Paramagnetic Carbenemetal Complexes. Part 2.[1] Synthesis and Spectroscopic Studies of Stable Electron-rich Olefin-derived Paramagnetic Carbenecarbonyl- and Carbenenitrosyl-iron(I) Complexes

By **Michael F. Lappert,* Jonathan J. MacQuitty,** and **Peter L. Pye,** School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

The synthesis of some new electron-rich olefin-derived carbeneiron(0) complexes (1)—(11) of the type $[\mathrm{Fe(CO)_3(L^{Me})L'}]$ $[\mathrm{L^{Me}} = \overline{\mathrm{CN(Me)CH_2CH_2N}}\mathrm{Me}$; L′ = $\mathrm{PMePh_2}$, $\mathrm{PEt_2Ph}$, $\mathrm{PPh_2H}$, $\mathrm{PPh_3}$, $\mathrm{AsPh_3}$, $\mathrm{P(C_6H_{11})_3}$, or $\mathrm{P(OPh)_3}]$, $[\{\mathrm{Fe(CO)_3(L^{Me})}\}_2(\mu\text{-dppe})]$, (8), and $[\mathrm{Fe_2(CO)_6(L^{Me})(dppe)}]$ is described, from the appropriate ligand with $[\mathrm{Fe(CO)_4(L^{Me})}]$. These complexes have then been used to produce paramagnetic carbeneiron(I) salts (12)—(38) by one-electron oxidation, generally by use of $\mathrm{Ag[BF_4]}$. The iron(I) salts are often chemically and thermally stable, nine examples, *e.g.* $[\mathrm{Fe(CO)_3(L^{Me})_2}][\mathrm{BF_4}]$, being fully characterised as crystalline materials. Oxidation of complex (8) yields the novel di-iron(I) dication $[\{\mathrm{Fe(CO)_3(L^{Me})}\}_2(\mu\text{-dppe})]^{2+}$ which contains two independent, non-interacting, low-spin d^7 iron atoms. The tricarbonyliron(I) complexes react with various neutral ligands to afford $[\mathrm{Fe(CO)_2(L^{Me})(L')L''}]^+$ cations and CO; such reactions are often followed by disproportionation, *e.g.* $[\mathrm{Fe(CO)_3(L^{Me})(PPh_3)}]^+$ gives $[\mathrm{Fe(CO)_2(L^{Me})(PPh_3)_2}]^+$ and $[\mathrm{Fe(CO)_4(L^{Me})}]^+$, which may have synthetic utility. The ligand $\mathrm{L^{Me}}$ assists stabilisation of the cationic iron(I) state by delocalising positive charge. Infrared and e.s.r. data provide an insight into the structure and stereochemistry of the iron(0) (trigonal-bipyramidal) and iron(I) (distorted square-pyramidal) complexes and suggest that the $\mathrm{L^{Me}}$ ligand is a better acceptor of the unpaired electron density than a tertiary phosphine.

CARBENEMETAL complexes have been extensively studied since 1964. Examples are known for most of the *d*-block elements, but until 1978 all isolable complexes were diamagnetic,[2,3] the central metal atom (usually in a low oxidation state) being in a low-spin d^2, d^4, d^6, d^8, or d^{10} environment. Likewise there were few stable paramagnetic complexes containing carbonyl ligands. In a preliminary publication we described some iron(I) complexes,[4] while in Part 1 cationic chromium(I) complexes were discussed.[1] We now provide full details relating to the synthesis, isolation, and spectroscopic characterisation of various stable, paramagnetic, low-spin d^7 carbeneiron(I) complexes and some of the new iron(0) precursors.

Prior to our work [1,4] there had been two reports [5,6] describing the formation of short-lived, thermally unstable, paramagnetic carbenemetal complexes, equations (i) (M = Cr or W, $\mathrm{C_{10}H_9Fe}$ = ferrocenyl) [5] and (ii) [6] (M = Cr, Mo, or W; R = Ph or OMe; R′ = aryl).

$$[\mathrm{M(CO)_5\{C(OEt)(C_{10}H_9Fe)\}}] \xrightarrow[\text{electrochemical}]{-1e^-} [\mathrm{M(CO)_5\{C(OEt)(C_{10}H_9Fe)\}}]^+ \quad \text{(i)}$$

$$[\mathrm{M(CO)_5\{C(R)R'\}}] \xrightarrow[\text{Na-K}]{+1e^-} [\mathrm{M(CO)_5\{C(R)R'\}}]^- \quad \text{(ii)}$$

The e.s.r. spectra of the radical anions of equation (ii) were taken as indicating that the odd electron was mainly carbene centred, but in neither instance was a complex isolated.

A stable oxidation state of I is rare for iron; a stable d^7 environment is only well known for cobalt(II). Among the established iron(I) complexes are the yellow-brown $[\mathrm{Fe(pdma)(CO)_2I}]$ [pdma = *o*-phenylenebis(dimethylarsine)],[7] and various salts of formula $[\mathrm{Fe(CO)_3(PR_3)_2}][\mathrm{BF_4}]$, although the latter were only identified spectroscopically in solution.[8]

RESULTS AND DISCUSSION

We have previously reported [9] some electron-rich olefin-derived carbeneiron(0) complexes, *e.g.* $[\mathrm{Fe(CO)_3(L^{Me})_2}]$ and $[\mathrm{Fe(CO)_3(L^{Me})(PR_3)}]$ [R = Ph or Et, $\mathrm{L^{Me}} = \overline{\mathrm{CN(Me)CH_2CH_2N}}\mathrm{Me}$]. We have now extended the series to compounds (1)—(11) (Table 1 and Scheme 1), in order to be able to examine the relative stabilities and properties of a wider range of iron(I) complexes. The latter were prepared from the iron(0) derivatives, generally by one-electron oxidation, using AgX (X = $\mathrm{BF_4}$, $\mathrm{PF_6}$, or $\mathrm{SbF_6}$). The iron(0) complexes $[\mathrm{Fe(CO)_3(L^{Me})L'}]$ [L′ = $\mathrm{AsPh_3}$, $\mathrm{P(C_6H_{11})_3}$, $\mathrm{P(OPh)_3}$, $\mathrm{PPh_2H}$, $\mathrm{PEt_2Ph}$, $\mathrm{PPh_3}$, or $\mathrm{PMePh_2}$] were usually synthesised by irradiation of $[\mathrm{Fe(CO)_4(L^{Me})}]$ and the appropriate neutral ligand in an inert, often paraffinic, solvent. Of particular interest was the reaction between the potentially chelating ligand 1,2-bis(diphenylphosphino)ethane (dppe) and $[\mathrm{Fe(CO)_4(L^{Me})}]$, which, photochemically or thermally, gave the bridged di-iron(0) complex $[\{\mathrm{Fe(CO)_3(L^{Me})}\}_2(\mu\text{-dppe})]$, (8), rather than the simple mononuclear dicarbonyl complex $[\mathrm{Fe(CO)_2(L^{Me})(dppe)}]$. The ability of dppe to bridge the metal atoms in this manner has been observed before for $\mathrm{Fe^0}$,[10,11] *e.g.* in $[\{\mathrm{Fe(CO)_4}\}_2(\mu\text{-dppe})]$. Photochemical synthesis also yields a secondary red-brown product, $[\mathrm{Fe_2(CO)_6(L^{Me})(dppe)}]$, (11). Infrared spectroscopy indicates bridging carbonyls for the latter (which analyses satisfactorily) but it has not been further characterised. It is, however, interesting to note the loss of a carbene fragment during its formation, a rare occurrence with little precedent among imidazolidinylidenemetal complexes.[2]

TABLE 1

Characterisation data for new electron-rich olefin-derived carbeneiron(0) [and an iron(II)] complexes

	Complex	Yield/ %	M.p. (θ_c/°C)	Colour	Analysis [a]/% C	H	N
(1)	$[Fe(CO)_4(L^{CH_2Ph})]$	80	58	Pale yellow	60.0 (60.3)	4.3 (4.3)	6.9 (6.7)
(2)	$[Fe(CO)_3(L^{CH_2Ph})(PPh_3)]$	90	165	Yellow	69.8 (69.9)	5.3 (5.1)	4.3 (4.3)
(3) [b]	$[Fe(AsPh_3)(CO)_3(L^{Me})]$	90		Bright yellow			
(4)	$[Fe(CO)_3(L^{Me})\{P(C_6H_{11})_3\}]$	90	208	Bright yellow	59.9 (60.2)	8.3 (8.3)	5.4 (5.4)
(5) [b]	$[Fe(CO)_3(L^{Me})(PPh_2H)]$	70	106	Yellow			
(6) [b]	$[Fe(CO)_3(L^{Me})(PMePh_2)]$	40		Yellow			
(7) [b]	$[Fe(CO)_3(L^{Me})(PEt_2Ph)]$	60		Yellow			
(8)	$[\{Fe(CO)_3(L^{Me})\}_2(\mu\text{-dppe})]$	90	196	Pale yellow	57.3 (57.6)	5.1 (5.1)	6.2 (6.4)
(9)	$[Fe(CO)_3(L^{Me})\{P(OPh)_3\}]$	80	96	Cream	57.1 (57.2)	4.8 (4.6)	5.1 (5.1)
(10)	$[FeBr(\eta\text{-}C_3H_5)(CO)_2(L^{Me})]$	40 [c]		Dark yellow	35.7 (36.2)	4.6 (4.5)	8.4 (8.4)
(11)	$[Fe_2(CO)_6(L^{Me})(dppe)]$	40		Red-brown	65.6 (65.5)	5.1 (5.0)	4.1 (4.1)

[a] Calculated values are given in parentheses. [b] Characterised solely by the i.r. spectrum. [c] Crude yield very high; quoted yield is of material obtained after five recrystallisations.

