

Synthesis, X-Ray Crystal Structure and Magnetic Properties of the Six-coordinated Intermediate-spin Iron(II) Complex $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^2\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)(\sigma\text{-O=CMe}_2)]^+ \text{CF}_3\text{SO}_3^-$

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The σ -acetone complex $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^2\text{-dppe})(\sigma\text{-O=CMe}_2)]^+ \text{OSO}_2\text{CF}_3^-$ (**2**, dppe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) is cleanly synthesised by treatment of the hydride compound $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^2\text{-dppe})\text{H}]$ **1** with $\text{MeOSO}_2\text{CF}_3$ in Et_2O followed by crystallization from acetone–pentane; this compound, characterized by a single crystal X-ray diffraction, exhibits unexpected paramagnetic behaviour for a six-coordinated 18-electron iron(II) organometallic species.

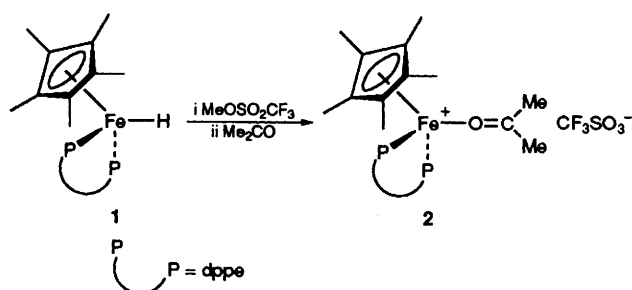
The oxidation state +2 is very common in iron coordination chemistry and the diamagnetic ground state of octahedral d^6 iron(II) derivatives with cyclic organic ligands ($\eta^4\text{-C}_4\text{Ph}_4$, $\eta^5\text{-C}_5\text{R}_5$, $\eta^6\text{-C}_6\text{R}_6$) is well established.¹ To the best of our knowledge, six-coordinated 18-electron iron(II) compounds having two unpaired electrons are unknown in such series. In contrast, this electronic structure is typical of the five-coordinated trigonal-bipyramidal^{1b–3} and four-coordinated tetrahedral iron(II) complexes.⁴ This is a consequence of the small crystal field splitting in a low coordination state. Here, we report the synthesis, X-ray crystal structure and unexpected magnetic properties of the first paramagnetic six-coordinated d^6 organoiron(II) species, namely the σ -acetone complex $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^2\text{-dppe})(\sigma\text{-O=CMe}_2)]^+ \text{OSO}_2\text{CF}_3^-$ **2**.

The hydride compound $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\text{dppe})\text{H}]$ **1**⁵ and $\text{MeOSO}_2\text{CF}_3$ were reacted (Et_2O , +20 °C) to give a greenish solid, which slowly precipitated from the solvent. After washing with pentane and drying under vacuum, the solid residue was dissolved in acetone to give the σ -acetone complex $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^2\text{-dppe})(\sigma\text{-O=CMe}_2)]^+ \text{OSO}_2\text{CF}_3^-$ **2** (94% yield after recrystallization from acetone–pentane, Scheme 1).[†] The σ coordination mode of the dimethyl ketone was assigned on the basis of the IR $\nu_{\text{C=O}}$ (1664 cm^{-1} , Nujol) and compares well with the values already reported for the related compounds $[\text{Fe}(\text{C}_5\text{H}_5)(\text{dmpe})(\text{Me}_2\text{CO})]\text{BF}_4$ ⁶ and $[\text{Fe}(\text{C}_5\text{H}_5)(\text{dppe})(\text{Me}_2\text{CO})]\text{PF}_6$.⁷ The X-ray crystal structure of **2** confirmed the coordination of the ketone ligand to the metal centre (Fig. 1).[‡]

The geometry of **2** is roughly an octahedral polyhedron, assuming the pentamethylcyclopentadienyl group occupies three ligand sites and the dppe and acetone occupy the other three sites. The bond distances involving the dppe ligand are comparable with values reported for related systems.⁸ The $\text{Fe}-(\eta^5\text{-C}_5\text{Me}_5)$ bond distances in **2** range from 2.108(5) to 2.129(5) Å, with an average $\text{Fe}-\text{C}_{\text{ring}}$ distance of 2.117 Å and are similar to those found for parent compounds.^{8,9} The $\text{Fe}-\text{O}$ bond length of 2.031(4) Å is slightly long in comparison with the data available in the literature.¹⁰ However, the $\text{Fe}-\text{O}$ bond distance gives no evidence that the acetone ligand is only weakly associated with the metal; rather, it indicates a relatively strong interaction between the iron atom and this ligand. The normal $\text{Fe}-\text{O}$ bond length agrees well with the

