Reduction–Oxidation Properties of Organotransition-metal Complexes. Part 13.[1] Cationic Iron(II) Carbonyls *via* the Radical Coupling, and Substitution Reactions of $[Fe(CO)_3(PPh_3)_2]^+$:† Synthetic and Electron Spin Resonance Spectroscopic Studies

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The radical cation $[Fe(CO)_3(PPh_3)_2]^+$ (1) undergoes oxidative-substitution reactions with the diamagnetic ligands S_2CPPh_3 and $[S_2CNMe_2]^-$ to give *cis,trans*-$[Fe(CO)_2(PPh_3)_2(S_2CR)]^Z$ (R = PPh$_3$, Z = 2; R = NMe$_2$, Z = 1); the dithiocarbamato-complex is also prepared from $Me_2NC(S)SSC(S)NMe_2$. Radical–radical coupling occurs between (1) and NO or NO$_2$ to give $[Fe(CO)_2(NO)(PPh_3)_2]^+$ and *mer,trans*-$[Fe(NO_2)(CO)_3(PPh_3)_2]^+$ respectively. On thermolysis, the nitro-complex yields CO$_2$ and the nitrosyl derivative *via* *cis,trans*-$[Fe\{C(O)ONO\}(CO)_2(PPh_3)_2]^+$. The spin trapping of $[Fe(CO)_3(PPh_3)_2]^+$ with Bu^{t}NO, and the formation of paramagnetic complexes with 1,2-diketones, have been studied by e.s.r. spectroscopy; *cis,trans*-$[Fe(CO)_2(PPh_3)_2(O_2C_6Cl_4)]^+$, from 3,4,5,6-tetrachloro-*p*-benzoquinone, has been isolated and fully characterised.

We have recently described [2] the synthesis of the radical cation $[Fe(CO)_3(PPh_3)_2][PF_6]$ (1) and revealed its intermediacy in the oxidative-elimination reactions of $[Fe(CO)_3(PPh_3)_2]$ (2) with halogens, X$_2$. The formation of $[FeX_2(CO)_3(PPh_3)]$ involves reactions (i) and (ii) which may be represented, overall, by equation (iii).

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

$$[Fe(CO)_3(PPh_3)_2]^+ + [FeX(CO)_3(PPh_3)_2] \longrightarrow [Fe(CO)_3(PPh_3)_2] + [FeX(CO)_3(PPh_3)_2]^+ \quad \text{(ii)}$$

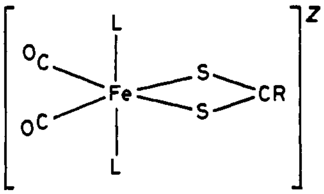
$$2[Fe(CO)_3(PPh_3)_2]^+ + X^- \longrightarrow [Fe(CO)_3(PPh_3)_2] + [FeX(CO)_3(PPh_3)_2]^+ \quad \text{(iii)}$$

We now detail [3] studies which show that equation (iii) also applies to the reactions of (1) with other diamagnetic substrates. In addition, radical–radical coupling reactions between (1) and NO or NO$_2$, the spin trapping of (1) with Bu^{t}NO, and the substitution reactions of (1) with 1,2-diketones are described.

RESULTS AND DISCUSSION

Oxidative-substitution Reactions of (1).—The addition of CS$_2$ and PPh$_3$ to deep green (1) in CH$_2$Cl$_2$ results in CO evolution and the formation of a red solution containing equimolar quantities of (2) and $[Fe(CO)_2(PPh_3)_2(S_2CPPh_3)][PF_6]_2$ (3). The salt (3) may be isolated as red crystals either by addition of diethyl ether to the mixture or by evaporation to dryness, extraction of (2) with toluene, and recrystallisation of the residue from CH$_2$Cl$_2$–n-hexane.

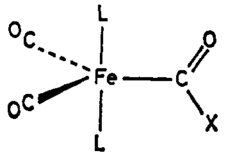
Formation of the chelated, zwitterionic ligand S$_2$CPPh$_3$ from CS$_2$ and PPh$_3$ has previously been demonstrated with $[Ir(NCMe)(CO)(PPh_3)_2][BF_4]$, *X*-ray studies [4] verifying the structure of *trans*-$[Ir(CO)(PPh_3)_2(S_2CPPh_3)][BF_4]$. The iridium complex shows [5] ν(CS) absorptions in the i.r. spectrum at 1 106 and 1 012 cm^{-1} (Nujol); corresponding bands at 1 120 and 1 100 cm^{-1} are observed for (3).