The initial experiment which led us to explore carbeneiron(I) chemistry was the observation that upon addition of di-iodine at ambient temperature to yellow $[Fe(CO)_3(L^{Me})_2]$, *en route* to brown $[Fe(CO)_2(L^{Me})_2I_2]$,[9] an intermediate persistent green colour was produced without apparent CO evolution after addition of half a molar portion of I_2. An e.s.r. spectrum of this solution showed a singlet, with $g_{av.}$ *ca.* 2.044, similar to $g_{av.}$ for the small number of previously observed iron(I) species; this suggested the presence of $[Fe^{I}(CO)_3(L^{Me})_2]I$. Many other oxidants were found to convert $[Fe(CO)_3(L^{Me})_2]$ into $[Fe(CO)_3(L^{Me})_2]^+$ (Table 2), *e.g.* Al_2Cl_6, MeI, Ph_3CCl, or tetracyanoethylene (tcne), but the most generally useful reagents were $Ag[BF_4]$, $Ag[PF_6]$, or $Ag[SbF_6]$; as far as anion dependence and stability is concerned, the iron(I) hexafluorophosphates are the most robust.

The general synthetic route (Schemes 2 and 3) to the new iron(I) complexes (Tables 3—5) was to add a stoicheiometric quantity of oxidant (AgX) to a tetrahydrofuran (thf) or CH_2Cl_2 solution of the iron(0) precursor, at various temperatures (−60 °C to ambient) depending on the thermal stability of the resulting complex. Nine such complexes [(12)—(20)] (Table 3) were isolated as crystalline materials. Others, (21)—(38), were generated for spectroscopic studies only, but this does not necessarily imply that they are thermally unstable. Several complexes, notably $[Fe(CO)_4(L^R)]X$ ($R = Me$ or CH_2Ph, $X = BF_4$), $[Fe(CN)(CO)_2(L^{Me})(PPh_3)]$, $[Fe(L^{Me})(NO)_2(PPh_3)]X$, and to a lesser extent $[Fe(AsPh_3)(CO)_3(L^{Me})]X$, however, could only be clearly observed below −20 °C. E.s.r. data are shown in Table 5, together with qualitative indications about the stability of the complexes.

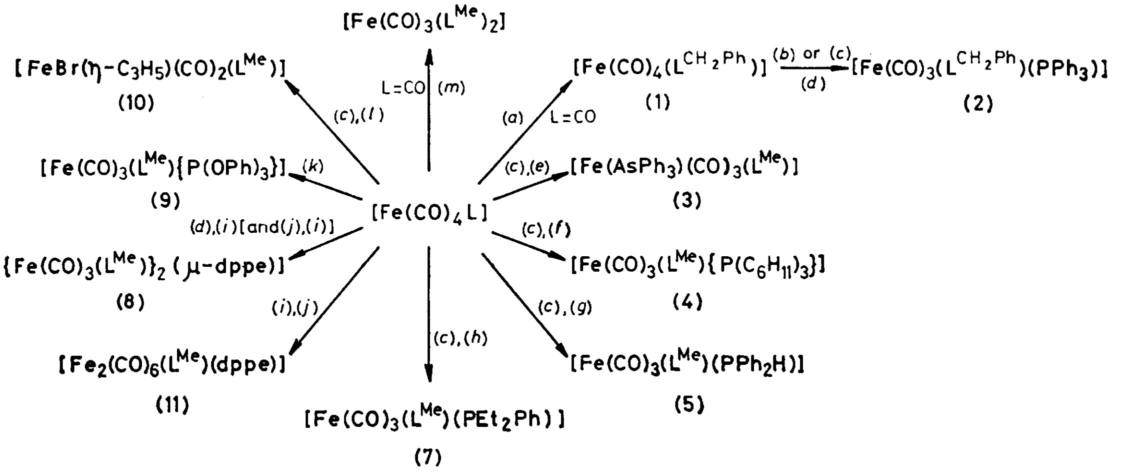
TABLE 2

Some oxidising agents used for the conversion $[Fe(CO)_3(L^{Me})_2] \longrightarrow [Fe(CO)_3(L^{Me})_2]X$

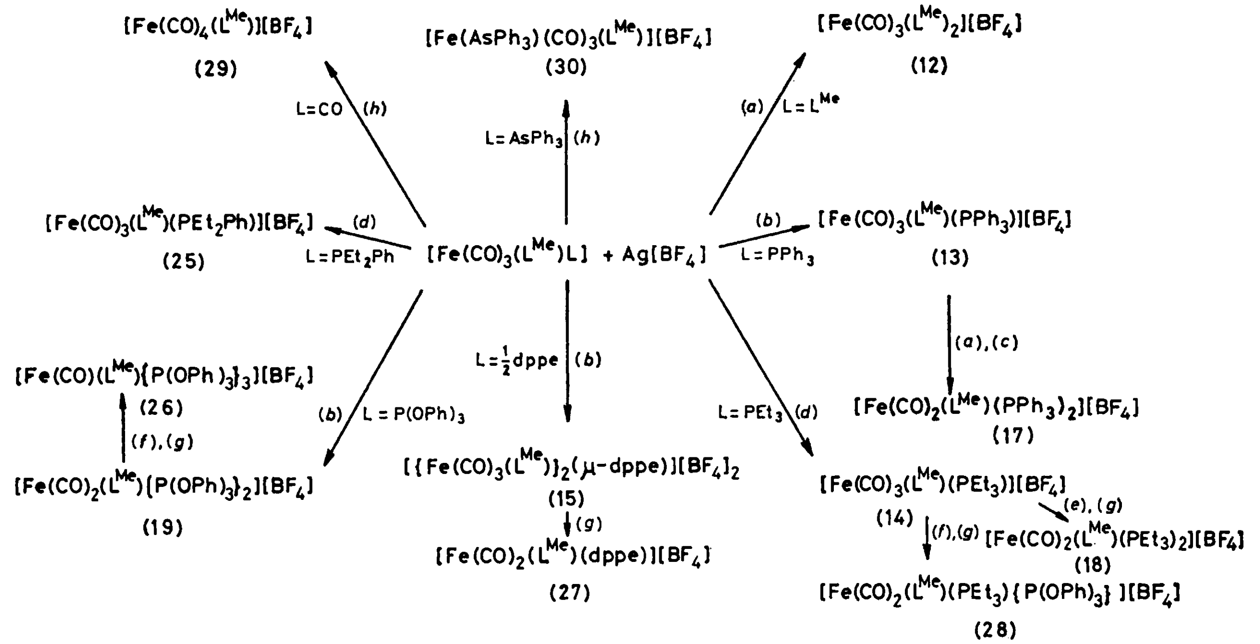
Oxidant	$g_{av.}$ [a]	Anion, X^-	Colour of salt
I_2	2.0438	I^-	Green
$Ag[BF_4]$	2.0433	$[BF_4]^-$	Green
$AlCl_3$	2.0436	$[AlCl_4]^-$	Green
MeI	2.0437	I^-	Green
Ph_3CCl	2.0438 [b]	Cl^-	Green
tcne	2.0438 [c]	tcne$^-$	Purple
Ag[CN]	2.0435	$[CN]^-$	Blue

[a] In CH_2Cl_2 at 20 °C. [b] Ph_3C^- spectrum also observed. [c] tcne$^{-\cdot}$ spectrum also observed.

Neutral carbeneiron(I) complexes have proved more difficult to synthesise. Thus, whereas treatment with



SCHEME 1 Synthetic routes to electron-rich olefin-derived carbeneiron(0) complexes; $L = L^{Me}$ except where stated otherwise. (*a*) Hexane, 65 °C; $L^{CH_2Ph}{}_2$; (*b*) MeC_6H_{11}, 100 °C; (*c*) $h\nu$, hexane, 25 °C; (*d*) PPh_3; (*e*) $AsPh_3$; (*f*) $P(C_6H_{11})_3$; (*g*) PPh_2H; (*h*) PEt_2Ph; (*i*) dppe; (*j*) $h\nu$, toluene, 25 °C; (*k*) hexane, 25 °C, $P(OPh)_3$; (*l*) allyl bromide; (*m*) decalin, 180 °C, $L^{Me}{}_2$.



