Isolation and Characterization of a Cationic 19-Electron Iron(III) Hydride Complex; Electron Transfer Induced Hydride Migration by Carbon Monoxide at an Iron(III) Centre

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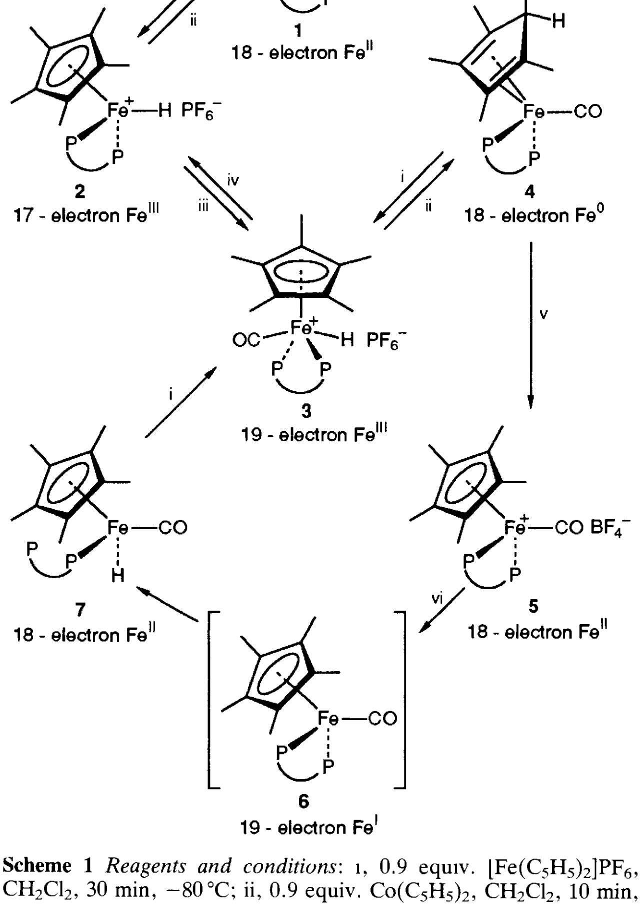
The first hypervalent 19-electron metal hydride complex [Fe(C_5Me_5)(dppe)(CO)H]PF_6 **3**, synthesized from the 17-electron iron(III) hydride complex [Fe(C_5Me_5)(dppe)H]PF_6 **2**, is isolated and its structure is established by IR, Mössbauer and ESR data; reaction of the iron(III) complex **2** with carbon monoxide causes hydride transfer to the C_5Me_5 ligand through an electrochemical chemical electrochemical (ECE)-like pathway [dppe = ethylenebis-(diphenylphosphine)].

It is increasingly recognised that transition metal hydride complexes constitute an important class of compounds because of their involvement in catalytic and stoichiometric processes as organometallic and inorganic radicals.[1] However, stable 17-electron metal hydride complexes resulting from the oxidation of corresponding 18-electron neutral species are very rare; most of these cation radicals previously studied have been short-lived, their major mode of decomposition being deprotonation.[2a–c] 19-Electron metal radicals are also rare, their reactivity is not very well understood, and metal hydride or metal alkyl compounds with such an electronic structure are unknown.[2d] Recently, we successfully synthesised and characterised the 17-electron iron(III) hydride complex [Fe(C_5Me_5)(dppe)H]PF_6 **2**, resulting from the one-electron oxidation of [Fe(C_5Me_5)(dppe)H] **1**.[3] We now report here the first example of an isolated 19-electron iron(III) hydride complex [Fe(C_5Me_5)(dppe)(CO)H]PF_6 **3**, evidence for its 19-electron structure, and a preliminary account of its reactivity.

The 17-electron compound **2** binds CO reversibly at −80 °C to give cleanly the unusual Fe^{III} 19-electron adduct [Fe(C_5Me_5)(η^2-dppe)(CO)H]PF_6 **3**, isolated as a dark-green powder in 98% yield.† This compound is stable below −60 °C, but above this temperature it readily releases CO both in the solid state and in solution, regenerating pure **2** (Scheme 1). The 19-electron complex **3** was characterised by its IR spectrum in Nujol, which revealed a strong C–O stretching absorption at 1940 cm^{-1}, obscuring the Fe–H signal. The Mössbauer spectrum of a powdered sample of **3** recorded at zero field is characteristic of a pure iron(III) complex. It displays a doublet [4.2 K, isomeric shift (IS) = 0.304 mm s^{-1} (*vs.* Fe), quadrupole splitting (QS) = 0.715 mm s^{-1}] with two lines of unequal intensity due to the magnetic relaxation phenomenon at the iron(III) centre. The Mössbauer parameters are well differentiated from those previously obtained for **2**[3] [4.2 K, IS = 0.260 mm s^{-1} (*vs.* Fe), QS = 0.84 mm s^{-1},] and are a consequence of the change in the ligand field symmetry induced by the CO binding to the metal.[4]

