17-Electron Alkynyl Complexes of Cyclopentadienyliron(III)

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The complexes $[\mathrm{Fe(C{\equiv}CR)(L\text{-}L)(\eta\text{-}C_5R'_5)}]$ [R = Bu^t, $\mathrm{CO_2Me}$, $\mathrm{CO_2Et}$, $\mathrm{SiMe_3}$, Ph or $\mathrm{CH_2OMe}$, L–L = $\mathrm{Ph_2PCH_2PPh_2}$ (dppm), R′ = H; R = Bu^t or Ph, L–L = $\mathrm{Ph_2PCH_2CH_2PPh_2}$ (dppe), R′ = Me] undergo reversible one-electron oxidation at a platinum electrode in $\mathrm{CH_2Cl_2}$. Chemical oxidation with $[\mathrm{Fe(\eta\text{-}C_5H_5)_2}][\mathrm{PF_6}]$ gave the isolable salts $[\mathrm{Fe(C{\equiv}CR)(dppe)(\eta\text{-}C_5Me_5)}][\mathrm{PF_6}]$ (R = Bu^t or Ph) which Mössbauer spectroscopy suggests to be complexes of Fe$^{\mathrm{III}}$. The ESR spectra of these salts, and of the cations $[\mathrm{Fe(C{\equiv}CR)(dppm)(\eta\text{-}C_5H_5)}]^+$ (R = Bu^t, $\mathrm{CO_2Me}$, $\mathrm{CO_2Et}$ or Ph), generated by *in situ* oxidation with $[\mathrm{Fe(\eta\text{-}C_5H_5)_2}][\mathrm{PF_6}]$, are similar to those of low-spin d^5 complexes of Cr$^{\mathrm{I}}$, Mn$^{\mathrm{II}}$ and Fe$^{\mathrm{III}}$.

In a series of papers, Whiteley and co-workers have demonstrated that the oxidative dimerisation of the alkynyl complex $[\mathrm{Mo(C{\equiv}CPh)(dppe)(\eta\text{-}C_7H_7)}]$ (dppe = $\mathrm{Ph_2PCH_2CH_2PPh_2}$) to the divinylidene-bridged dication $[\mathrm{Mo_2(\mu\text{-}C_4Ph_2)(dppe)_2(\eta\text{-}C_7H_7)_2}]^{2+}$ (ref. 1) involves the initial formation of the isolable 17-electron cation $[\mathrm{Mo(C{\equiv}CPh)(dppe)(\eta\text{-}C_7H_7)}]^+$.[2] The same group showed[3] that analogous cyclopentadienyl complexes $[\mathrm{M(C{\equiv}CPh)(dppe)(\eta\text{-}C_5R_5)}]$ (M = Fe or Ru, R = H or Me) also underwent one-electron oxidation although neither the resulting monocations nor any dimeric products could be isolated. We now report on the electron-transfer reactions of a range of cyclopentadienyliron alkynyls, the isolation and characterisation of the stable salts $[\mathrm{Fe(C{\equiv}CR)(dppe)(\eta\text{-}C_5Me_5)}][\mathrm{PF_6}]$ (R = Bu^t or Ph), and Mössbauer and ESR spectroscopic studies which define the 17-electron alkynyl cations as complexes of low spin Fe$^{\mathrm{III}}$.

Results and Discussion

Synthesis of $[\mathrm{Fe(C{\equiv}CR)(dppe)(\eta\text{-}C_5Me_5)}]$ (R = Bu^t *or* Ph).—The complexes $[\mathrm{Fe(C{\equiv}CR)(dppe)(\eta\text{-}C_5Me_5)}]$ (R = Bu^t or Ph) were prepared in a two-step process involving formation of the corresponding vinylidenes followed by deprotonation.[3–5] Thus, the addition of a terminal alkyne, HC≡CR (R = Bu^t or Ph), to $[\mathrm{FeCl(dppe)(\eta\text{-}C_5Me_5)}]$ and $\mathrm{NH_4PF_6}$ in methanol gave, after 16 h, a brown-orange solution from which the orange vinylidene complexes $[\mathrm{Fe(C{=}CHR)(dppe)(\eta\text{-}C_5Me_5)}][\mathrm{PF_6}]$ (R = Bu^t or Ph) were isolated in 80–90% yield. The complex $[\mathrm{Fe(C{=}CHPh)(dppe)(\eta\text{-}C_5Me_5)}][\mathrm{PF_6}]$ has been reported previously[3] but the present synthesis is more convenient, giving a higher yield, and the spectroscopic data are slightly different.