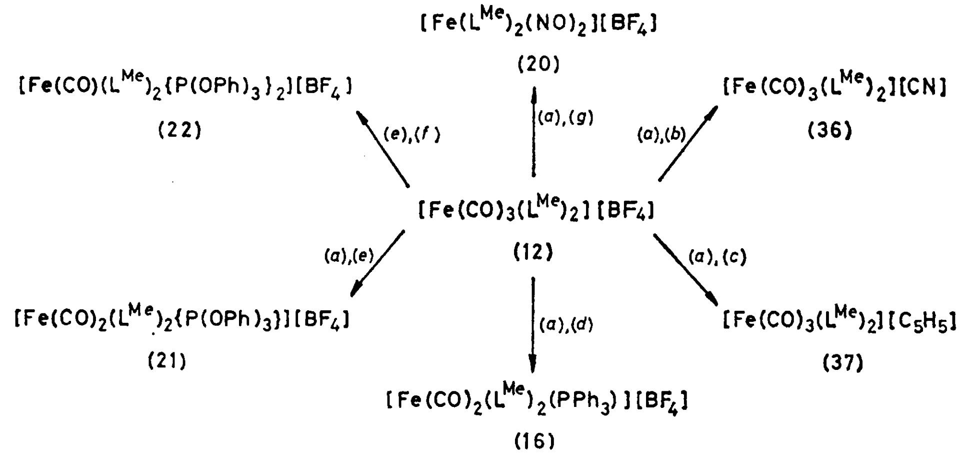
SCHEME 2 Synthetic routes to paramagnetic carbeneiron(I) complexes. (*a*) thf, 20 °C; (*b*) thf, −10 °C; (*c*) PPh_3; (*d*) thf, 0 °C; (*e*) PEt_3; (*f*) $P(OPh)_3$; (*g*) CH_2Cl_2, 40 °C; (*h*) CH_2Cl_2, −50 °C

TABLE 3

Characterisation data for electron-rich olefin-derived paramagnetic carbeneiron(I) complexes isolated as crystalline salts

	Complex	Yield/ %	M.p. (θ_c/°C)	Colour	Analysis [a]/% C	H	N
(12)	$[Fe(CO)_3(L^{Me})_2][BF_4]$	80	109	Very dark green	36.9 (36.9)	5.1 (4.9)	13.2 (13.2)
(13)	$[Fe(CO)_3(L^{Me})(PPh_3)][BF_4]$	80		Dark green	53.1 (53.1)	4.6 (4.3)	4.8 (4.8)
(14)	$[Fe(CO)_3(L^{Me})(PEt_3)][BF_4]$	60		Very dark green	38.0 (37.9)	5.9 (5.7)	5.9 (6.3)
(15)	$[\{Fe(CO)_3(L^{Me})\}_2(\mu\text{-dppe})][BF_4]_2$ [b]	80	130 (decomp.)	Dark green	47.5 (48.1)	4.5 (4.3)	5.6 (5.4)
(16)	$[Fe(CO)_2(L^{Me})_2(PPh_3)][BF_4]$	90		Very dark green	54.0 (54.8)	5.9 (5.4)	8.3 (8.5)
(17)	$[Fe(CO)_2(L^{Me})(PPh_3)_2][BF_4]$ [c]	95		Green	62.7 (62.8)	4.8 (4.9)	3.4 (3.6)
(18)	$[Fe(CO)_2(L^{Me})(PEt_3)_2][BF_4]$	70		Dark blue-green	42.7 (42.8)	7.6 (7.6)	5.6 (5.3)
(19)	$[Fe(CO)_2(L^{Me})\{P(OPh)_3\}_2][BF_4]$	70		Grass-green	55.0 (56.3)	4.7 (4.4)	3.5 (3.1)
(20)	$[Fe(L^{Me})_2(NO)_2][BF_4]$	20		Brown	29.7 (30.1)	4.7 (5.0)	21.2 (21.0)

[a] Calculated values are given in parentheses. [b] $\chi_g = 2.35 \times 10^{-6}$ c.g.s. units at 293 K, determined by the Faraday method on the solid; hence $\chi_m = 2\,467.5 \times 10^{-6}$ c.g.s. units (per binuclear unit), whence $\chi'_m = 2\,986 \times 10^{-6}$ c.g.s. units (after applying the diamagnetic correction) and $\mu_{eff.} = 2.65$ B.M. (per binuclear unit). [c] $\mu_{eff.} = 1.68$ B.M. (^1H n.m.r. in CH_2Cl_2).



SCHEME 3 Some reactions of $[Fe(CO)_3(L^{Me})_2][BF_4]$, (12). (*a*) thf, 25 °C; (*b*) K[CN]; (*c*) $Na[C_5H_5]$; (*d*) PPh_3; (*e*) $P(OPh)_3$; (*f*) thf, 40 °C; (*g*) NO

TABLE 4

Selected i.r. data (cm^{-1}) for electron-rich olefin-derived carbeneiron(I) complexes

	Complex	Solvent	ν(CO)	$\nu(CN_2)$
(1)	$[Fe(CO)_4(L^{CH_2Ph})]$	Nujol	2 042m, 1 955s, 1 936s	1 494mw
(2)	$[Fe(CO)_3(L^{CH_2Ph})(PPh_3)]$	Nujol	1 959w, 1 848vs	1 490mw
(3)	$[Fe(AsPh_3)(CO)_3(L^{Me})]$	CH_2Cl_2	1 956w, 1 860s	
(4)	$[Fe(CO)_3(L^{Me})\{P(C_6H_{11})_3\}]$	Nujol	1 942mw, 1 857m, 1 840s	1 504mw
(5)	$[Fe(CO)_3(L^{Me})(PPh_2H)]$	Nujol	1 958w, 1 875vs	1 503mw
(6)	$[Fe(CO)_3(L^{Me})(PMePh_2)]$	Nujol	1 948w, 1 853vs	1 508m
(7)	$[Fe(CO)_3(L^{Me})(PEt_2Ph)]$	CH_2Cl_2	1 960w, 1 852s	
(8)	$[\{Fe(CO)_3(L^{Me})\}_2(\mu\text{-}dppe)]$	Nujol	1 860vs	1 502mw
(9)	$[Fe(CO)_3(L^{Me})\{P(OPh)_3\}]$	Nujol	1 900vs	1 498mw
(10)	$[FeBr(\eta\text{-}C_3H_5)(CO)_2(L^{Me})]$	Nujol	2 008s, 1 954s	1 510ms
(11)	$[Fe_2(CO)_6(L^{Me})(dppe)]$	Nujol	1 925, 1 870, 1 810, and others	1 500w
(12)	$[Fe(CO)_3(L^{Me})_2][BF_4]$	CH_2Cl_2	2 058m, 1 978vs, 1 964 (sh)	1 522ms
(13)	$[Fe(CO)_3(L^{Me})(PPh_3)][BF_4]$	CH_2Cl_2	2 067m, 2 001s, 1 985s	1 526ms
(14)	$[Fe(CO)_3(L^{Me})(PEt_3)][BF_4]$	CH_2Cl_2	2 061m, 1 992s, 1 976s	1 525ms
(15)	$[\{Fe(CO)_3(L^{Me})\}_2(\mu\text{-}dppe)][BF_4]_2$	CH_2Cl_2	2 065m, 2 004s, 1 980s	1 528ms
(16)	$[Fe(CO)_2(L^{Me})_2(PPh_3)][BF_4]$	CH_2Cl_2	1 973s, 1 904s	1 513ms
(17)	$[Fe(CO)_2(L^{Me})(PPh_3)_2][BF_4]$	CH_2Cl_2	1 980s, 1 918s	1 517ms
(18)	$[Fe(CO)_2(L^{Me})(PEt_3)_2][BF_4]$	CH_2Cl_2	1 969s, 1 900s	1 515ms
(19) [a]	$[Fe(CO)_2(L^{Me})\{P(OPh)_3\}_2][BF_4]$	CH_2Cl_2	2 022s, 1 960s	
(20)	$[Fe(L^{Me})_2(NO)_2][BF_4]$	CH_2Cl_2	1 781s,[b] 1 710s [b]	1 530s
(21)	$[Fe(CO)_2(L^{Me})_2\{P(OPh)_3\}][BF_4]$	CH_2Cl_2	1 996s, 1 933s	1 540s
(22)	$[Fe(CO)(L^{Me})_2\{P(OPh)_3\}_2][BF_4]$	CH_2Cl_2	1 887s	
(23)	$[Fe(CO)(L^{Me})(PPh_3)_2(TeL^{Et})][BF_4]$ [c]	CH_2Cl_2	1 861s	
(24)	$[Fe(CO)_2(L^{Me})(PMePh_2)_2][BF_4]$	CH_2Cl_2	1 981s, 1 913s	
(25)	$[Fe(CO)_3(L^{Me})(PEt_2Ph)][BF_4]$	CH_2Cl_2	2 060m, 1 995s, 1 970s	
(26)	$[Fe(CO)(L^{Me})\{P(OPh)_3\}_3][BF_4]$	CH_2Cl_2	1 880s	
(27)	$[Fe(CO)_2(L^{Me})(dppe)][BF_4]$	CH_2Cl_2	1 990s, 1 928s	
(28)	$[Fe(CO)_2(L^{Me})(PEt_3)\{P(OPh)_3\}][BF_4]$	CH_2Cl_2	1 994s, 1 929s	
(30)	$[Fe(AsPh_3)(CO)_3(L^{Me})][BF_4]$	CH_2Cl_2	2 040s, 1 980s, 1 970m	
(32)	$[Fe(CO)_2(L^{Me})(PEt_2Ph)_2][BF_4]$	CH_2Cl_2	1 964s, 1 898s	

[a] Shown in equation (vi) as the PF_6 analogue. [b] ν(NO). [c] For other metal complexes having TeL^R as ligand see M. F. Lappert, T. R. Martin, and G. M. McLaughlin, *J. Chem. Soc., Chem. Commun.*, 1980, 635.