(3; R = PPh$_3$, Z = 2)
(4; R = NMe$_2$, Z = 1)
L = PPh$_3$

The *cis,trans* structure of (3; R = PPh$_3$, Z = 2) follows from the presence of two i.r. carbonyl absorptions of similar intensity (Table 1), and the ^{31}P n.m.r. spectrum, in CD$_2$Cl$_2$, which shows a doublet, J_{PP} = 10 Hz, at 50.35 p.p.m. (downfield of H$_3$PO$_4$) due to the *trans*-phosphine ligands, and a triplet, J_{PP} = 10 Hz, at 19.88 p.p.m. due to the *C*-bonded PPh$_3$ group.

Complex (1) undergoes a similar reaction with Na$[S_2CNMe_2]$ giving equimolar quantities of (2) and $[Fe(CO)_2(PPh_3)_2(S_2CNMe_2)][PF_6]$ (4). In this case, however, the monocationic product is more readily prepared *via* the radical-coupling reaction described below.



(5; L = PPh$_3$, X = halide)

The mechanism by which (3) and (4) are formed from (1) is probably similar to that for the reaction between (1) and halide ions [equations (i) and (ii)]. No evidence has been found, however, for analogues of the paramagnetic intermediate $[FeX(CO)_3(PPh_3)_2]$ (5; X = halide).[2] Although we have suggested that (5) is a 19-electron species containing a direct Fe–X bond we cannot, in retrospect, rule out the structure shown. Such a complex, containing a halogeno-acyl group, would be paramagnetic but with a 17-electron configuration for the metal centre. An alternative mechanism

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† Tricarbonylbis(triphenylphosphine)iron(1+).

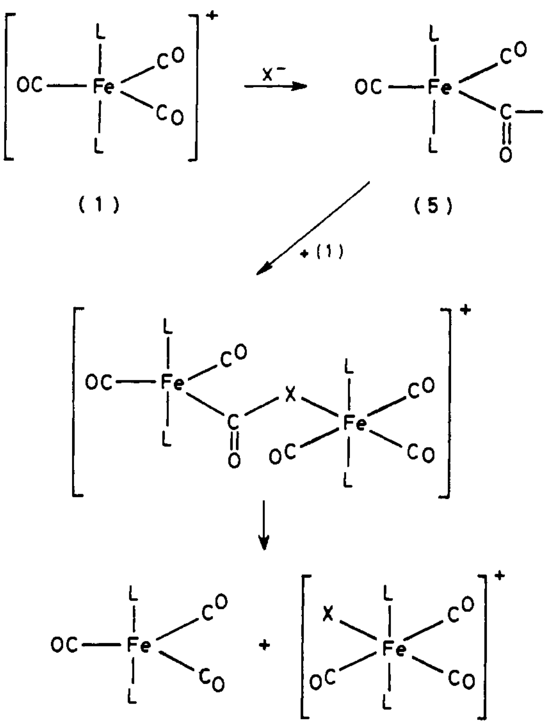
TABLE 1

Analytical and i.r. carbonyl data for cationic iron carbonyl complexes

	Complex	Analysis (%)[a]			
		C	H	N	$\tilde{\nu}$(CO)[b]/(cm^{-1})
(3)	$[Fe(CO)_2(PPh_3)_2(S_2CPPh_3)][PF_6]_2$	54.1(54.1)	3.9(3.6)	5.0(5.1)[c]	2 052, 2 011
(4)	$[Fe(CO)_2(PPh_3)_2(S_2CNMe_2)][PF_6]$	54.1(54.6)	4.4(4.0)	1.4(1.6)	2 024, 1 983
(7)	$[Fe(NO_2)(CO)_3(PPh_3)_2][PF_6]$	54.4(54.7)	4.3(3.5)	1.7(1.6)	2 113m, 2 073(sh)[d], 2 053br
(10)	$[Fe(CO)_2(PPh_3)_2(O_2C_6Cl_4)][PF_6]$	52.2(51.4)	3.3(2.9)		2 061, 2 021

[a] Calculated values are given in parentheses. [b] In CH_2Cl_2. [c] Sulphur analysis. [d] $\tilde{\nu}(NO_2)$ (Nujol) = 1 410 cm^{-1}.

for the reaction between (1) and X^-, based on the formation of this intermediate, is shown in the Scheme. Clearly this mechanism might also apply to the formation of (3) and (4) although species in which *S*-donor ligands, such as $[S_2CNMe_2]^-$, are bonded to the carbon of co-ordinated CO are unknown.