The ^{1}H NMR spectra of $[\mathrm{Fe(C{=}CHR)(dppe)(\eta\text{-}C_5Me_5)}][\mathrm{PF_6}]$ (R = Bu^t or Ph) show a characteristic triplet for the H atom bound to the β-carbon atom of the vinylidene ligand [R = Bu^t, δ 3.43 ($^4J_{\mathrm{PH}}$ = 3.6); R = Ph, δ 5.14 ($^4J_{\mathrm{PH}}$ = 4.3 Hz)]. Similarly, the ^{13}C NMR spectra show a triplet [R = Bu^t, δ 354.3 ($^2J_{\mathrm{PC}}$ = 32); R = Ph, δ 361.2 ($^2J_{\mathrm{PC}}$ = 33 Hz)] and a doublet [R = Bu^t, δ 130.9 ($^1J_{\mathrm{CH}}$ = 155); R = Ph, δ 126.5 ($^1J_{\mathrm{CH}}$ = 152 Hz)] for the C$_\alpha$ and C$_\beta$ vinylidene carbon atoms.[4] The IR spectra also show the presence of the vinylidene ligand with ν(C=C) at 1631 (R = Bu^t) and 1613 cm^{-1} (R = Ph).

The complexes $[\mathrm{Fe(C{=}CHR)(dppe)(\eta\text{-}C_5Me_5)}][\mathrm{PF_6}]$ (R = Bu^t or Ph) are readily deprotonated by KOBu^t in tetrahydrofuran (thf), giving the corresponding alkynyl complexes $[\mathrm{Fe(C{\equiv}CR)(dppe)(\eta\text{-}C_5Me_5)}]$ (R = Bu^t or Ph) as thermally stable orange solids in 80 and 98% yield respectively. The IR spectra show bands at 2066 (R = Bu^t) and 2049 cm^{-1} (R = Ph), characteristic of ν(C≡C),[6] and the ^{13}C NMR resonances were unequivocally assigned on the basis of the observed C–P coupling constants. Thus, for $[\mathrm{Fe(C{\equiv}CPh)(dppe)(\eta\text{-}C_5Me_5)}]$, C$_\beta$ appears as a singlet (δ 120.5) at higher field than the triplet of the C$_\alpha$ atom (δ 137.4, J_{PC} = 40 Hz), whereas $[\mathrm{Fe(C{\equiv}CBu^t)(dppe)(\eta\text{-}C_5Me_5)}]$ exhibits a different pattern with a triplet at δ 107.0 and a singlet at δ 125.3, for C$_\alpha$ and C$_\beta$ respectively. Such a dependence of the chemical shifts of the C$_\alpha$ and C$_\beta$ atoms on the alkynyl substituents has been observed previously.[3,5,7] A well defined singlet is observed in the ^{31}P NMR spectrum of $[\mathrm{Fe(C{\equiv}CBu^t)(dppe)(\eta\text{-}C_5Me_5)}]$ at 75 °C in $\mathrm{C_6D_6}$. At lower temperatures the signal broadens; further studies of the apparent fluxional behaviour of this complex are in progress.[8]