The 19-electron structure of **3** is established by the analysis of the ESR spectrum (Fig. 1). Carbon monoxide was bubbled for 1 min into a quartz tube containing a CH_2Cl_2–$ClCH_2CH_2Cl$ solution of **2** cooled to −80 °C. The ESR spectrum recorded at 77 K exhibits three broad and complex *g* tensor components (g_1 = 2.0019, g_2 = 2.0367, g_3 = 2.0777). These values clearly contrast with those determined under the same conditions for the 17-electron hydride **2** (g_1 = 1.9944, g_2 = 2.0430, g_3 = 2.4487). These three well-separated features for the latter correspond to the three components of the *g*-tensor expected for species having octahedral symmetry. The g_1 and g_2 values are close to the free electron *g* value (*g* = 2.0023), whereas the g_3 value is much bigger, as usually observed for 17-electron iron(III) compounds having a singly occupied HOMO with predominant $d_{x^2-y^2}$ character.[5] In the case of the 19-electron CO adduct **3** the *g*-tensor components are much closer to the free electron *g* value, indicating that the HOMO is significantly more separated in energy from the doubly occupied orbitals than for the 17-electron iron(III) complex. The multiline ESR spectrum of **3** is due to nuclear



Scheme 1 *Reagents and conditions*: i, 0.9 equiv. [Fe(C_5H_5)$_2$]PF_6, CH_2Cl_2, 30 min, −80 °C; ii, 0.9 equiv. Co(C_5H_5)$_2$, CH_2Cl_2, 10 min, 20 °C; iii, CO (1 atm), CH_2Cl_2, 30 min, −80 °C; iv, powdered **3**, 1 h, 20 °C or in CH_2Cl_2 solution, 30 min, 20 °C; v, 1.1 equiv. HBF_4·Et_2O, Et_2O, 4 h, −80 °C; vi, ref. 10

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† *Selected spectroscopic data for new compounds*: [Fe(C_5Me_5)(dppe)(CO)H]PF_6 **3**. IR ν_{CO}/cm^{-1} (Nujol) 1940s; Mössbauer (4.2 K) IS = 0.304 mm s^{-1} (*vs.* Fe), QS = 0.715 mm s^{-1}; ESR (77 K) g_1 = 2.0019, g_2 = 2.0367, g_3 = 2.0777, a_1 (^{31}P) = 17.70, a_1 (^{31}P) = 18.00, a_1 (^{31}P) = 17.10, a_1 (^1H) = 12.00, a_1 (^1H) = 6.20, a_1 (^1H) = 5.00 G, (1 G = 10^{-4} T). [Fe(η^4-C_5Me_5H)(dppe)CO] **4**. Satisfactory C, H, P analyses were obtained; IR ν_{CO}/cm^{-1} (Nujol) 1880; Mössbauer (298 K) IS = −0.046 mm s^{-1} (*vs.* Fe), QS = 1.452 mm s^{-1}; ^1H NMR (20 °C, CD_2Cl_2) δ 2.34 (m, CH_2, 4H), 2.20 (b, 1H, C_5Me_5H), 1.89 (s, C_5Me_5H, 6H), 0.82 (s, C_5Me_5H, 6H), 0.26 (d, C_5Me_5H, $^3J_{PH}$ 7 Hz, 3H); ^{13}C NMR (20 °C, CD_2Cl_2), δ 222.0 (t, CO, $^2J_{PC}$ 16 Hz), 93.5, 63.1 (s, C_5Me_5H), 61.1 (d, C_5Me_5H, J_{CH} 137 Hz); ^{31}P NMR (20 °C, CD_2Cl_2) δ 86.3 (s, dppe).