Ag[CN] of $[Fe(CO)_3(L^{Me})(PPh_3)]$ gave the thermally unstable $[Fe(CN)(CO)_2(L^{Me})(PPh_3)]$, use of $[Fe(CO)_3(L^{Me})_2]$ afforded the salt $[Fe(CO)_3(L^{Me})_2][CN]$, (36), also obtained by treatment of $[Fe(CO)_3(L^{Me})_2][BF_4]$, (12), with K[CN]. Similarly, reaction of the salt (12) with $Na[C_5H_5]$ only gave the anion-exchanged salt $[Fe(CO)_3(L^{Me})_2][C_5H_5]$, (37), and not $[Fe(\eta\text{-}C_5H_5)(L^{Me})_2]$; the evidence is based solely on i.r. and e.s.r. spectroscopy.

TABLE 5

E.s.r. and thermal-stability data for carbeneiron(I) complexes [a]

	Complex	$g_{av.}$	$a(^{31}P)/mT$	Approximate temperature (°C) at which stable in solution
(12)	$[Fe(CO)_3(L^{Me})_2][BF_4]$	2.043	— (s)	>20
(13)	$[Fe(CO)_3(L^{Me})(PPh_3)][BF_4]$	2.047	2.26 (d)	<10
(14)	$[Fe(CO)_3(L^{Me})(PEt_3)][BF_4]$	2.046	2.39 (d)	>20
(15)	$[\{Fe(CO)_3(L^{Me})\}_2(\mu\text{-}dppe)][BF_4]_2$	2.045	2.38 (d)	<10
(16)	$[Fe(CO)_2(L^{Me})_2(PPh_3)][BF_4]$	2.045	1.85 (d)	>20
(17)	$[Fe(CO)_2(L^{Me})(PPh_3)_2][BF_4]$	2.047	2.03 (t)	>20
(18)	$[Fe(CO)_2(L^{Me})(PEt_3)_2][BF_4]$	2.046	2.22 (t)	>20
(19) [b]	$[Fe(CO)_2(L^{Me})\{P(OPh)_3\}_2][BF_4]$	2.048	3.15 (t)	>20
(20)	$[Fe(L^{Me})_2(NO)_2][BF_4]$	2.034	— (s)	>20
(21)	$[Fe(CO)_2(L^{Me})_2\{P(OPh)_3\}][BF_4]$	2.043	1.84 (d)	>20
(22)	$[Fe(CO)(L^{Me})_2\{P(OPh)_3\}_2][BF_4]$	2.045	2.67 (d), 3.68 (d)	>20
(24)	$[Fe(CO)_2(L^{Me})(PMePh_2)_2][BF_4]$	2.045	2.24	>20
(25)	$[Fe(CO)_3(L^{Me})(PEt_2Ph)][BF_4]$	2.046	2.42	<20
(26)	$[Fe(CO)(L^{Me})\{P(OPh)_3\}_3][BF_4]$	2.050	3.35 (t), 1.58 (d)	>20
(27)	$[Fe(CO)_2(L^{Me})(dppe)][BF_4]$	2.048	1.91 (t)	>20
(28)	$[Fe(CO)_2(L^{Me})(PEt_3)\{P(OPh)_3\}][BF_4]$	2.047	2.46 (d) (Et), 2.77 (d) (OPh)	>20
(29) [b]	$[Fe(CO)_4(L^{Me})][BF_4]$	2.049	— (s)	<−40
(30)	$[Fe(AsPh_3)(CO)_3(L^{Me})][BF_4]$	2.048	2.29 (q) [c]	<−10
(31)	$[Fe(CN)(CO)_2(L^{Me})(PPh_3)]$	2.043	1.67 (d)	<−20
(32)	$[Fe(CO)_2(L^{Me})(PEt_2Ph)_2][BF_4]$	2.045	2.18 (t)	>20
(33)	$[Fe(CO)_3(L^{Me})(PPh_2H)][SbF_6]$	2.046	2.48 (d)	20
(34)	$[Fe(L^{Me})(NO)_2(PPh_3)][BF_4]$	2.036	2.44 (d)	<−40
(35)	$[Fe(CO)_4(L^{CH_2Ph})][PF_6]$	2.043	— (s)	<−50

[a] All run in CH_2Cl_2 solution at temperatures from −60 to +25 °C. [b] Shown in equation (vi) as the PF_6 analogue. [c] Value for $a(^{75}As)$.

The iron(II) complex $[FeBr(\eta\text{-}C_3H_5)(CO)_2(L^{Me})]$, (10), has, however, been successfully reduced (by the olefin $L^R{}_2$, R = Me or Et) to the neutral green $[Fe(\eta\text{-}C_3H_5)(CO)_2\text{-}L^{Me}]$, and further data on this and related complexes are described below.

When a thf solution of an allyliron halide $[Fe(\eta\text{-}C_3H_5)(CO)_2L(X)]$ (X = Br or I; L = CO, phosphine, or L^{Me}) was stirred with an electron-rich olefin $L^R{}_2$ (R = Me, Et, or CH_2Ph) at room temperature the solution turned bright green within 10 min. The colour was persistent, except for the case of L = CO where the solution became pink, attributed to dimerisation. We interpret these results (Table 6) in terms of equation (iii); the same carbene compounds, characterised spectroscopically, could also be prepared according to equation (iv). The allyliron(I) complexes of L^{Me} and L^{Et} decompose when thf is removed; however, the L^{CH_2Ph} complex was isolated as a solid and is soluble in toluene. Compounds $L^R{}_2$ react immediately with $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$ in thf to give $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$; no e.s.r. signal is observed.

TABLE 6

Selected i.r. and e.s.r. spectroscopic data for thf solutions of the complexes $[Fe(\eta\text{-}C_3H_5)(CO)_2L]$ *

L	$g_{av.}$	$a(^{31}P)$/ mT	$\nu(CO)/cm^{-1}$
CO	2.045		2 049, 1 965
PMe_2Ph	2.048	0.72	1 957, 1 892
PPh_3	2.050	1.69	1 956, 1 893
PEt_3	2.046	1.15	1 947, 1 889
L^{Me}	2.051		1 968, 1 907
L^{Et}	2.051		1 963, 1 906
L^{CH_2Ph}	2.050		1 960, 1 906

* These data were obtained by Dr. M. J. S. Gynane.

The iron(I) salts are susceptible to neutral-ligand exchange reactions, notably CO displacement. These sometimes occur spontaneously in solution at ambient temperatures without addition of ligand, and are accompanied by grey decomposition products, *e.g.* equations (v) and (vi). Some evidence for the type of spontaneous disproportionation shown in equations (v) and (vi) was obtained by a variable-temperature e.s.r. experiment carried out on the $Ag[PF_6]\text{–}CH_2Cl_2$ oxidation of $[Fe(CO)_3(L^{Me})\{P(OPh)_3\}]$, (9). At −60 °C the spectrum shows a doublet, assigned as the cation of the salt (38), which on warming decays rapidly giving a stable triplet, attributed to the cation of salt (19), and a superimposed singlet, assigned to the cation of salt (29) [equation (vi)], the latter being unstable above −20 °C. Salts (19) and (29) (shown as BF_4 salts in Scheme 3) were prepared independently and characterised, spectroscopically for (29) and completely for (19). Above −20 °C, $[Fe(CO)_4(L^{Me})]^+$ rapidly decomposes, evolving CO and precipitating an uncharacterised grey material. Addition of ligand and consequent disproportionation, however, provides a high-yield route (Schemes 2 and 3) to new iron(I) complexes not directly accessible from iron(0) precursors (because these are as yet unknown).