Electrochemical Studies.—Cyclic voltammetry (CV) shows that each of the complexes $[\mathrm{Fe(C{\equiv}CR)(L\text{-}L)(\eta\text{-}C_5R'_5)}]$ [R = Bu^t, $\mathrm{CO_2Me}$, $\mathrm{CO_2Et}$, $\mathrm{SiMe_3}$, Ph or $\mathrm{CH_2OMe}$, L–L = dppm ($\mathrm{Ph_2PCH_2PPh_2}$), R′ = H; R = Bu^t or Ph, L–L = dppe, R′ = Me] undergoes reversible [$(i_\mathrm{p})_{\mathrm{ox}}/(i_\mathrm{p})_{\mathrm{red}} = 1.0$], diffusion-controlled [$(i_\mathrm{p})_{\mathrm{ox}}/v^{\frac{1}{2}}$ = constant, for scan rates, v, from 50 to 200 mV s^{-1}] oxidation at a platinum electrode in $\mathrm{CH_2Cl_2}$ (Table 1). The magnitude of the oxidation potential, varying from −0.28 to 0.30 V, indicates the electron-richness of $[\mathrm{Fe(C{\equiv}CR)(L\text{-}L)(\eta\text{-}C_5R'_5)}]$ and is a function of the electron-withdrawing properties of both R and R′; substitution of H by Me on the C$_5$ ring lowers E° by *ca.* 160 mV, and a shift in the same sense is induced by the use of donor substituents on the alkynyl ligand, in the order (E°) Bu^t < Ph, $\mathrm{SiMe_3}$ < $\mathrm{CH_2OMe}$, $\mathrm{CO_2R''}$ (R″ = Me or Et). The oxidation potentials of the $\mathrm{C_5Me_5}$ alkynyls are slightly less negative than those of $[\mathrm{FeR(dppe)(\eta\text{-}C_5Me_5)}]$ (R = Me or $\mathrm{CH_2OMe}$[9]). It is also noteworthy that the oxidation of the parent complex $[\mathrm{Fe(C{\equiv}CH)(dppm)(\eta\text{-}C_5H_5)}]$ is chemically irreversible [$(E_\mathrm{p})_{\mathrm{ox}}$ = 0.09 V, v = 200 mV s^{-1}]; deprotonation of the $\mathrm{C_2H}$ group may occur after electron loss.

Table 1 Cyclic voltammetric data[a] for $[Fe(C{\equiv}CR)(L\text{–}L)(\eta\text{-}C_5R'_5)]$

R	R′	L–L	$E°/V$[b]
H	H	dppm	0.09(I)
CO_2Me	H	dppm	0.30
CO_2Et	H	dppm	0.29
$SiMe_3$	H	dppm	0.06
CH_2OMe	H	dppm	0.02
Ph	H	dppm	0.04
Bu^t	H	dppm	−0.12
Ph	H	dppe	0.08[c]
Ph	Me	dppe	−0.13[d]
Bu^t	H	dppe	−0.06[c]
Bu^t	Me	dppe	−0.28

[a] In CH_2Cl_2 at a platinum-bead electrode. Under the conditions used the potentials for the couples $[Fe(\eta\text{-}C_5H_5)_2]^+$–$[Fe(\eta\text{-}C_5H_5)_2]$ and $[Fe(\eta\text{-}C_5Me_5)_2]^+$–$[Fe(\eta\text{-}C_5Me_5)_2]$ are 0.47 and −0.09 V respectively. [b] $E°$ for reversible wave unless otherwise stated. The oxidation peak potential, $(E_p)_{ox}$, at a scan rate of 200 mV s^{-1} is given for an irreversible (I) wave. [c] Data from ref. 3; the original values have been converted into the same reference scale on the basis of the value cited for the ferrocene–ferrocenium couple. [d] Also reported in ref. 3.

Table 2 Mössbauer parameters for $[FeR(dppe)(\eta\text{-}C_5Me_5)]^z$ (T = 77 K)

R	z	Iron oxidation state	Isomer shift	Quadrupole splitting
			mm^{-1}	
C_2Bu^t	0	II	0.28	2.00
C_2Bu^t	1	III	0.26	0.85
C_2Ph	0	II	0.28	2.02
C_2Ph	1	III	0.25	0.90
Me*	0	II	0.15	1.95
Me*	1	III	0.35	0.76

* Data from ref. 9.

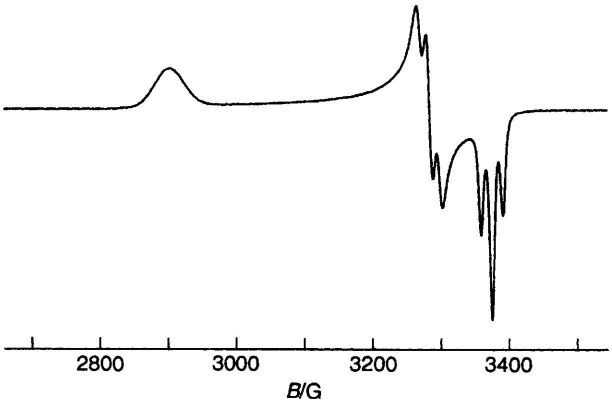

Fig. 1 The ESR spectrum of $[Fe(C{\equiv}CBu^t)(dppm)(\eta\text{-}C_5H_5)]^+$ in CH_2Cl_2–$C_2H_4Cl_2$ (1:1) at 110 K; G = 10^{-4} T

