Stable Paramagnetic Carbenemetal Complexes; Syntheses and Properties of Low Spin d^7 (1,3-Dimethylimidazolidin-2-ylidene)iron(I) Tetrafluoroborates†

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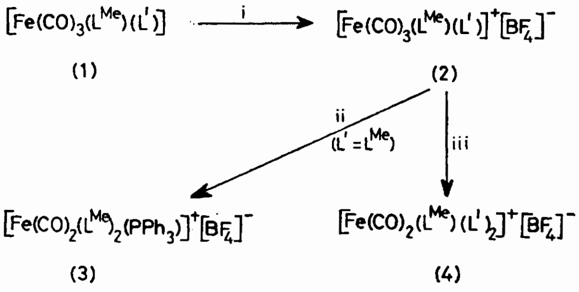
Summary Stable (at *ca.* 20 °C), green, crystalline, paramagnetic carbeneiron(I) salts (a) $[Fe(CO)_2(L^{Me})(L')(L'')]^+[BF_4]^-$ $[L^{Me} = -\overline{CN(Me)CH_2CH_2N}Me]$ (**2**; L′ = L^{Me}, PPh_3 or PEt_3, and L″ = CO), (**3**; L′ = PPh_3, L″ = L^{Me}), and [**4**; L′ = L″ = PPh_3, PEt_3, or $P(OPh)_3$], and (b) $[Fe_2(CO)_6(L^{Me})_2(\mu\text{-}Ph_2PCH_2CH_2PPh_2)]^{2+}[BF_4]^-_2$ (**6**) are obtained by $AgBF_4$ oxidation of an appropriate Fe^0 precursor (**1**) or (**5**), or from (**2**) by CO–PPh_3 exchange or disproportionation; i.r. [ν(CO)] and e.s.r. (*g* and *a*(P)] measurements on (**2**)—(**4**) and (**6**), and cyclic voltammetric data ($E_{\frac{1}{2}}$) on a neutral Fe^0 complex indicate that while the odd electron is substantially metal-centred, the carbene ligand L^{Me} contributes to stability by its strong Fe–C bond and delocalisation of positive charge.

WE report the first stable crystalline and characterised (analysis, i.r., e.s.r., and μ_{eff}) *paramagnetic* carbenemetal complexes, the green iron(I) tetrafluoroborates (**2**)—(**4**) (Scheme 1 and Table) and the unusual di-iron(I) analogue (**6**) (Scheme 2) (both of interest also as stable paramagnetic Fe^I complexes). Three synthetic procedures were employed (Scheme 1: i, ii, and iii). Evidence for (iii) as a disproportionation rather than a ligand displacement reaction is illustrated by the $AgPF_6$–CH_2Cl_2 oxidation (i) of $[Fe(CO)_3(L^{Me})\{P(OPh)_3\}]$ in the cavity of an e.s.r. spectrometer. At −60 °C, there appears a doublet assigned to $[Fe(CO)_3(L^{Me})\{P(OPh)_3\}]^+$; which, upon warming, decays, giving way to a triplet, assigned to $[Fe(CO)_2(L^{Me})\{P(OPh)_3\}_2]^+$, and a singlet (which is unstable above −20 °C), assigned to $[Fe(CO)_4(L^{Me})]^+$.



SCHEME 1. Synthesis and reactions of (1,3-dimethylimidazolidin-2-ylidene)iron(I) tetrafluoroborates: i, $AgBF_4$–THF, 20 °C (L′ = L^{Me}, PPh_3, or PEt_3) or −60 °C [L′ = $P(OPh)_3$]; ii, PPh_3–THF, 20 °C; iii, THF (or L′–THF), >20 °C (L′ = PPh_3 or PEt_3) or −20 °C [L′ = $P(OPh)_3$]. Some data on compounds (**2**)—(**4**) are in the Table; all analysed satisfactorily. A low temperature species (**2**, L′ = CO) is assigned merely on the basis of e.s.r. spectroscopy in CH_2Cl_2 (g = 2·049) at −60 °C.

