p.p.m., singlet] spectra consistent with the *cis,trans*-dicarbonylbis(phosphine) complex [**5**; $ML_n = Fe(CO)_2(PPh_3)_2$].

Complex (**1**) also reacts at room temperature in CH_2Cl_2 with $Me_2NC(S)SSC(S)NMe_2$ which may be regarded as a source of $Me_2NC(S)S$ radicals. After column chromatography, yellow crystals of the dithiocarbamate complex *cis,trans*-$[Fe(CO)_2(PPh_3)_2(S_2CNMe_2)][PF_6]$ (**6a**) are isolated in moderate yield [45%, $\nu(CO)(CH_2Cl_2)$ 2 024(s) and 1 981(s) cm^{-1}; ^1H n.m.r. (CD_3NO_2) τ 2·50 (30H, m, P*Ph*$_3$) and 7·69 (6H, s, *Me*)].



(5)



(6) L = PPh_3
a ; X = NMe_2, Z = +1
b ; X = PPh_3, Z = +2

The newly discovered[2] mechanism for the oxidative-elimination reaction between (**2**) and iodine, to give $[FeI_2(CO)_3(PPh_3)]$, includes steps in which (**1**) is involved in the formation of an unusual 19-electron intermediate (**7**) and its subsequent oxidation to (**8**) (Scheme).

$$\underset{(\mathbf{1})}{[Fe(CO)_3(PPh_3)_2]^+} + I^- \rightarrow \underset{(\mathbf{7})}{[FeI(CO)_3(PPh_3)_2]} \quad (a)$$

$$(\mathbf{1}) + (\mathbf{7}) \rightleftharpoons (\mathbf{2}) + \underset{(\mathbf{8})}{[FeI(CO)_3(PPh_3)_2]^+} \quad (b)$$

The equation for the combined reactions (a) and (b), *i.e.* $2(\mathbf{1}) + I^- \rightarrow (\mathbf{2}) + (\mathbf{8})$ suggested that (**1**) would react with other diamagnetic ligands in a second route to Fe^{II} carbonyl complexes. Thus (**1**) and $[S_2CNMe_2]^-$ (2:1 ratio) afford equimolar quantities of (**2**)‡ and (**6a**), and (**1**) and the zwitterionic ligand $R_3\overset{+}{P}\overset{-}{C}S_2$ (R = Ph or Bu^n) give (**2**) and the red, crystalline dicationic complex *cis, trans*-$[Fe(CO)_2(PPh_3)_2(S_2CPPh_3)][PF_6]_2$ [**6b**; 50%, $\nu(CO)$ (CH_2Cl_2) 2 052(s) and 2 011(s) cm^{-1}; $\nu(CS)$(Nujol) 1 120(med) and 1 100(med) cm^{-1}; ^{31}P n.m.r. (CD_2Cl_2) δ 50·35 p.p.m. (d, J_{PP} = 10 Hz, *P*Ph$_3$) and 19·8 p.p.m. (t, J_{PP} = 10 Hz, $(S_2C\mathit{P}Ph_3)$)].

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† ^{31}P chemical shifts to high frequency of H_3PO_4.

‡ The neutral complex (**2**) is readily removed from mixtures with the salts (**6a**) or (**6b**) by toluene washing.

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