Synthesis of $[Fe(C{\equiv}CR)(L\text{–}L)(\eta\text{-}C_5R'_5)]^+$.—The cations $[Fe(C{\equiv}CR)(L\text{–}L)(\eta\text{-}C_5R'_5)]^+$ can be generated in solution either chemically or electrochemically and in two cases stable salts have been isolated and fully characterised. Exhaustive controlled-potential electrolysis at a platinum-basket electrode (0.3 V, in CH_2Cl_2) of $[Fe(C{\equiv}CPh)(dppm)(\eta\text{-}C_5H_5)]$ resulted in the passage of 0.96 F mol^{-1} and the formation of a green solution. This solution showed a reversible reduction wave at a potential, and with a height, identical to those for the oxidation of $[Fe(C{\equiv}CPh)(dppm)(\eta\text{-}C_5H_5)]$ confirming the quantitative formation of the monocation $[Fe(C{\equiv}CPh)(dppm)(\eta\text{-}C_5H_5)]^+$ in a one-electron process. Similar electrolytic oxidation of $[Fe(C{\equiv}CCO_2Me)(dppm)(\eta\text{-}C_5H_5)]$, at 0.6 V, resulted in the passage of 0.9 F mol^{-1} but the cyclic voltammetric wave due to the primary redox product, namely $[Fe(C{\equiv}CCO_2Me)(dppm)(\eta\text{-}C_5H_5)]^+$, was considerably diminished relative to that of the neutral precursor. Clearly, the cation $[Fe(C{\equiv}CCO_2Me)(dppm)(\eta\text{-}C_5H_5)]^+$, though stable on the CV time-scale, is less so on the longer time-scale of electrolysis.

The addition of $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ to $[Fe(C{\equiv}CPh)(dppm)(\eta\text{-}C_5H_5)]$ [$\nu(C{\equiv}C)$ 2071 cm^{-1}][5] in CH_2Cl_2 gave a green solution the IR spectrum of which showed $\nu(C{\equiv}C)$ at 2030 cm^{-1}. Similar shifts to lower wavenumber have been observed on one-electron oxidation of $[Mo(C{\equiv}CPh)(dppe)(\eta\text{-}C_7H_7)]$,[2] providing further evidence for the formation of $[Fe(C{\equiv}CPh)(dppm)(\eta\text{-}C_5H_5)]^+$. A similar reaction, between $[Fe(C{\equiv}CBu^t)(dppm)(\eta\text{-}C_5H_5)]$ and $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$, gave a purple solution but neither $[Fe(C{\equiv}CBu^t)(dppm)(\eta\text{-}C_5H_5)][PF_6]$ nor $[Fe(C{\equiv}CPh)(dppm)(\eta\text{-}C_5H_5)][PF_6]$ could be isolated in an analytically pure form. By contrast, the $\eta\text{-}C_5Me_5$ analogues proved to be more robust.

The addition of 1 equivalent of $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ to $[Fe(C{\equiv}CR)(dppe)(\eta\text{-}C_5Me_5)]$ in CH_2Cl_2 resulted in a rapid colour change from orange to mauve (R = Bu^t) and black-blue (R = Ph). Addition of pentane to the reaction mixtures then gave $[Fe(C{\equiv}CR)(dppe)(\eta\text{-}C_5Me_5)][PF_6]$ (R = Bu^t or Ph) as air and thermally stable microcrystalline solids in 80% yield. The stability of these species, relative to that of their $\eta\text{-}C_5H_5$ analogues, may be kinetic in origin in that they are likely to be highly sterically crowded.