Previously there was only low temperature e.s.r. (Cr^{-1}, Mo^{-1}, or W^{-1})[1] or electrochemical (Cr^I or W^I)[2] evidence for the existence of transient paramagnetic carbenemetal complexes in solution.

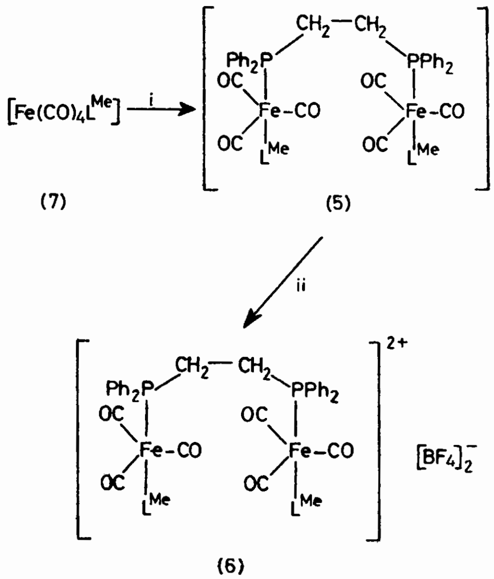
Oxidation of a CH_2Cl_2 or tetrahydrofuran (THF) solution of the yellow[3] $[Fe(CO)_3(L^{Me})_2]$ gave an intense green Fe^I complex (g = 2·044), using tetracyanoethylene, trityl chloride (procedures previously used[4] to obtain Mo^I complexes from $[Mo(CO)_2\{Me_2P(CH_2)_2PMe_2\}_2]$), or a deficiency of iodine. An excess of the reagent afforded the brown $[Fe^{II}(CO)_2(L^{Me})_2I_2]$.[3]

TABLE. I.r. and e.s.r. data[a] for complexes (**2**)—(**4**).

Compound	ν(CO)/cm⁻¹	*g*	*a*(P)/G
(**2**; L′ = L^{Me})	2058ms, 1978vs	2·044	
(**2**; L′ = PPh_3)	2067s, 2001vs ,1985s	2·047	22·6
(**2**; L′ = PEt_3)	2061vs, 1992s, 1976vs	2·046	23·9
(**3**; L′ = PPh_3)	1973vs, 1904vs	2·045	18·5
(**4**; L′ = PPh_3)	1980s, 1918vs	2·047	20·3
(**4**; L′ = PEt_3)	1969s, 1900vs	2·046	22·2
[**4**; L′ = $P(OPh)_3$]	2022vs, 1960vs	2·042	31·5

[a] In CH_2Cl_2 at 20 °C.

The facility of the conversion (**2**) → (**4**), $[Fe(CO)_3(L^{Me})(L')]^+ \rightarrow [Fe(CO)_2(L^{Me})(L')_2]^+$, decreases in the sequence L′ = $P(OPh)_3$ > PPh_3 > PEt_3 > L^{Me}, and reflects the decreasing π-acceptor and increasing σ-donor strength of L′.



SCHEME 2. Binuclear μ-bis(diphenylphosphino)ethane-di-iron(0) and -di-iron(I) complexes: i, $Ph_2PCH_2CH_2PPh_2$, $h\nu$, PhMe, 25 °C; ii, $AgBF_4$–THF, 20 °C; (**7**), from $[Fe(CO)_5]$-$L^{Me}{}_2$, n-C_6H_{14}, 65 °C (see ref. 3) (**5**), [ν(CO) 1860s cm⁻¹]; (**6**), [ν(CO) 2070s, 2005s, and 1985s cm⁻¹], g = 2·045, a(P) = 23·8 G; each of (**5**)—(**7**) gave satisfactory microanalyses.