$$[Fe(\eta\text{-}C_3H_5)(CO)_2L(X)] + \tfrac{1}{4}L^R{}_2 \xrightarrow[20\,°C]{thf} [Fe(\eta\text{-}C_3H_5)(CO)_2L] + \tfrac{1}{2}[L^R\text{–}X]X \quad \text{(iii)}$$

$$[FeBr(\eta\text{-}C_3H_5)(CO)_2(PPh_3)] + L^R{}_2 \xrightarrow[10\ min,\ 20\,°C]{thf} [Fe(\eta\text{-}C_3H_5)(CO)_2(PPh_3)] \xrightarrow[20\,°C]{12\ h} [Fe(\eta\text{-}C_3H_5)(CO)_2(L^R)] \quad \text{(iv)}$$

$$2[Fe(CO)_3(L^{Me})(PPh_3)][BF_4] \longrightarrow [Fe(CO)_2(L^{Me})(PPh_3)_2][BF_4] + [Fe(CO)_4(L^{Me})][BF_4] \quad \text{(v)}$$

$$\underset{(38)}{2[Fe(CO)_3(L^{Me})\{P(OPh)_3\}][PF_6]} \longrightarrow \underset{(19)}{[Fe(CO)_2(L^{Me})\{P(OPh)_3\}_2][PF_6]} + \underset{(29)}{[Fe(CO)_4(L^{Me})][PF_6]} \quad \text{(vi)}$$

The ease with which one or more CO ligands are displaced appears to depend upon (*i*) the electron-richness at the metal (influenced by the electronic character of the ligands) and (*ii*) the incoming ligand. Thus, the higher the π acceptor : σ donor ratio of the co-ordinated ligands and the attacking nucleophile the more readily are carbonyl groups substituted. For example, the salt $[Fe(CO)_3(L^{Me})_2]^+$, (12), reacts with L = PPh_3 or $P(OPh)_3$ to give $[Fe(CO)_2(L^{Me})_2L]^+$ at 25 °C, but only $P(OPh)_3$ is able to react further to give $[Fe(CO)_2(L^{Me})\{P(OPh)_3\}_2]\text{-}[BF_4]$, (19). As noted above, $[Fe(CO)_3(L^{Me})\{P(OPh)_3\}]^+$, (38), is particularly prone to CO loss, this occurring rapidly even at −20 °C; with an excess of phosphite, species such as $[Fe(CO)_2(L^{Me})L_2]^+$ and $[Fe(CO)(L^{Me})L_3]^+$ are observed. The salt $[Fe(CO)_3(L^{Me})(PR_3)]^+$ reacts smoothly with PR_3 affording $[Fe(CO)_2(L^{Me})(PR_3)_2]^+$ (R = Ph or Et). The least labile tricarbonyl complexes are $[Fe(CO)_3(L^{Me})_2]^+$, (12), and $[Fe(CO)_3(L^{Me})(PEt_3)]^+$, (14), both of which contain ligands of greatest σ donor : π acceptor ratio. The dicarbonyl salt $[Fe(CO)_2(L^{Me})\text{-}(PPh_3)_2][BF_4]$, (17), is probably the most stable of the iron(I) complexes, being inert to dioxygen in the solid and to some extent in solution, and only slowly affected by aerated water.

Of considerable interest is the di-iron(I) cation $[\{Fe(CO)_3(L^{Me})\}_2(\mu\text{-dppe})]^{2+}$, (15), which contains two magnetically independent low-spin d^7 metal centres. The observed magnetic susceptibility ($\chi_g = 2.35 \times 10^{-6}$ c.g.s. units, obtained by the Faraday method at 20 °C) corresponds to $\mu_{eff.}$ for the binuclear complex of 2.65 B.M.* (or *ca.* 1.88 B.M. per iron atom) and corresponds approximately to the spin-only value of 2.45 B.M. for two isolated unpaired electrons, one from each Fe atom. This salt is moderately stable, but slowly deteriorates in the solid state at 25 °C. In solution, slow decomposition also occurs, probably to yield $[Fe(CO)_2(L^{Me})\text{-}(dppe)][BF_4]$, (27), characterised by e.s.r. and i.r. spectroscopy.

To extend the range of paramagnetic carbeneiron derivatives, some attempts were made to generate $[Fe(L^{Me})_2(NO)_2]^+$, (20). Rather surprisingly this cation was obtained by the reaction of $[Fe(CO)_3(L^{Me})_2]^+$, (12), with NO, $[Fe(L^{Me})_2(NO)_2]$ also being produced. The diamagnetic $[Fe(CO)_2(L^{Me})_2(NO)]^+$ cation might have

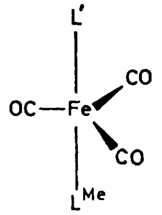
---

* Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2.

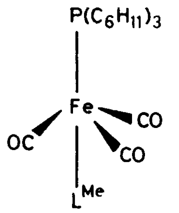
been expected, by analogy with the reaction of $[Fe(CO)_3(L^{Me})(PPh_3)]^+$, (13), which with NO gave $[Fe(CO)_2(L^{Me})(NO)(PPh_3)]^+$.[4] The cation $[Fe(L^{Me})_2(NO)_2]^+$, (20), was also obtained by the more conventional AgX (X = BF_4 or PF_6) oxidation of $[Fe(L^{Me})_2(NO)_2]$.

We consider that at least in part the stability of these paramagnetic cations is due to the capacity of the carbene ligand L^{Me} substantially to delocalise the positive charge,[12,13] and therefore the cation (12) with two L^{Me} ligands is especially robust. Consistent with this, there is an increase of *ca.* 20—30 cm^{-1} in ν(CN_2) compared with the iron(0) precursors.

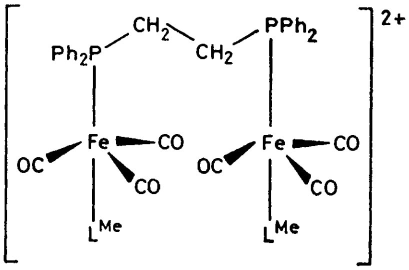
We find that complexes containing the ligand $L^{CH,Ph}$ {*e.g.* $[Fe(CO)_4(L^{CH,Ph})]^+$} are significantly less stable, consistent with our previous observation that $L^{CH,Ph}$ is less able to stabilise a cationic metal environment than L^{Me} or L^{Et}.[13] It is noteworthy that the analogous phosphine complexes, *e.g.* $[Fe(CO)_3(PPh_3)_2]^+$, are markedly less stable than our complexes, suggesting that PPh_3 is not so effective as L^{Me} at charge delocalisation. Also, in such bis(phosphine) complexes, loss of CO would occur more readily, more stable cations such as $[Fe(CO)_2(PPh_3)_3]^+$ being formed by decomposition similar to that of equation (v).



(I)



(II)



(III)

L' = PPh_2H, $PMePh_2$, PEt_2Ph,
$P(OPh)_3$, or $AsPh_3$

Cyclic voltammetry * upon $[Fe(CO)_3(L^{Me})(PPh_3)]$ in CH_2Cl_2 indicates a reversible one-electron oxidation [on a time scale too fast to detect the disproportionation reaction of equation (v)] with $E_{\frac{1}{2}} = 0.12$ V, *cf.* 0.34 V for $[Fe(CO)_3(PPh_3)_2]$.[8] This provides additional evidence for the increased ease of oxidation and stability forthe L^{Me}-containing complexes, and explains the contrasting effects of I_2 on $[Fe(CO)_3(PPh_3)_2]$ [8] and the carbene-iron(0) analogues discussed here. A possible synthetic route to novel trisubstituted iron(0) derivatives *via* suitable reducing agents is the reversible one-electron reduction of $[Fe(CO)_2(L^{Me})(PPh_3)_2][BF_4]$ ($E_{\frac{1}{2}} = 0.50$ V), but this has not yet been investigated on a preparative scale.

Spectroscopic Properties.—The new iron(0) complexes of the type $[Fe(CO)_3(L^{Me})L']$ generally show carbonyl-stretching modes [ν(CO)] in their i.r. spectra (Table 4) compatible with D_{3h} or C_{3v} local symmetry,[14] (I). Thus a very strong *e* mode is observed, together with a formally i.r. inactive a_1 mode as a very weak higher-frequency feature. However, when L' = $P(C_6H_{11})_3$, this more bulky phosphine causes the *e* mode to be split and the a_1 band to become of medium-weak intensity, indicating a significant deviation of the CO ligands from the equatorial plane, *i.e.* as in (II).

The di-iron(0) dppe-bridged complex $[\{Fe(CO)_3(L^{Me})\}_2(\mu\text{-dppe})]$, (8), exhibits only one very strong ν(CO) band, at 1 860 cm^{-1}. This compares with the polymeric $[\{Fe(CO)_3(dppe)\}_n]$,[10,11] with ν(CO) at 1 887 cm^{-1}, similar to that (1 886 cm^{-1}) found in $[Fe(CO)_3(PPh_3)_2]$.[14] On this basis, the structure (III) is assigned for the dication (15); ν(CO) values for complexes containing L^{Me} (or other L^R) ligands are generally lower than those in the tertiary phosphine analogues.