The paramagnetic salts $[Fe(C{\equiv}CR)(dppe)(\eta\text{-}C_5Me_5)][PF_6]$ (R = Bu^t or Ph) were characterised by elemental analysis and by cyclic voltammetry which showed reduction waves at potentials identical to those of the oxidation waves of $[Fe(C{\equiv}CR)(dppe)(\eta\text{-}C_5Me_5)]$ (R = Bu^t or Ph). The magnetic moments of 1.50 (R = Bu^t) and 1.60 (R = Ph) (determined by the Evans method[10]) and the Mössbauer spectra, recorded at zero field, of the crystalline salts (Table 2) are in accord with the presence of low-spin iron(III) centres. The temperature-independent quadrupole doublets are well differentiated from those of the neutral precursors showing the cationic products to be free from iron(II) impurities. In addition, the unequal intensities of the two lines are typical of 'piano-stool' iron(III) complexes and can be explained by magnetic relaxation phenomena.[9] The Mössbauer isomer shifts of the iron-(II) and -(III) alkynyl complexes are similar whereas the quadrupole splittings of the latter are much smaller than those of the former. The Mössbauer parameters of $[Fe(C{\equiv}CR)(dppe)(\eta\text{-}C_5Me_5)]^+$ (R = Bu^t or Ph) are different from those of related alkyl derivatives such as $[FeMe(dppe)(\eta\text{-}C_5Me_5)][PF_6]$[9] as a consequence of the change in the ligand-field symmetry induced by the alkynyl ligand bound to the iron centres.[11]

We have found no evidence for dimer formation from either the isolable cations $[Fe(C{\equiv}CR)(dppe)(\eta\text{-}C_5Me_5)]^+$ (R = Bu^t or Ph) or during the decomposition of the less-stable C_5H_5 analogues even though $[Fe_2(\mu\text{-}C_4Me_2)(dppe)_2(\eta\text{-}C_5H_5)_2]^{2+}$, formally the product of dimerisation of $[Fe(C{\equiv}CMe)(dppe)(\eta\text{-}C_5H_5)]^+$, has been fully characterised.[12] As in the case of $[Mo(C{\equiv}CR)(dppe)(\eta\text{-}C_7H_7)]^+$, where C–C linking occurs for R = Ph {giving $[Mo_2(\mu\text{-}C_4Ph_2)(dppe)_2(\eta\text{-}C_7H_7)_2]^{2+}$} but $[Mo(C{=}CHBu^t)(dppe)(\eta\text{-}C_7H_7)]^+$ is formed for R = Bu^t,[1] steric factors may play an important role.

ESR Spectroscopy.—The fluid-solution ESR spectra of the cations $[Fe(C{\equiv}CR)(L\text{–}L)(\eta\text{-}C_5R'_5)]^+$ show broad singlets; that of $[Fe(C{\equiv}CBu^t)(dppm)(\eta\text{-}C_5H_5)]^+$ [at 270 K, in CH_2Cl_2–$C_2H_4Cl_2$ (1:1)] is centred at g = 2.116. However, in low-temperature glasses the spectra show three well separated features corresponding to the three components of the g tensor; the spectrum of $[Fe(C{\equiv}CBu^t)(dppm)(\eta\text{-}C_5H_5)]^+$ at 110 K is shown in Fig. 1. In the case of the $\eta\text{-}C_5H_5$ derivatives, the two high-field features are split into 1:2:1 triplets by hyperfine coupling with the two equivalent ^{31}P nuclei; partial resolution is

Table 3 ESR spectroscopic data for $[Fe(C{\equiv}CR)(L{-}L)(\eta\text{-}C_5R'_5)]^+$ *

R	R′	L–L	g_1	g_2	g_3	10^4A_1/ cm^{-1}	10^4A_2/ cm^{-1}
CO_2Me	H	dppm	1.989	2.046	2.366	16.5	16.5
CO_2Et	H	dppm	1.990	2.046	2.362	16.4	16.5
Ph	H	dppm	1.993	2.050	2.347	14.6	14.4
Bu^t	H	dppm	1.994	2.049	2.318	15.1	14.2
Ph	Me	dppe	1.975	2.033	2.464	—	—
Bu^t	Me	dppe	1.980	2.036	2.442	13	—

* At 77 or 90 K in CH_2Cl_2–$C_2H_4Cl_2$ (1 : 1)

observed on the high-field feature in the spectrum of $[Fe(C{\equiv}CBu^t)(dppe)(\eta\text{-}C_5Me_5)]^+$. In no case is the low-field feature resolved into a triplet, but the width of this feature could easily conceal a triplet splitting comparable to those observed on the high-field features. Thus the phosphorus coupling appears to be nearly isotropic. The ESR parameters are given in Table 3.