It is interesting that compound (**6**) has two independent iron atoms in the low spin d^7 configuration, rather than an Fe–Fe bond as in known[5] binuclear dimetallocycles. This

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† No reprints available.

is shown by its magnetic moment at 20 °C [3·48 (by ^{1}H n.m.r. spectrometry in CH_2Cl_2) or 3·5 (solid state, Faraday method)] which is almost exactly twice the value of 1·68 B.M. (by ^{1}H n.m.r. spectrometry in CH_2Cl_2 at 20 °C) for $[Fe(CO)_2(L^{Me})(PPh_3)_2]^+[BF_4]^-$.

Comparison of our e.s.r. spectroscopic data (Schemes 1 and 2 and Table) with those reported for other Fe^I systems,[6] particularly $[Fe(CO)_3(L')_2]^+PF_6^-$ (L' = a tertiary phosphine or phosphite),[7] show that the unpaired electron is still mainly localised on the Fe atom. Values of a(P) are larger, possibly owing to the higher σ-donor–π-acceptor ratio of L^{Me} compared to PR_3 or $P(OR)_3$. The i.r. spectroscopic data show the expected increases in ν(CO) upon oxidation of $Fe^0 \rightarrow Fe^I$. The trigonal bipyramidal structure of the Fe^0 precursor becomes distorted upon oxidation, *e.g.*, three ν(CO) bands of approximately equal intensity are observed in $[Fe(CO)_3(L^{Me})(PPh_3)]^+BF_4^-$, compared with one very strong band in the Fe^0 precursor.

Cyclic voltammetry on $[Fe(CO)_3(L^{Me})(PPh_3)]$ in CH_2Cl_2 indicates a reversible one-electron oxidation (the time-scale is too fast to detect possible disproportionation), with $E_{\frac{1}{2}}$ = 0·12 V compared with $E_{\frac{1}{2}}$ = 0·34 V for $[Fe(CO)_3(PPh_3)_2]$;[7] L^{Me} therefore increases the ease of oxidation. This may explain why iodine does not effect a simple one-electron oxidation for the latter complex. The complex $[Fe(CO)_2(L^{Me})(PPh_3)_2]^+BF_4^-$ undergoes reversible one-electron reduction ($E_{\frac{1}{2}}$ = − 0·50 V) and this suggests an unusual synthetic route to novel tri-substituted Fe^0 derivatives (*cf.*, ref. 3), *e.g.*, *via* Na–Hg reduction of the appropriate Fe^I precursors ($E_{\frac{1}{2}}$ *vs.* S.C.E., 0·2M in $Bu^n_4N^+BF_4^-$).

The new cations vary in thermal, aerial, and hydrolytic sensitivity, from $[Fe(CO)_4(L^{Me})]^+$ (only observable below −20 °C) to $[Fe(CO)_2(L^{Me})(PPh_3)_2]^+$, and are insensitive to air or water even in solution and thermally very stable. The general and unexpected stability of the majority of the Fe^I tetrafluoroborates is attributed mainly to the high σ-donor strength of the carbene ligand.[3] A d^7 low spin system (as in Fe^I) may be favoured because of Jahn–Teller stabilisation.

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[1] P. J. Krusic, U. Klabunde, C. P. Casey, and T. F. Block, *J. Amer. Chem. Soc.*, 1976, **98**, 2015.
[2] M. K. Lloyd, J. A. McCleverty, D. G. Orchard, J. A. Connor, M. B. Hall, I. H. Hillier, E. H. Jones, and G. K. McEwen, *J.C.S. Dalton*, 1973, 1743.
[3] M. F. Lappert and P. L. Pye, *J.C.S. Dalton*, in the press.
[4] J. A. Connor and P. I. Riley, *J.C.S. Chem. Comm.*, 1976, 634.
[5] R. J. Haines and A. L. DuPreez, *J. Organometallic Chem.*, 1970, **21**, 181.
[6] H. D. Murdoch and E. A. C. Lucken, *Helv. Chim. Acta*, 1964, **47**, 1517.
[7] N. G. Connelly and K. R. Somers, *J. Organometallic Chem.*, 1976, **113**, C39.