SCHEME L = PPh_3, X = halogen

Radical-coupling Reactions of (1).—The reaction of (1) with halogens, X_2, as shown in equation (iv), may be regarded as an example of radical–radical coupling.[2]

$$2[Fe(CO)_3(PPh_3)_2]^+ + X_2 \longrightarrow 2[FeX(CO)_3(PPh_3)_2]^+ \quad (iv)$$

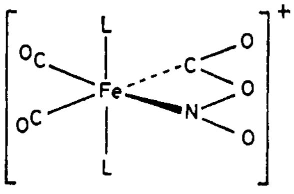
Similar reactions occur with other paramagnetic substrates. Thus, (4) may be prepared from (1) and $Me_2NC(S)SSC(S)NMe_2$, as a source of Me_2NCS_2 radicals, in yields superior to those from the oxidative-substitution reaction between (1) and $[S_2CNMe_2]^-$ (see above). The *cis,trans* structure of (4; R = NMe_2, *Z* = 1) gives rise to an i.r. carbonyl spectrum similar to that of (3) but with the two absorptions shifted to lower wavenumber (Table 1); the singlet resonance at δ 2.31, in the ^{1}H n.m.r. spectrum, verifies the presence of equivalent methyl groups on the dithiocarbamate ligand.

The dropwise addition of a solution of NO gas in CH_2Cl_2 to (1) results in the immediate, and quantitative, formation of an orange solution of $[Fe(CO)_2(NO)(PPh_3)_2][PF_6]$ (6), a complex previously prepared from (2) and $[NO][PF_6]$.[6] The coupling of (1) with NO to give $[Fe(CO)_3(NO)(PPh_3)_2]^+$, which might contain a 'bent' nitrosyl ligand, is followed by decarbonylation to give (6).

Solutions of NO_2 gas and (1) in CH_2Cl_2 react similarly, giving yellow crystals of *mer,trans*-$[Fe(NO_2)(CO)_3(PPh_3)_2][PF_6]$ (7) on addition of hexane. The spectral properties of (7) reveal its close similarity to the halogeno-complexes $[FeX(CO)_3(PPh_3)_2][PF_6]$ (X = Cl, Br, or I).[2] The i.r. carbonyl spectrum (Table 1) is typical of a *mer*-tricarbonyl group, and the singlet at 38.52 p.p.m. in the ^{31}P n.m.r. spectrum defines the *trans*-bis(phosphine) geometry.

In CH_2Cl_2 the i.r. carbonyl spectrum of (7) slowly changes so that two new absorptions, of equal intensity, are observed at 2 064 and 2 021 cm^{-1}. In addition, the ^{31}P n.m.r. spectrum shows a new singlet absorption at 50.36 p.p.m. Similar changes occur at room temperature in acetone, but solutions of (7) under reflux afford (6) (^{31}P n.m.r., 58.98 p.p.m.).

The intermediate in the thermolysis of (7), complex (8), could not be isolated pure [it is either contaminated with (6) or (7)] but its i.r. and ^{31}P n.m.r. spectra suggest the presence of a *cis*-dicarbonyl group and two phosphine ligands in mutually *trans* positions. The identities of (6) and (7) suggest that (8) has the structure shown, in which the *cis*-bonded nitro- and carbonyl ligands are linked prior to CO_2 elimination. The same bidentate ligand has been postulated in $[Ni(NO_2)\{C(O)ONO\}(PEt_3)_2]$, an intermediate in the formation of $[Ni(NO_2)(NO)(PEt_3)_2]$ from $[Ni(NO_2)_2(PEt_3)_2]$ and CO.[7]



(8; L = PPh_3)

Reactions of (1) *with the Spin Trap*, Bu^tNO, *and with*

1,2-Diketones.—The reactions of (1), described above, result in the isolation of diamagnetic cationic carbonyls which may be regarded, at least formally, as iron(II) complexes. The spin trap, Bu^{t}NO, and certain 1,2-diketones also react with (1) to give paramagnetic species which can also be formulated as iron(II) compounds with the unpaired electron largely ligand-based.