observation that the pseudo-octahedral geometry is not distorted from those of related complexes in the $\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\text{dppe})$ series as shown by the values of the $\text{P}(1)\text{-Fe-P}(2)$, $\text{P}(1)\text{-Fe-O}$ and $\text{P}(2)\text{-Fe-O}$ angles, which are always slightly below 90° and strongly diverge from the bond angles values found in the trigonal-bipyramidal complexes.^{2,11} The $\text{Fe}-\text{P}$ bond lengths of 2.242(2) and 2.269(2) Å are typical for octahedral low-spin iron(II) species⁸ and undoubtedly, these $\text{Fe}-\text{P}$ distances reflect six-coordination of the metal centre. The $\text{C}=\text{O}$ bond length of 1.212(7) Å is consistent with those of other σ -acetone complexes which range from 1.216(8) to 1.242(8) Å.¹² The $\text{Fe}-\text{O}-\text{C}$ angle of 152.5(4)° is rather large with respect to literature values that range from 129.4 to 153.2°.¹²

Given the structural data, and the description of analogous C_5H_5 complexes,^{6,7} the paramagnetic behaviour of **2** is completely unexpected. The solid ketone complex **2** exhibits a magnetic moment $\mu_{\text{eff}} = 2.90 \mu_{\text{B}}$ (SQUID method) in the range 77–300 K. In acetone solution, a similar value was determined ($3.18 \mu_{\text{B}}$, 310 K, Evans' method). Such values correspond to two unpaired electrons.² The powder ESR spectrum of the iron(II) derivative **2** at 77 K consists of three signals. The relevant parameters are $g = 9.95$ and $g' = 4.264$ for the two low-field unresolved signals and a high-field well-resolved octahedral structure with three anisotropic parameters $g''_1 = 2.0677$, $g''_2 = 2.1051$ and $g''_3 = 2.3730$. The high-field component g''_3 shows hyperfine splitting due to magnetic interaction between the unpaired electron and the phosphorus nucleus spin of the dppe ligand ($I = 1$, $a''_3 = 21 \text{ G}$). An increase in the temperature to 298 K induces a dramatic and reversible disappearance of all the absorption signals. These findings are consistent, as indicated also by the experimental μ_{eff} value, with a $S = 1$ spin Hamiltonian which explains both the temperature dependence of the iron(II) powder spectra and the low-field absorptions at liquid-nitrogen temperature.² The iron(II) acetone complex **2** displays ESR parameters in frozen THF solution, which are in good agreement with those of the powder spectra, indicating



Scheme 1

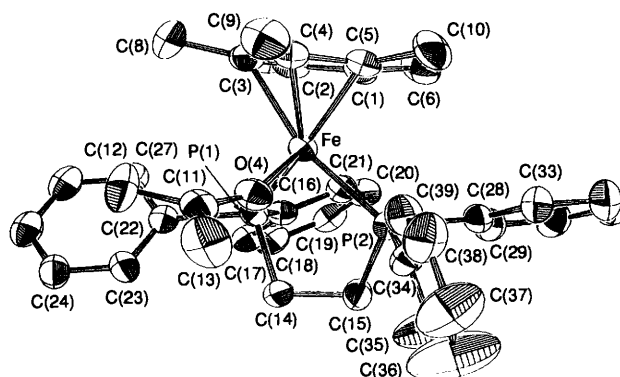


Fig. 1 Structure of **2**

that it maintains the same geometry in solution. Minor variations of the g'' tensor components are observed between the powder and solution spectra, which could be related to the effect of the solvent on the overall line shape as already described.¹³

Such magnetic properties have not previously been reported for an octahedral 18-electron d^6 organometallic complex.¹⁴ It is a well known direct consequence of ligand-field theory that truly regular octahedral complexes cannot possess a ground state of intermediate spin. They show either $S = 0$ or 2 electronic configurations.^{1b} However, there are a few complexes in which the symmetry is very low, and the intermediate $S = 1$ state is the adopted ground level.¹⁵ On the other hand, it cannot be excluded that our experimental data could result from the effective coexistence of $S = 0$ and $S = 2$ species as has already been observed for inorganic derivatives.¹⁶ Surprisingly, ^1H NMR data reported for the related complex $[\text{Fe}(\text{C}_5\text{H}_5)(\text{dppe})(\text{Me}_2\text{CO})]\text{PF}_6$ do not suggest that it is paramagnetic, one might expect that related iron ketone complexes should also be paramagnetic since the ligand field of C_5Me_5 is stronger than that of C_5H_5 .