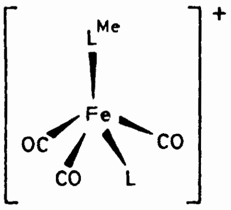
There are two main changes, (*i*) and (*ii*), in ν(CO) upon $Fe^0 \longrightarrow Fe^I$ oxidation. (*i*) There is a high-frequency shift, >100 cm^{-1}, due to the decrease in back bonding and the concomitant increase in the CO bond order. For instance, (*a*) $[Fe(CO)_3(L^{Me})_2]$ has ν(CO) at 1 959vw and 1 840vs cm^{-1},[9] whereas the corresponding cation (12) has ν(CO) at 2 058mw, 1 978vs, and 1 964(sh) cm^{-1}; (*b*) $[Fe(CO)_3(L^{Me})(PPh_3)]$ has ν(CO) at 1 962vw and 1 870vs cm^{-1}, whereas the corresponding cation (13) has ν(CO) at 2 067ms, 2 001s, and 1 985s cm^{-1}; or $[Fe(CO)_2(L^{Me})(PEt_3)_2]^+$, (18), has ν(CO) at 1 969s and 1 900s cm^{-1} whereas $[Fe(CO)_2(PEt_3)_3]$ has ν(CO) at 1 880s and 1 820 cm^{-1}.[14] (*ii*) In the tricarbonyl complexes the very weak a_1 mode increases considerably in intensity and the *e* band is generally clearly split, indicating a significant deviation from the idealised trigonal-bipyramidal (t.b.p.) geometry of the iron(0) complex. In several instances the three bands approach each other in intensity. The iron(I) complex $[Fe(pdma)(CO)_2I]$ probably has an approximately square-based bipyramidal (s.b.p.) geometry,[7] *via* $d_{x^2-y^2}sp^3$ hybridisation (rather than $d_{z^2}sp^3$); on this basis, the geometry adopted by a particular complex depends upon the ligands in the complex and their effect on the relative energies of the d_{z^2} and $d_{x^2-y^2}$ orbitals. We consider the tricarbonyl complexes, and

---

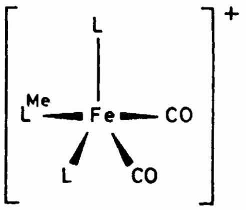
* $E_{\frac{1}{2}}$ *versus* the saturated calomel electrode (s.c.e.), 0.2 mol dm^{-3} in $[NBu^n_4][BF_4]$ throughout, at a platinum electrode.

especially $[Fe(CO)_3(L^{Me})_2]^+$, to favour a considerably distorted t.b.p. geometry, whereas the dicarbonyl complexes may well be closer to an s.b.p. ligand arrangement, *i.e.* (IV) and (V). A further effect of the $Fe^0 \longrightarrow Fe^I$ oxidation is to increase both the frequency (by 20—30 cm^{-1}) and the intensity of the $\nu(CN_2)$ band. This is consistent with significant delocalisation of the positive charge into the N–C–N framework of the imidazolidine ring, thereby assisting in stabilisation of the cations.

A comparison of the *g* values of the carbeneiron(I) salts (Table 5) with earlier data,[8,10] *e.g.* on $[Fe(\eta\text{-}C_3H_5)(CO)_2(PR_3)]$,[15] indicates that the unpaired electron is still mainly centred on the iron atom. However, *g* values for the cations $[Fe(CO)_2(L^{Me})L_2]^+$ [L = PPh_3, PEt_3, or $P(OPh)_3$] are rather lower than for $[Fe(CO)_3L_2]^+$,[8] suggesting that L^{Me} has a slightly larger share of the unpaired electron density than a CO ligand in an analogous complex. Similarly, *g* values for $[Fe(CO)_3(L^{Me})L]^+$ are lower than those for $[Fe(CO)_3L_2]^+$ [L = PPh_3, PEt_3, or $P(OPh)_3$], suggesting that L^{Me} also has more of the unpaired electron density than a tertiary phosphine or phosphite ligand. This supports the above proposal that the ability of L^{Me} to accept some spin density and positive charge may well be a contributing factor in the enhanced thermal and chemical stability of *carbeneiron*(I) complexes compared with other iron(I) analogues.



(IV)



(V)

L = P donor

The $a_{av.}(^{31}P)$ constants of the carbeneiron(I) salts (Table 5) are generally similar to those reported for iron(I) phosphorus-containing complexes;[8,15] however, $a_{av.}$ in $[Fe(CO)_2(L^{Me})L_2]^+$ is slightly larger than in the related $[Fe(CO)_3L_2]^+$.[8] Although $a_{av.}(^{31}P)$ is dependent on the residual spin density in the phosphorus 3*s* orbital, there is also the possibility of some of the electron spin being delocalised into orbitals of the substituents at P or other non-*s* phosphorus orbitals. Hence a simple rationalisation of the precise distribution of the unpaired electron density between the metal and the P ligand from $a_{av.}(^{31}P)$ changes would be simplistic. The available data, however, suggest that more of the unpaired electron density is located in the 3*s* orbitals of the P ligands in $[Fe(CO)_2(L^{Me})L_2]^+$ complexes than, for instance, in $[Fe(CO)_3L_2]^+$.[8]

The e.s.r. spectra of the cations $[Fe(CO)(L^{Me})_2\{P(OPh)_3\}_2]^+$, (22), and $[Fe(CO)(L^{Me})\{P(OPh)_3\}_3]^+$, (26), show inequivalence of the phosphite ligands on the e.s.r. time scale (and therefore slow exchange, with $\Delta G^\ddagger > ca.$ 20 kJ mol^{-1}). For the salt $[Fe(CO)(L^{Me})_2\{P(OPh)_3\}_2]^+$, (22), two doublets (rather than a triplet) and for (26) a doublet of triplets (rather than a quartet) (Figure 2) are seen at 20 °C. These observations indicate a more stereochemically rigid environment in these complexes and suggest that these cations are closer to s.b.p. geometry [(VI) and (VII)] rather than t.b.p., especially for (26). This may well be due to the higher level of substitution in these complexes.

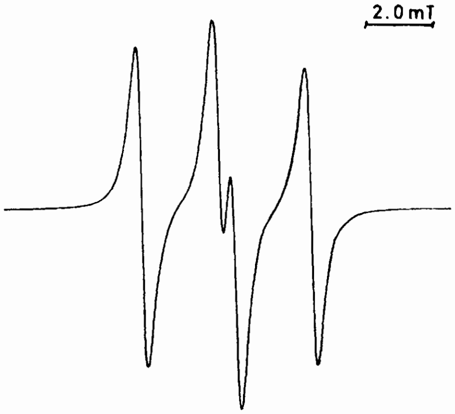


FIGURE 1 E.s.r. spectrum assigned to $[Fe(CO)_2(L^{Me})(PEt_3)\{P(OPh)_3\}][BF_4]$, (28), in CH_2Cl_2 at 20 °C

The e.s.r. spectra of the dicarbonyliron(I) complexes containing two phosphorus ligands invariably show equivalence, on the e.s.r. time scale, of the PR_3 groups a triplet being observed in each case; *e.g.* in $[Fe(CO)_2(L^{Me})(PR_3)_2]^+$ [R = Ph (17), Et (18), or OPh (19); or R_3 = $MePh_2$ (24)]. Even at lower temperatures (*ca.* −60 °C) the spectra are unchanged, indicating that the phosphorus ligands are equivalent, *e.g.* as in (VIII) or (IX); if the salts are of approximate s.b.p. geometry, as in (IX), then the phosphines are mutually *trans*, as the stronger σ-donating L^{Me} is preferentially *trans* to CO. Some support for this comes from a study of $[Fe(CO)_2(L^{Me})(PEt_3)\{P(OPh)_3\}]^+$, (28), the e.s.r. spectrum of which shows $a_{av.}(^{31}P)$ values consistent with the two P ligands being *trans* to each other and in the equatorial plane (Figure 1).

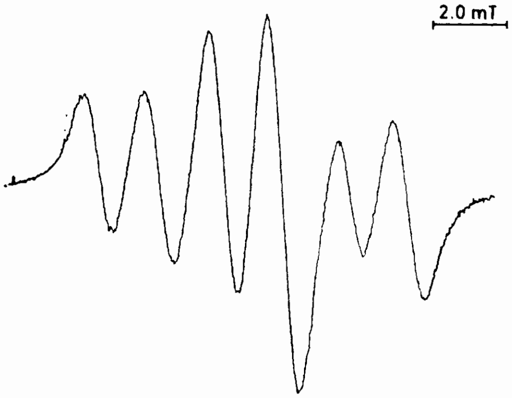
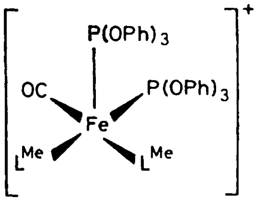
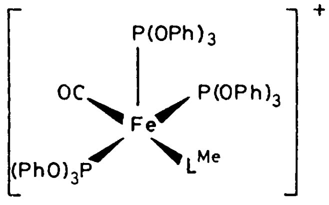


FIGURE 2 E.s.r. spectrum assigned to $[Fe(CO)(L^{Me})\{P(OPh)_3\}_3][BF_4]$, (26), in CH_2Cl_2 at 20 °C

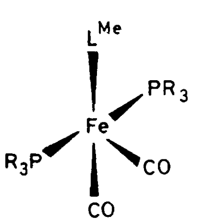
The general thermal stability and chemical inertness of the carbeneiron(I) salts to disproportionation to yield complexes of Fe^0 and Fe^{II} suggests that other paramagnetic carbenemetal complexes in unusual oxidation states may well be accessible. Chromium(I) derivatives have recently been obtained [1] and we have e.s.r. evidence for carbenenickel(I) species.[16]



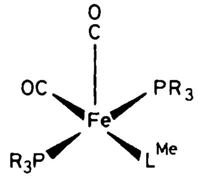
(VI)



(VII)



(VIII)



(IX)

EXPERIMENTAL

General Procedures.—All reactions were carried out under an atmosphere of dry argon using conventional Schlenk-tube techniques. Hydrocarbon and ether solvents were dried over and distilled from sodium wire (ether solvents were distilled from sodium–benzophenone) under dry dinitrogen before use, and dichloromethane was dried over and distilled from P_4O_{10}, also under dry dinitrogen. Before use all solvents were degassed by the freeze–thaw technique. All glass apparatus was cleaned using a base (K[OH]–EtOH) rather than acid (H_2CrO_4) bath.