TABLE 2

E.s.r. spectral data for $[M(CO)_m(PPh_3)_nL]^Z$ [a]

M	m	n	L	Z	$g_{av.}$	$A_{iso.}(^{31}P)$/ (G)	$A_{iso.}(^{1}H)$/ (G)	$A_{iso.}$(other)/ (G)	Ref.
Fe	3	2	Bu^{t}NO	1	2.002 7	3.2		19.1 [b]	This work
Mn	4	1	Bu^{t}NO	0		3.86		19.44,[b] 11.33 [c]	9
Fe	2	2	MeC(O)C(O)Me	1	2.002 6	22.8	7.6		This work
Mn	2	2	MeC(O)C(O)Me	0		26.3	6.65	8.75 [c]	18 [d]
Fe	2	2	MeC(O)C(O)Ph	1	2.001 9	23.0	6.4 [e]		This work
Fe	2	2	PhC(O)C(O)Ph	1	2.001 7	23.3			This work
Mn	4	0	PhC(O)C(O)Ph	0	2.004 1		0.92(H_o), 0.43(H_m), 1.32(H_p)	5.76 [c]	20 [d]
Fe	2	2	Furil	1	2.001 5	21.3			This work
Fe	2	2	*o*-Chloranil	1	2.000 9	36.5			This work
Mn	4	0	*o*-Chloranil	0	2.004 3			9.13,[c] 0.5[f]	20 [d]
Fe	2	2	1,2-Naphthoquinone	1	2.000 7	25.3			This work
Fe	2	2	Phenanthrenequinone	1	2.001 3	22.5	1.8, 0.4 [g]		This work
Mn	4	0	Phenanthrenequinone	0	2.002 8		1.72, 0.40	5.50 [c]	17 [d]

[a] In CH_2Cl_2 unless stated otherwise. [b] ^{14}N coupling. [c] ^{55}Mn coupling. [d] In toluene. [e] Coupling to methyl protons. Further unresolved coupling to the phenyl protons (< 1 G) is also observed. [f] Coupling to two chlorine atoms. [g] Coupling to protons $H^{1,3}$ and $H^{2,4}$ respectively.

The addition of solid $(Bu^tNO)_2$ to a dilute solution of (1) in CH_2Cl_2 results in the formation of the spin-trapped adduct $[Fe(CO)_3\{N(O)Bu^t\}(PPh_3)_2]^+$ (9) as shown by e.s.r. spectroscopy (Table 2). The spectrum of (9), shown in Figure 1, consists of a 1 : 1 : 1 triplet, due to the coupling of the free electron to one nitrogen atom (^{14}N, $I = 1$), further split into 1 : 2 : 1 triplets by coupling to two equivalent phosphorus atoms (^{31}P, $I = \frac{1}{2}$). The $g_{av.}$ value of (9) is close to that of the free electron and $A_{iso.}(^{31}P)$ is small suggesting the free electron to be localised largely on the N(O)Bu^t ligand.

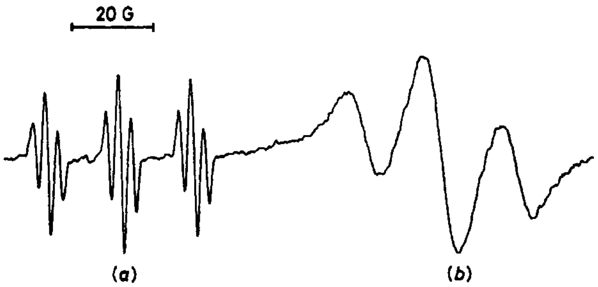


FIGURE 1 E.s.r. spectrum in CH_2Cl_2 at room temperature of (*a*) $[Fe(CO)_3\{N(O)Bu^t\}(PPh_3)_2]^+$ in the presence of (*b*) $[Fe(CO)_3(PPh_3)_2]^+$

The spin trapping of metal carbonyl radicals such as $\cdot Mn(CO)_5$ has been demonstrated previously,[8-10] but only in one case, that of $[Mn_2(CO)_9\{N(O)R\}]^+$, has a cation radical been so detected.[8] That (1) can be spin-trapped as (9) suggests, then, under favourable circumstances, more short-lived radical cations such as $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$ [11,12] and $[Fe(CO)_3(C_8H_8)]^+$ [1] might also be observed.