The *g* tensors and ^{31}P couplings are qualitatively similar to those reported for the isoelectronic chromium(I) and manganese(II) complexes $[Cr(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$,[13] $[Cr(CO)_2(PMe_3)(\eta\text{-}C_5Me_5)]$,[14] $[Mn(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]^+$ and $[Mn(CO)L_2(\eta\text{-}C_5H_5)]^+$ ($L = PMe_3$, L_2 = dppm or dppe).[15] The *g* tensors are also quite similar to those of the related iron(III) and ruthenium(III) 'piano-stool' complexes $[FeR(dppe)(\eta\text{-}C_5Me_5)]^z$ ($z = +1$, $R = CH_2OH$[16] or CH_2OMe;[17] $z = 0$, $R = CHOMe$[17]), $[FeMe\{P(OMe)_3\}_2(\eta\text{-}C_5Me_5)]^+$,[18] $[FeL(S_2CNMe_2)(dppe)(\eta\text{-}C_5Me_5)]^+$ (L = CO, MeCN, Me_2CO or CH_2Cl_2),[19] $[Fe(C_5H_5Me_2)(\eta\text{-}C_5H_5)]^+$ ($C_5H_5Me_2$ = 2,4-dimethylpentadienyl)[20] and $[RuX(CO)(PEt_3)(\eta\text{-}C_5Ph_5)]^+$ (X = Br or COMe).[21] In all cases, $1.98 < g_{min} < 2.00$, $2.01 < g_{inter} < 2.05$, and $g_{max} \approx 2.1$ (Cr), 2.2 (Mn), and 2.3–2.4 (Fe). A spectrum remarkably similar to those of the present complexes was assigned[22] to the iron(I) radical $[Fe(PPh_3)_2(\eta\text{-}C_5H_5)]$, formed by treating $[Fe(\eta\text{-}C_5H_5)(\eta^6\text{-}C_6H_5Me)]$ with PPh_3 in thf; the ESR parameters [g = 1.99, 2.08, and 2.30; $A_1(^{31}P)$ 20 × 10^{-4} cm^{-1}, A_2 and A_3 unresolved] seem more consistent with an iron(III) complex.

Molecular orbital (MO) calculations for $[Cr(CO)_2L(\eta\text{-}C_5H_5)]$ (L = CO or PH_3)[14] and $[Fe(CH_2OH)(PH_3)_2(\eta\text{-}C_5H_5)]^+$, both with imposed C_s symmetry, have shown that three MOs can be identified with the 't_{2g}' set, *i.e.* a relatively low-lying orbital, 1a′, and two closely spaced orbitals, 2a′ and 1a″. For the iron(III) species and chromium(I) carbonyl, 2a′ is predicted to be singly occupied (the SOMO), whereas 1a″ is the SOMO in the chromium(I) phosphine complex. In either case, the *g* tensor is expected to have one component substantially larger (spin–orbit mixing of 2a′ and 1a″), one component somewhat larger (spin–orbit mixing of 1a′ with the SOMO) and one component slightly less than g_e (mixing of the SOMO with a high-lying orbital). The only ESR observable which distinguishes between $^2A'$ and $^2A''$ ground states is the orientation of the principal axes, and dilute single-crystal studies of $[Cr(CO)_3(\eta\text{-}C_5H_5)]$,[23] $[Cr(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$[13] and $[Cr(CO)_2(PMe_3)(\eta\text{-}C_5Me_5)]$[14] have confirmed the extended Hückel molecular orbital (EHMO) predictions. While it is tempting to accept the EHMO predictions of $^2A'$ for the ground state in iron(III) complexes, the increasing values of g_{max} in the series Cr^I, Mn^{II}, Fe^{III} suggest that the separation of the $^2A'$ and $^2A''$ states decreases in the series. This is also consistent with the generally poorer resolution of the iron spectra as the ground state/excited state spacing decreases. The ordering is likely, therefore, to be a very delicate function of ligand character and conformation.

