## The Radical Cation [Fe(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>: 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<sub>2</sub>, etc.) and diamagnetic ([S<sub>2</sub>-

CNR<sub>2</sub>]<sup>-</sup>, S<sub>2</sub>CPR<sub>3</sub>, etc.) ligands, respectively, to give iron(II) carbonyl derivatives such as [Fe(NO<sub>2</sub>)(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> and  $[Fe(CO)_2(PPh_3)_2(S_2CPPh_3)]^{2+}$ .

WHEREAS many mononuclear metal carbonyl derivatives are known<sup>1</sup> to undergo one-electron transfer reactions the chemistry of the products is virtually unexplored. We now report that the paramagnetic, formally Fe<sup>I</sup>, complex  $[Fe(CO)_3(PPh_3)_2][PF_6]$  (1)<sup>2</sup> is the precursor to a range of novel Fe<sup>11</sup> carbonyls which cannot be prepared directly from  $[Fe(CO)_3(PPh_3)_2]$  (2).



In CH<sub>2</sub>Cl<sub>2</sub>, NO gas and (1) undergo radical-radical coupling to give quantitative yields of [Fe(CO)<sub>2</sub>(NO)- $(PPh_3)_2$  [PF<sub>6</sub>]<sup>3</sup> {**3**; <sup>31</sup>P n.m.r. [(CD<sub>3</sub>)<sub>2</sub>CO],  $\delta$  58.98 p.p.m.,<sup>†</sup> singlet]. A similar reaction with NO2 affords yellow crystals of mer, trans-[Fe(NO<sub>2</sub>) (CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>][PF<sub>6</sub>] {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<sup>-1</sup>; <sup>31</sup>P n.m.r. [(CD<sub>3</sub>)<sub>2</sub>CO], δ 38.52 p.p.m., singlet] which on heating under reflux in acetone yields (3). Oxygen transfer from co-ordinated NO<sub>2</sub> to CO, to give  $CO_2$  and a nitrosyl ligand, is thought<sup>4</sup> to occur via intermediates such as (5). In refluxing CH<sub>2</sub>Cl<sub>2</sub> (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  $2.025(s) \text{ cm}^{-1}$ ] and <sup>31</sup>P n.m.r. [ $\delta$  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<sub>2</sub>Cl<sub>2</sub> with Me<sub>2</sub>NC(S)SSC(S)NMe<sub>2</sub> which may be regarded as a source of Me<sub>2</sub>NC(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<sup>-1</sup>; <sup>1</sup>H n.m.r. (CD<sub>3</sub>NO<sub>2</sub>)  $\tau$  2.50 (30H, m, PPh<sub>3</sub>) and 7.69 (6H, s, Me)].



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

$$[Fe(CO)_{3}(PPh_{3})_{2}]^{+} + I^{-} \rightarrow [FeI(CO)_{3}(PPh_{3})_{2}] (a)$$
(1)
(7)
(1) + (7)  $\rightleftharpoons$  (2) + [FeI(CO)\_{3}(PPh\_{3})\_{2}]^{+} (b)
(8)

The equation for the combined reactions (a) and (b), *i.e.*  $2(1) + I^+ \rightarrow (2) + (8)$  suggested that (1) would react with other diamagnetic ligands in a second route to Fe<sup>II</sup> carbonyl complexes. Thus (1) and  $[S_2CNMe_2]^-$  (2:1) ratio) afford equimolar quantities of (2)<sup>+</sup> and (6a), and (1)and the zwitterionic ligand  $R_3 PCS_2$  (R = Ph or Bu<sup>n</sup>) give (2) and the red, crystalline dicationic complex cis, trans-[Fe(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(S<sub>2</sub>CPPh<sub>3</sub>)][PF<sub>6</sub>]<sub>2</sub> [**6b**; 50%,  $\nu$ (CO) (CH<sub>2</sub>Cl<sub>2</sub>) 2 052(s) and 2 011(s) cm<sup>-1</sup>; v(CS)(Nujol) 1 120(med) and 1 100(med) cm<sup>-1</sup>; <sup>31</sup>P n.m.r. (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  50.35 p.p.m. (d,  $J_{PP} = 10 \text{ Hz}, PPh_3$  and 19.8 p.p.m. (t,  $J_{PP} = 10 \text{ Hz},$  $(S_2CPPh_3)$ ].

K. B. and P. K. B. thank the S.R.C. for Research Studentships.

(Received, 6th May 1980; Com. 474.)

 $^{+31}$ P chemical shifts to high frequency of H<sub>3</sub>PO<sub>4</sub>.

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

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