E.s.r. spectroscopy has also been used to identify *cis,trans*-$[Fe(CO)_2(L\text{-}L)(PPh_3)_2]^+$ (10), the product of the room-temperature reaction between (1) and 1,2-diketones (L-L) in CH_2Cl_2. The spectra (Table 2) suggest that the complexes are best formulated as iron(II) species bonded to the radical anion of L-L, with $g_{av.}$ and $A_{iso.}(^{1}H)$ parameters similar to those of the unco-ordinated anions $L\text{-}L^-$ (Table 3).[13-16] However, all of the products show hyperfine coupling to the two equivalent phosphorus atoms implying some delocalisation onto the $Fe(CO)_2(PPh_3)_2$ unit. In some cases, additional hyperfine coupling to the protons of the chelate ligand is observed.

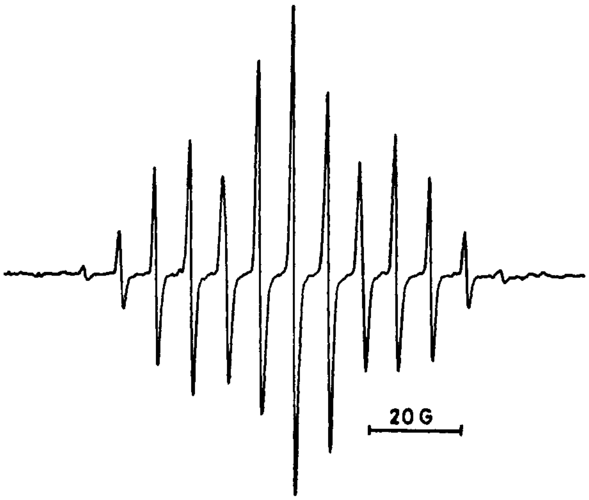


FIGURE 2 E.s.r. spectrum in CH_2Cl_2 at room temperature of [10; L-L = MeC(O)C(O)Me]

Thus, the e.s.r. spectrum of [10; L-L = MeC(O)C(O)Me] (Figure 2) consists of 13 lines with coupling of the free electron to six equivalent methyl protons and two phosphorus atoms; $A_{iso.}(^{31}P)$ is, fortuitously, $3A_{iso.}(^{1}H)$. The spectrum of [10; L-L = MeC(O)C(O)Ph] also shows

TABLE 3

E.s.r. data for 1,2-diketone radical anions, $[L-L]^-$

L–L	$g_{av.}$	$A_{iso.}(^1H)/(G)$	Ref.
MeC(O)C(O)Me [a]	2.004 8	7.00	13
MeC(O)C(O)Ph		$3.43(H_{Me})$, $1.84(H_p)$, $1.59(H_o)$, $0.53(H_m)$	14
PhC(O)C(O)Ph		$1.12(H_p)$, $0.99(H_o)$, $0.36(H_m)$	15
o-Chloranil	2.005 3		16
Phenanthrenequinone	2.004 9	$1.67(H^3)$, $1.34(H^1)$, $0.42(H^4)$, $0.21(H^2)$ [b]	21

[a] *cis* Isomer. [b] Numbering as in structure of (10; L–L = phenanthrenequinone)

coupling to the methyl protons (Table 2), and the 1 : 2 : 1 triplet of 1 : 2 : 2 : 1 quartets is further split by the coupling to the phenyl protons [$A_{iso.}(^1H) < 1.0$ G*]. By contrast, no proton coupling was observed for [10; L–L = PhC(O)C(O)Ph or furil].

The spectrum generated by the addition of 1,2-naphthoquinone to (1) is also poorly resolved, but that with phenanthrenequinone (Figure 3) consists of a 1 : 2 : 1 triplet, each component of which is split into a quintet of quintets due to coupling to the two sets of ring protons $H^{1,3}$ and $H^{2,4}$.