Experimental

The complexes $[Fe(C{\equiv}CR)(dppm)(\eta\text{-}C_5H_5)]$ ($R = Bu^t$, CO_2Me, $SiMe_3$, Ph,[5] CO_2Et or CH_2OMe[24]) and $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$[25] were prepared by published methods. Samples for ESR spectroscopy were prepared under an atmosphere of dry nitrogen, using dried, distilled and deoxygenated solvents.

Electrochemical studies were carried out as previously described[26] or by using a PAR 362 instrument (at Rennes). All potentials are standardised against the $[Fe(\eta\text{-}C_5H_5)_2]^+$–$[Fe(\eta\text{-}C_5H_5)_2]$ and $[Fe(\eta\text{-}C_5Me_5)_2]^+$–$[Fe(\eta\text{-}C_5Me_5)_2]$ couples as internal standards (E° = 0.47 and −0.09 V respectively). Infrared spectra were recorded on a Nicolet 5ZDX FT spectrometer and Mössbauer spectra with a 2.5 × 10^{-2} C (9.25 × 10^8 Bq) ^{57}Co source using a symmetric triangular sweep mode,[27] and NMR spectra on a Bruker AM300 calibrated against tetramethylsilane (^1H and ^{13}C) or H_3PO_4 (^{31}P). X-Band ESR spectra were recorded on a Bruker ESP-300E spectrometer, at 77 K in liquid nitrogen or at 90 K using a variable-temperature probe, and calibrated against a solid sample of the diphenylpicrylhydrazyl (dpph) radical. Microanalyses were carried out by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol or at the Centre for Microanalyses of the CNRS at Lyon-Villeurbanne.

$[Fe(C{=}CHBu^t)(dppe)(\eta\text{-}C_5Me_5)][PF_6]$.—To $[FeCl(dppe)(\eta\text{-}C_5Me_5)]$ (1.54 g, 2.46 mmol) in MeOH (20 cm^3) at 20 °C was added $Bu^tC{\equiv}CH$ (303 µl, 2.46 mmol) and NH_4PF_6 (0.40 g, 2.45 mmol). The solution was stirred for 16 h and then the solvent was removed under vacuum. The residue was extracted with CH_2Cl_2, the extract was concentrated *in vacuo*, and diethyl ether was added to precipitate the product as an orange powder, yield 1.74 g (87%) (Found: C, 61.4; H, 5.9. $C_{42}H_{49}F_6FeP_3$ requires C, 61.8; H, 6.1%). IR (Nujol): ν(C=C) 1631 cm^{-1}. NMR ($CDCl_3$, 20 °C): ^1H, δ 7.50–7.12 (20 H, m, Ph), 3.43 (1 H, t, $^4J_{PH}$ 3.6, $CHBu^t$), 2.91, 2.51 (4 H, 2m, CH_2) and 1.51 (15 H, s, C_5Me_5); ^{13}C, δ 354.3 (t, $^2J_{PC}$ 32, C_α), 133.7–128.5 (C_6H_5), 130.9 (d, $^1J_{CH}$ 155, C_β), 98.9 (s, C_5Me_5), 33.0 (s, CMe_3), 32.5 [q, $^1J_{CH}$ 126, CMe_3], 29.6 (tt, $^1J_{CH}$ 135, $^1J_{PC}$ 23, CH_2 of dppe) and 10.2 (q, $^1J_{CH}$ 128 Hz, C_5Me_5); ^{31}P NMR, δ 89.60.

The complex $[Fe(C{=}CHPh)(dppe)(\eta\text{-}C_5Me_5)][PF_6]$ was prepared by the same method in 97% yield (Found: C, 63.4; H, 5.6. $C_{44}H_{45}F_6FeP_3$ requires C, 63.2; H, 5.4%). IR (Nujol): ν(C=C) 1613 cm^{-1}. NMR ($CDCl_3$, 20 °C): ^1H, δ 7.62–6.35 (25 H, m, Ph), 5.14 (1 H, t, $^4J_{PH}$ 4.3, $CHPh$), 3.06, 2.50 (4 H, 2m, CH_2) and 1.58 (15 H, s, C_5Me_5); ^{13}C, δ 361.2 (t, $^2J_{PC}$ 33 Hz, C_α), 134.1–126.9 (C_6H_5), 126.5 (dt, $^1J_{CH}$ 152, $^3J_{PC}$ 4.8, C_β), 101.1 (s, C_5Me_5), 29.7 (tm, $^1J_{CH}$ 136, CH_2 of dppe) and 10.6 (q, $^1J_{CH}$ 128 Hz, C_5Me_5); ^{31}P, δ 88.0.