Analyses were performed in the microanalytical department of the University by Mr. and Mrs. A. G. Olney or by the Butterworth Microanalytical Consultancy. All spectra were run under an atmosphere of dry argon or dinitrogen, and i.r. spectra were obtained from a Perkin-Elmer 457 instrument as Nujol mulls or as CH_2Cl_2 solutions, using an expanded scale (×10) calibrated against polystyrene film at 1 801.5 cm^{-1}. E.s.r. spectra were recorded on a Varian E3 spectrometer with a V-4557 variable-temperature unit, using samples in quartz e.s.r. tubes fitted with ground-glass-jointed Pyrex T pieces. Coupling constants were obtained directly from the spectra after field-sweep calibration using Fremy's salt, and $g_{av.}$ values are quoted relative to dpph (diphenylpicrylhydrazyl).

The starting materials [Fe(CO)$_4$(L^{Me})], [Fe(CO)$_3$(L^{Me})$_2$], [Fe(CO)$_3$(L^{Me})(PR$_3$)] (R = Et or Ph), and [Fe(L^{Me})$_2$(NO)$_2$] were prepared by the published procedures.[9]

Synthesis of New Compounds.*—[Fe(CO)$_3$(L^{Me})L′] [L′ = P(C$_6$H$_{11}$)$_3$ *or* AsPh$_3$]. Typically, to a solution of [Fe(CO)$_4$(L^{Me})] (0.27 g, 1.0 mmol) in hexane (20 cm^3) was added an excess of ligand (1.5 mmol), and the mixture was stirred and irradiated (4—8 h) to afford the yellow crystalline *tricarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)-(*tricyclohexylphosphine*)*iron*(0) or -(*triphenylarsine*)*iron*(0). The product was filtered off, washed with hexane (3 × 5 cm^3), and dried *in vacuo*.

[Fe(CO)$_3$(L^{Me})L′] (L′ = PEt$_2$Ph, PPh$_2$H, *or* PMePh$_2$). A mixture of [Fe(CO)$_4$(L^{Me})] (0.27 g, 1.0 mmol) and the ligand (1.5 mmol) in hexane (20 cm^3) was irradiated (8 h) and the resulting mixture was cooled overnight (−30 °C, 18 h). The crude product was recrystallised from toluene–hexane (−30 °C, 48 h) to afford *tricarbonyl*(*diethylphenylphosphine*)-(1,3-*dimethylimidazolidin*-2-*ylidene*)*iron*(0), *tricarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*diphenylphosphine*)*iron*(0), or *tricarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*methyldiphenylphosphine*)*iron*(0), respectively.

(*a*) [{Fe(CO)$_3$(L^{Me})}$_2$(μ-dppe)] *and* (*b*) [Fe$_2$(CO)$_6$(L^{Me})(dppe)]. (*a*) Irradiation (8 h) of a mixture of [Fe(CO)$_4$(L^{Me})] (1 mmol) and Ph$_2$PCH$_2$CH$_2$PPh$_2$ (dppe) (1.2 mmol) in toluene afforded a pale yellow precipitate of μ-(1,2-*bis*-*diphenylphosphino*)*ethane*-*bis*[*tricarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)*iron*(0)].

(*b*) Addition of hexane to the red solution and cooling (−30 °C, 72 h) gave small red-brown crystals of [1,2-*bis*(*diphenylphosphino*)*ethane*]*hexacarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)*di*-*iron*(0).

A mixture of [Fe(CO)$_4$(L^{Me})] (0.27 g, 1.0 mmol) and dppe (0.57 g, 1.5 mmol) in MeC$_6$H$_{11}$ (20 cm^3) was refluxed (8 h) to afford only the phosphine-bridged complex as a pale yellow microcrystalline powder.

[Fe(CO)$_3$(L^{Me}){P(OPh)$_3$}]. A mixture of [Fe(CO)$_4$(L^{Me})] (0.27 g, 1.0 mmol) and dried distilled P(OPh)$_3$ (0.47 g, 1.5 mmol) in hexane (20 cm^3) was stirred (30 °C, 6 h). The solution was filtered, hexane removed *in vacuo* to *ca*. 10 cm^3, and cooled (−30 °C, 72 h) to afford *tricarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*triphenyl phosphite*)*iron*(0), as small white crystals.

[FeBr(η-C$_3$H$_5$)(CO)$_2$(L^{Me})]. A mixture of [Fe(CO)$_4$(L^{Me})] (0.27 g, 1.0 mmol) and distilled allyl bromide (0.48 g, 4.0 mmol) in pentane (20 cm^3) was irradiated (25 °C, 24 h). The crude product was removed periodically by filtration and recrystallised from toluene–hexane (−30 °C, 48 h) to give small yellow-brown crystals of η-*allylbromodicarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)*iron*(II).

[Fe(CO)$_3$(L^{Me})$_2$][BF$_4$]. To a stirred solution of [Fe(CO)$_3$(L^{Me})$_2$] (0.34 g, 1.0 mmol) in thf (25 cm^3) at 25 °C was added Ag[BF$_4$] (0.20 g, 1.0 mmol) in portions over a period of *ca*. 10 min. The mixture was stirred (20 °C, 20 min) and filtered through a sinter (porosity 3) containing dried and degassed Celite. Tetrahydrofuran was removed *in vacuo* until crystallisation commenced. The solution was cooled (−30 °C, 48 h) to afford extremely dark green crystals of the product *tricarbonylbis*(1,3-*dimethylimidazolidin*-2-*ylidene*)-*iron*(I) *tetrafluoroborate*, which was filtered off, washed with OEt$_2$ (1 × 2 cm^3, 2 × 5 cm^3), and dried *in vacuo*.

[Fe(CO)$_3$(L^{Me})(PEt$_3$)][BF$_4$]. To a stirred solution of [Fe(CO)$_3$(L^{Me})(PEt$_3$)] (0.36 g, 1.0 mmol) in thf (15 cm^3) at 20 °C was added Ag[BF$_4$] (0.20 g, 1.0 mmol) in portions over *ca*. 10 min, and the mixture treated as above. Tetrahydrofuran was removed at −20 °C *in vacuo* until crystallisation commenced (*ca*. 5 cm^3) and cooling (−30 °C, 72 h) gave very dark green crystals of *tricarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*triethylphosphine*)*iron*(I) *tetra*-

---

* The first two complexes, containing the L^{CH_2Ph} rather than the L^{Me} carbene ligand, were prepared by methods as described [9] for the L^{Me} analogues.

fluoroborate; this was filtered off, washed with OEt_2 (3×5 cm^3), and dried *in vacuo*. (Addition of OEt_2 dropwise to the thf solution may assist the crystallisation.)

$[Fe(CO)_3(L^{Me})(PPh_3)][BF_4]$. To a stirred solution of $[Fe(CO)_3(L^{Me})(PPh_3)]$ (0.47 g, 1.0 mmol) in thf (30 cm^3) cooled to -20 °C was added dropwise (5 min) a solution of $Ag[BF_4]$ (0.20 g, 1.0 mmol) in thf (5 cm^3). The mixture was stirred (10 min) and filtered as above, ensuring the temperature remained below 0 °C. Tetrahydrofuran was removed *in vacuo* until crystallisation commenced and the solution was then cooled (-30 °C, 72 h) to afford *tricarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*triphenylphosphine*)*iron*(I) *tetrafluoroborate* as dark green microcrystals which were filtered off, washed with OEt_2 (3×5 cm^3), and dried *in vacuo*.

$[Fe(CO)_2(L^{Me})(PPh_3)_2][BF_4]$. To a stirred solution of $[Fe(CO)_3(L^{Me})(PPh_3)]$ (0.47 g, 1.0 mmol) in thf (30 cm^3) at 30 °C was added PPh_3 (0.28 g, 1.2 mmol) and then $Ag[BF_4]$ (0.20 g, 1.0 mmol) in portions over 10 min; the mixture was stirred (30 min) and filtered as before. Tetrahydrofuran was removed *in vacuo* until crystallisation commenced, whereupon the solution was cooled (-30 °C, 72 h) to deposit small dark green crystals of *dicarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)*bis*(*triphenylphosphine*)*iron*(I) *tetrafluoroborate*, which were filtered off, washed with OEt_2 (3×5 cm^3), and dried *in vacuo*.