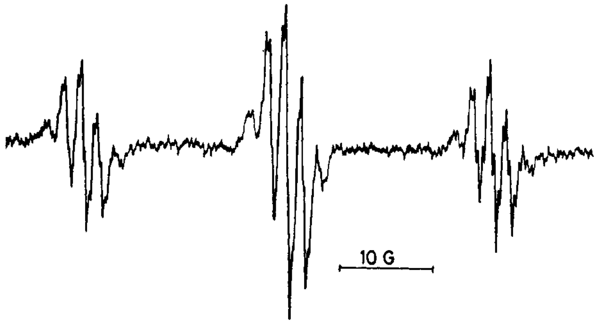
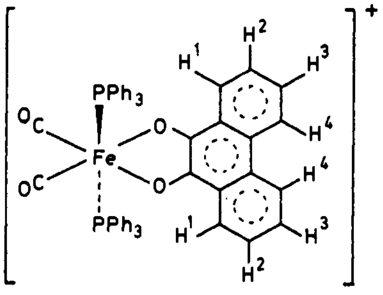


FIGURE 3 E.s.r. spectrum in CH_2Cl_2 at room temperature of (10; L–L = phenanthrenequinone)



(10; L—L = phenanthrenequinone)

The e.s.r. spectra do not, by themselves, show complex (10) to be $[Fe(CO)_2(PPh_3)_2(1,2\text{-diketone})]^+$. Indeed, in all of the examples so far described, isolation and further characterisation was not possible. However, the addition of 3,4,5,6-tetrachloro-*p*-benzoquinone (*o*-chloranil) to (1) in CH_2Cl_2 gives a green-black solution from which a near-quantitative yield of *cis,trans*-$[Fe(CO)_2(PPh_3)_2(O_2C_6Cl_4)][PF_6]$ is isolable. Elemental analysis, the observation of two carbonyl bands of equal intensity in the i.r. spectrum (Table 1), and a 1 : 2 : 1 triplet in the e.s.r. spectrum (Table 2) serve to confirm the *cis,trans* geometry proposed for (10).

Many studies have been made [17-21] of the generation of 1,2-diketone derivatives of the radical $\cdot Mn(CO)_5$. There is some evidence [19] for the initial formation of $[Mn(CO)_5(1,2\text{-diketone})]$, but the more persistent e.s.r. spectra are assigned to the chelated tetracarbonyls $[Mn(CO)_4(1,2\text{-diketone})]$. Although such species are not isolable, the successful characterisation of (10; L–L = *o*-chloranil) and the similarities between the e.s.r. spectra of (10) and the isoelectronic manganese complexes (Table 2) is further evidence for the chelation of the 1,2-diketone ligands.

Conclusions.—The oxidative-substitution and radical-coupling reactions of (1), and the formation of isolable 1,2-diketone derivatives, illustrates the synthetic potential of organotransition-metal radical cations. It is particularly noteworthy that the reactions described do not occur with the diamagnetic precursor to (1), namely $[Fe(CO)_3(PPh_3)_2]$ (2). Indeed, we have already shown that (1) is an intermediate in the reactions of (2) with halogens, and may also be so in the reaction with $[NO]^+$. That many organometallic complexes can be oxidised to reactive radical cations is also becoming apparent [1,11,12] and the spin trapping of (1) with Bu^tNO bodes well for the identification of other, more short-lived species.

EXPERIMENTAL

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. The complex $[Fe(CO)_3(PPh_3)_2][PF_6]\cdot 0.5CH_2Cl_2$ was prepared by the published method,[2] *o*-quinones were purchased from Aldrich Chemical Co., and NO gas was purified by passage through a cold trap (−78 °C) before use. Infrared spectra were recorded on Perkin-Elmer PE 257 or PE 457 spectrometers and calibrated against the absorption band of polystyrene at 1 601 cm^{-1}. Phosphorus-31 n.m.r. spectra were recorded on a JEOL FX90Q instrument and calibrated against 85% aqueous H_3PO_4 as external reference. *X*-Band e.s.r. spectra were recorded on a Varian Associates 4502/15 instrument and were calibrated against a solid sample of the diphenylpicrylhydrazyl radical. Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