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† Satisfactory C, H, P, elemental analyses were obtained. Crystal data for **2**: $\text{C}_{40}\text{H}_{45}\text{F}_3\text{FeO}_4\text{P}_2\text{S}$, $M = 796.66$, monoclinic, $P2_1/c$, $a = 15.375(4)$, $b = 13.227(9)$, $c = 20.142(9)$ Å, $\beta = 109.20(5)$, $V = 3868(3)$ Å³, $D_c = 1.368$ g cm⁻³, $Z = 4$, $F(000) = 1664$, $\lambda(\text{Mo-K}\alpha) = 0.71069$ Å, scan type $\omega/2\theta$ ($\theta_{\text{max}} = 50^\circ$, $t_{\text{max}} = 60$ s), 3735 independent observed data [$I > 4\sigma(I)$] were collected at 294 K on an Enraf-Nonius diffractometer. The structure was solved by direct methods and Fourier techniques, and refined by full-matrix least squares analysis to $R = 0.050$, $R_w = 0.047$. Atomic coordinates, bond

lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

- (a) *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, Pergamon, New York, 1987, vol. IV; (b) F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn., Wiley Interscience, New York, 1988.
- C. Bianchini, F. Laschi, D. Masi, F. M. Ottaviani, A. Pastor, M. Peruzzini, P. Zanello and F. Zanobini, *J. Am. Chem. Soc.*, 1993, **115**, 2723.
- Y. Kubo, A. Yamamoto and S. Ikeda, *J. Organomet. Chem.*, 1972, **46**, C50–52.
- A. R. Hermes and G. S. Girolami, *Organometallics*, 1987, **6**, 763.
- C. Roger, P. Marseille, C. Salus, J.-R. Hamon and C. Lapinte, *J. Organomet. Chem.*, 1987, **336**, C13.
- W. E. Silverthorn *J. Chem. Soc., Chem. Commun.*, 1971, 1310.
- D. Sellmann and E. Kleinschmidt, *J. Organomet. Chem.*, 1977, **140**, 211.
- C. Roger, P. Hamon, L. Toupet, H. Rabaâ, J.-Y. Saillard, J.-R. Hamon and C. Lapinte, *Organometallics*, 1991, **10**, 1045; C. Roger, L. Toupet and C. Lapinte, *J. Chem. Soc., Chem. Commun.*, 1988, 713.
- Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, Pergamon, New York, 1987, vol. IX.
- M. B. Humphrey, W. M. Lamana, M. Brookhart and G. R. Husk; *Inorg. Chem.*, 1983, **22**, 3355; M. R. Churchill and J. Wormald, *Inorg. Chem.*, 1970, **9**, 2430; D. J. Darensbourg, C. S. Day and M. B. Fisher, *Inorg. Chem.*, 1981, **20**, 3577.
- I. Sacconi and M. Di Vaira, *Inorg. Chem.*, 1978, **17**, 810.
- D. M. Dalton, J. M. Fernandez, K. Emerson, R. D. Larsen, A. M. Arif and J. A. Gladysz, *J. Am. Chem. Soc.*, 1990, **112**, 9198 and references cited therein.
- G. Razuva, V. K. Cherkasov and G. A. Abamukov, *J. Organomet. Chem.*, 1978, **160**, 361.
- A paramagnetic behaviour was reported for the 16-electron d^6 complex $[\text{Fe}(\eta^5\text{-pentadienyl})(\text{PEt}_3)_2]\text{PF}_6$, J. R. Bleeke, R. J. Wittenbrink, T. W. Clayton, Jr. and M. Y. Chiang, *J. Am. Chem. Soc.*, 1990, **112**, 6539.
- E. König, *Coord. Chem. Rev.*, 1968, **4**, 471.
- L. Wiehl, G. Kiel, C. P. Köhler, H. Spiering and P. Gütllich, *Inorg. Chem.*, 1986, **25**, 1565.