$[Fe(C{\equiv}CBu^t)(dppe)(\eta\text{-}C_5Me_5)]$.—To a suspension of $[Fe(C{=}CHBu^t)(dppe)(\eta\text{-}C_5Me_5)][PF_6]$ (1.16 g, 1.40 mmol) in thf (30 cm^3) at 20 °C was added $KOBu^t$ (0.165 g, 1.47 mmol). After stirring the mixture for 2 h the solvent was removed under vacuum and the solid residue was extracted with toluene (3 × 30 cm^3). The solvent was then removed *in vacuo* and the crude residue was washed with pentane (10 cm^3) and dried to give the thermally stable product as an orange powder, yield 0.76 g (80%) (Found: C, 75.6; H, 7.2. $C_{42}H_{48}FeP_2$ requires C, 75.2; H, 7.2%). IR (Nujol): ν(C≡C) 2066 cm^{-1}. NMR (C_6D_6): ^1H (20 °C), δ 8.09–7.04 (20 H, m, Ph), 2.77, 1.98 (4 H, 2m, CH_2), 1.53 (15 H, s, C_5Me_5) and 1.25 (9 H, s, Bu^t); ^{13}C (75 °C), δ 140.7–127.3 (C_6H_5), 125.3 (s, C_β), 107.0 (t, $^2J_{PC}$ 40, C_α), 87.1 (s, C_5Me_5), 33.0 (q, $^1J_{CH}$ 126, CMe_3), 31.1 (m, CH_2 of dppe), 30.3 (s, CMe_3) and 10.5 (q, $^1J_{CH}$ 126 Hz, C_5Me_5); ^{31}P (75 °C), δ 100.4.

The complex $[Fe(C{\equiv}CPh)(dppe)(\eta\text{-}C_5Me_5)]$ was prepared by the same method, yield 98% (Found: C, 76.7; H, 6.4. $C_{44}H_{44}FeP_2$ requires C, 76.5; H, 6.4%). IR (Nujol): ν(C≡C) 2049 cm^{-1}. NMR (C_6D_6, 20 °C): ^1H, δ 8.05–6.96 (25 H, m, Ph), 2.65, 1.84 (4 H, 2m, CH_2), 1.54 (15 H, s, C_5Me_5); ^{13}C-$\{^1H\}$, δ 140.1–123.2 (C_6H_5), 137.4 (t, $^2J_{PC}$ 40 Hz, C_α), 120.5 (s, C_β), 87.9 (s, C_5Me_5), 3.12 (m, CH_2 of dppe) and 10.6 (s, C_5Me_5); ^{31}P-$\{^1H\}$, δ 100.0.

$[Fe(C{\equiv}CBu^t)(dppe)(\eta\text{-}C_5Me_5)][PF_6]$.—To $[Fe(C{\equiv}CBu^t)(dppe)(\eta\text{-}C_5Me_5)]$ (0.17 g, 0.24 mmol) in CH_2Cl_2 (10 cm^3) at

−80 °C was added $[Fe(\eta-C_5H_5)_2][PF_6]$ (73 mg, 0.22 mmol). The solution was stirred at −80 °C for 4 h and then reduced to very low volume *in vacuo*. Addition of pentane gave a precipitate which was recrystallised from CH_2Cl_2–diethyl ether to give mauve microcrystals, yield 0.16 g (78%) (Found: C, 61.4; H, 5.8. $C_{42}H_{48}F_6FeP_3$ requires C, 61.9; H, 5.9%). IR (Nujol): ν(C≡C) 2035 cm^{-1}.

Black microcrystals of the complex $[Fe(C{\equiv}CPh)(dppe)(\eta-C_5Me_5)][PF_6]$ were prepared by the same method in 80% yield (Found: C, 62.8; H, 5.5. $C_{44}H_{44}F_6FeP_3$ requires C, 63.2; H, 5.3%). IR (Nujol): ν(C≡C) 2022 cm^{-1}.

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