$[Fe(CO)_2(L^{Me})(PEt_3)_2][BF_4]$. To a stirred solution of $[Fe(CO)_3(L^{Me})(PEt_3)]$ (0.36 g, 1.0 mmol) in thf (20 cm^3) at 35 °C containing PEt_3 (0.14 g, 1.2 mmol) was added $Ag[BF_4]$ (0.20 g, 1.0 mmol) in portions (10 min). The mixture was stirred (1 h) and filtered as before. Tetrahydrofuran was removed *in vacuo* at -30 °C until crystallisation commenced (*ca.* 5 cm^3) and the solution was then cooled (-30 °C, 7 d) to afford dark green crystals of *dicarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)*bis*(*triethylphosphine*)*iron*(I) *tetrafluoroborate*, which was obtained by removal of the solvent by syringe, washed with OEt_2 (3×5 cm^3), and dried *in vacuo*. (Addition of OEt_2 dropwise to a small volume of thf may assist crystallisation on cooling.)

$[Fe(CO)_2(L^{Me})\{P(OPh)_3\}_2][BF_4]$. To a stirred solution of $[Fe(CO)_3(L^{Me})\{P(OPh)_3\}]$ (0.55 g, 1.0 mmol) (at *ca.* 0—10 °C) containing redistilled $P(OPh)_3$ (1.1 mmol) was added $Ag[BF_4]$ (0.20 g, 1.0 mmol) over 5 min and the mixture was stirred (30 min) and filtered as before. Tetrahydrofuran was removed *in vacuo* and the resulting oil was cooled at -50 °C under OEt_2 (10 cm^3). The solid was further washed (3×5 cm^3) with OEt_2 and dried *in vacuo* to give *dicarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)*bis*(*triphenyl phosphite*)*iron*(I) *tetrafluoroborate* as a grass-green powder.

$[\{Fe(CO)_3(L^{Me})\}_2(\mu\text{-dppe})][BF_4]_2$. To a stirred solution of $[\{Fe(CO)_3(L^{Me})\}_2(\mu\text{-dppe})]$ (0.74 g, 1.0 mmol) in thf (30 cm^3) cooled to -20 °C was added dropwise (over 10 min) a solution of $Ag[BF_4]$ (0.80 g, 2.0 mmol) in thf (5 cm^3). The resulting mixture was stirred (20 min), filtered as before below 0 °C, and thf was removed *in vacuo* until crystallisation commenced. The solution was then cooled (-30 °C, 48 h) to give small green crystals of μ-[1,2-*bis*(*diphenylphosphino*)*ethane*]-*bis*[*tricarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)*iron*(I)] *bis*(*tetrafluoroborate*).

$[Fe(CO)_2(L^{Me})_2(PPh_3)][BF_4]$. To a solution of $[Fe(CO)_3(L^{Me})_2][BF_4]$ (0.5 mmol) in thf (20 cm^3) was added PPh_3 (0.16 g, 0.6 mmol) in portions over 10 min. The mixture was stirred (30 min) at 35 °C, filtered, and the solvent slowly removed *in vacuo* until crystallisation commenced. The mixture was then cooled (-30 °C, 48 h) to afford *dicarbonylbis*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*triphenylphosphine*)*iron*(I) *tetrafluoroborate* as small very dark green crystals which were filtered off, washed with OEt_2 (3×5 cm^3), and dried *in vacuo*.

$[Fe(L^{Me})_2(NO)_2][BF_4]$. To a solution of $[Fe(L^{Me})_2(NO)_2]$ (0.14 g, 0.50 mmol) in thf (30 cm^3) was added $Ag[BF_4]$ (0.10 g, 0.5 mmol) in portions over 15 min and the mixture was stirred (20 °C, 1.5 h), and filtered as above, and the solvent slowly removed *in vacuo*. A small quantity of starting material precipitated and was filtered off. Further concentration of the solution and cooling (-30 °C, 72 h) afforded small brown crystals of *bis*(1,3-*dimethylimidazolidin*-2-*ylidene*)*dinitrosyliron*(I) *tetrafluoroborate*, which were filtered off, washed with OEt_2 (3×5 cm^3), and dried *in vacuo*. This material [as the hexafluorophosphate salt], together with $[Fe(L^{Me})_2(NO)_2]$, was also isolated on reaction of $[Fe(CO)_3(L^{Me})_2]$ with $[NO][PF_6]$ in CH_2Cl_2.

E.S.R. Spectroscopic Experiments.—*Generation of iron*(I) *complexes.* Typically, to a dry dioxygen-free solution of a known quantity of the appropriate iron(0) precursor in CH_2Cl_2, cooled to -60 °C, was added the required quantity of $Ag[BF_4]$, $Ag[PF_6]$, or $Ag[SbF_6]$ (as a CH_2Cl_2 solution or suspension). The mixture was allowed to warm slowly within the cavity of the e.s.r. spectrometer, spectra being recorded periodically until completion of the experiment.

Reactions followed by e.s.r. spectroscopy. Solutions of the iron(I) complexes in CH_2Cl_2 in e.s.r. tubes, prepared either *in situ* as above or by conventional Schlenk-tube techniques, were cooled (-60 °C) and the required quantity of ligand (usually as a standard solution in CH_2Cl_2) was added. The tube was allowed to warm slowly within the cavity of the e.s.r. spectrometer, spectra being recorded periodically until completion of the experiment.

In all e.s.r. spectroscopic experiments, for species sufficiently thermally stable at ambient temperatures, the CH_2Cl_2 solution studied was transferred anaerobically to an i.r. solution cell and the i.r. spectrum (carbonyl region) was recorded.

We thank Dr. C. J. Pickett for advice and facilities relating to the cyclic voltammetry experiments, Dr. M. J. S. Gynane for the data of Table 6, and the S.R.C. for support.

[0/1661 *Received*, 31*st October*, 1980]

REFERENCES

[1] Part 1, M. F. Lappert, R. W. McCabe, J. J. MacQuitty, P. L. Pye, and P. I. Riley, *J. Chem. Soc., Dalton Trans.*, 1980, 90.

[2] M. F. Lappert, *J. Organomet. Chem.*, 1975, **100**, 139.

[3] D. J. Cardin, B. Çetinkaya, and M. F. Lappert, *Chem. Rev.*, 1972, **72**, 545; F. A. Cotton and C. M. Lukehart, *Prog. Inorg. Chem.*, 1972, **16**, 487; E. O. Fischer, *Pure Appl. Chem.*, 1970, **24**, 407; 1972, **30**, 353; F. J. Brown, *Prog. Inorg. Chem.*, 1980, **27**, 1.

[4] M. F. Lappert, J. J. MacQuitty, and P. L. Pye, *J. Chem. Soc., Chem. Commun.*, 1977, 411.

[5] M. K. Lloyd, J. A. McCleverty, D. G. Orchard, J. A. Connor, M. B. Hall, I. H. Hillier, E. M. Jones, and G. K. McEwen, *J. Chem. Soc., Dalton Trans.*, 1973, 1743.

[6] P. J. Krusic, U. Klabunde, C. P. Casey, and T. F. Block, *J. Am. Chem. Soc.*, 1976, **98**, 2015.

[7] H. Nigam, R. S. Nyholm, and D. V. R. Rao, *J. Chem. Soc.*, 1959, 1397.

[8] N. G. Connelly and K. R. Somers, *J. Organomet. Chem.*, 1975, **113**, C39; P. K. Baker, N. G. Connelly, B. M. R. Jones, J. P. Maher, and K. R. Somers, *J. Chem. Soc., Dalton Trans.*, 1980, 579; P. K. Baker, K. Broadley, and N. G. Connelly, *J. Chem. Soc., Chem. Commun.*, 1980, 775.

[9] M. F. Lappert and P. L. Pye, *J. Chem. Soc., Dalton Trans.*, 1977, 2172.

[10] T. A. Manuel, *Inorg. Chem.*, 1963, **2**, 854.

[11] J. Lewis, R. S. Nyholm, A. G. Osborne, S. S. Sandhu, and M. H. B. Stiddard, *Chem. Ind.* (*London*), 1963, 1398.

[12] P. B. Hitchcock, M. F. Lappert, and P. L. Pye, *J. Chem. Soc., Dalton Trans.*, 1978, 826.

[13] M. F. Lappert and P. L. Pye, *J. Chem. Soc., Dalton Trans.*, 1978, 837.

[14] D. M. Adams, 'Metal–Ligand and Related Vibrations,' Edward Arnold, London, 1967, p. 121.

[15] H. D. Murdoch and E. A. C. Lucken, *Helv. Chim. Acta*, 1964, **47**, 1517.

[16] J. J. MacQuitty, D.Phil. Thesis, University of Sussex, 1979.