*Dicarbonylbis(triphenylphosphine)(triphenylphosphoniodithioformate-*S,S'*)iron Bis(hexafluorophosphate)*, $[Fe(CO)_2(PPh_3)_2(S_2CPPh_3)][PF_6]_2$.—The compound CS_2 (0.022 g, 0.29 mmol) was added to a mixture of $[Fe(CO)_3(PPh_3)_2][PF_6]\cdot 0.5CH_2Cl_2$ (0.23 g, 0.27 mmol) and PPh_3 (0.07 g, 0.27 mmol) in CH_2Cl_2 (20 cm^3). Carbon monoxide gas was

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* Throughout this paper: 1 G = 10^{-4} T.

evolved, and after 15 min the solution was deep red. Filtration and addition of diethyl ether (20 cm^3) gave red crystals of the *product*. Yield 0.085 g [50%, based on equation (iii)]. The complex is stable in air for long periods, and dissolves in polar solvents such as CH_2Cl_2 or acetone to give moderately air-stable red solutions.

Dicarbonyl(dimethyldithiocarbamato)bis(triphenylphosphine)iron Hexafluorophosphate, $[Fe(CO)_2(PPh_3)_2(S_2CNMe_2)][PF_6]$.—The compound $Me_2NC(S)SSC(S)NMe_2$ (0.030 g, 0.13 mmol) was added to a stirred solution of $[Fe(CO)_3(PPh_3)_2][PF_6]\cdot 0.5CH_2Cl_2$ (0.20 g, 0.23 mmol) in CH_2Cl_2 (15 cm^3). After 90 min, the yellow solution was filtered and n-hexane (30 cm^3) added to give a yellow precipitate. Chromatography on an alumina–CH_2Cl_2 column, eluting with CH_2Cl_2–acetone (9 : 1), gave a yellow solution from which pale yellow crystals of the *product* were obtained by addition of n-hexane and partial evaporation *in vacuo*. Yield 0.13 g (61%). The product is stable in air but darkens slowly on exposure to light. Solutions of the complex in polar solvents such as CH_2Cl_2 are air- and light-sensitive.

Tricarbonylnitrobis(triphenylphosphine)iron Hexafluorophosphate, $[Fe(NO_2)(CO)_3(PPh_3)_2][PF_6]$.—To $[Fe(CO)_3(PPh_3)_2][PF_6]\cdot 0.5CH_2Cl_2$ (0.2 g, 0.23 mmol) in CH_2Cl_2 (25 cm^3) was added dropwise a solution of NO_2 in CH_2Cl_2. On completion of the reaction, as monitored by i.r. spectroscopy, hexane was added to the yellow solution to give the *product* as a yellow solid. Yield 0.16 g (80%). The complex is soluble in polar solvents such as CH_2Cl_2 and acetone to give yellow solutions which slowly lose CO_2 with formation of $[Fe(CO)_2(NO)(PPh_3)_2][PF_6]$.

Thermolysis of $[Fe(NO_2)(CO)_3(PPh_3)_2][PF_6]$.—A solution of $[Fe(NO_2)(CO)_3(PPh_3)_2][PF_6]$ (0.25 g, 0.29 mmol) was heated under reflux in acetone (30 cm^3) for 3 h. After filtration, addition of hexane gave $[Fe(CO)_2(NO)(PPh_3)_2][PF_6]$ as a yellow-orange precipitate, yield 0.09 g (38%).

*Dicarbonyl(*o*-chloranil)bis(triphenylphosphine)iron Hexafluorophosphate*, $[Fe(CO)_2(PPh_3)_2(o\text{-}O_2C_6Cl_4)][PF_6]$.—To a stirred solution of $[Fe(CO)_3(PPh_3)_2][PF_6]\cdot 0.5CH_2Cl_2$ (0.4 g, 0.47 mmol) in CH_2Cl_2 (20 cm^3) was added *o*-chloranil (0.13 g, 0.53 mmol). After 5 min, the deep green solution was filtered and n-hexane added to precipitate the *product* as a dark green solid. Yield 0.45 g (93%). The complex is moderately air-stable, and soluble in polar solvents to give green-black air-sensitive solutions.

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