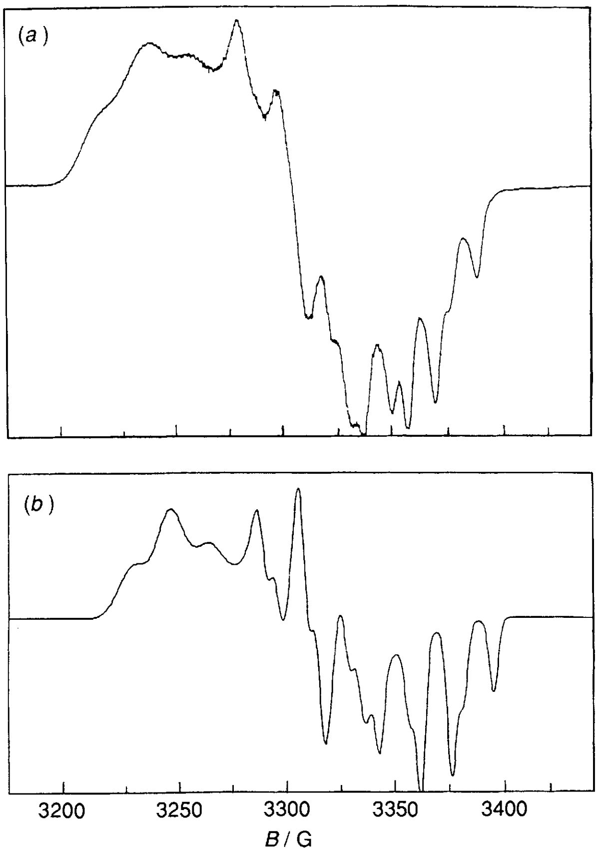

Fig. 1. ESR spectrum of [Fe(C_5Me_5)(η^2-dppe)(CO)H]BF_4 **3**; (*a*) experimental spectrum of CH_2Cl_2:$(ClCH_2)_2$ (1:1 v/v) solution at 77 K (*b*) computer-simulated spectrum

hyperfine coupling and there is considerable variation in linewidth (Fig. 1). However, the experimental spectrum can be described as a doublet of 1:2:1 triplets, consistent with the coordination to the iron atom of two equivalent ^{31}P and one ^1H nuclei; the complete set of the Hamiltonian parameters can be determined from the best fit between the experimental [Fig. 1(*a*)] and simulated spectra [Fig. 1(*b*)]. Taken with the IR data, this information clearly identifies the organometallic radical [Fe(C_5Me_5)(dppe)(CO)H]PF_6 **3** as a 19-electron species, with the C_5Me_5, the carbon monoxide, two phosphorus atoms and a hydrogen atom bound to the metal centre. Moreover, the equivalence of the spin parameters of the two phosphorus atoms supports a *trans* structure for **3**.[6]‡

The reactivity of the iron(III) hydride **3** is consistent with a 19-electron open shell electronic structure. Thus, upon one-electron reduction of the complex with cobaltocene at −80 °C in CH_2Cl_2 the orange solid complex [Fe(η^4C_5-Me_5H)(dppe)CO] **4** is obtained in 92% yield after crystallisation from pentane (Scheme 1).† Although η^4-coordination of cyclopentadiene ligands is well-documented, the formation of compound **4** constitutes a rare example of η^5-η^4-decoordination of the C_5Me_5 ligand.[7] Moreover, the reduction of **3**-d_1 affords **4**-d_1, suggesting that the transient 20-electron iron(II) hydride intermediate gives the Fe^0 compound **4** through a reductive-elimination process. The chemical reversibility of this reaction was established by carrying out the oxidation of the iron^0 complex **4** with a stoichiometric amount of ferrocenium ion at −80 °C in CH_2Cl_2. After 30 min the reaction reached completion, affording **3** quantitatively, which can be isolated as microcrystals by addition of cold diethyl ether and characterized by its IR and ESR spectra, or transformed into **2** by warming to room temperature. It is noteworthy that the result of the reaction sequence from **1** to **4** is a reductive displacement of the hydride by carbon monoxide through an ECE-like pathway.

Protonation of the complex **4** with the HBF_4–Et_2O complex in diethyl ether at −80 °C occurs cleanly and the known [Fe(C_5Me_5)(dppe)CO]BF_4 **5** precipitates as a golden yellow solid in 90% yield, identified by comparison of its IR and ^1H NMR spectra with the literature data.[8] The one-electron reduction of **5**, which has been previously reported, yields the hydride [Fe(C_5Me_5)(η^1-dppe)(CO)H] **7** *via* the 19-electron species [Fe(C_5Me_5)(η^2-dppe)(CO)] **6**.[9] It is of interest to note that the behaviour of the 19-electron complexes **3** and **6** is very different. Whereas the transient iron(I) intermediate **6** releases a phosphine ligand, the dppe is coordinated as an η^2 chelating ligand in the iron(III) hydride **3**. Moreover, an equilibrium between the 19-electron species **3** and a 17-electron isomeric complex [Fe(C_5Me_5)(η^1-dppe)(CO)H]PF_6 cannot be assumed, since the latter should be thermodynamically easier to reduce than **3**, and the reduction of **3** would then provide the iron hydride **7** instead of the isolated iron^0 compound **4**. On the other hand, the independent chemical oxidation of the hydride complex **7** with 1 equiv. of ferrocenium ion in CH_2Cl_2 at −80 °C affords after 30 min the paramagnetic complex **3**. Thus, the change in the chelation of the dppe ligand at the iron(III) centre, induced by the one-electron oxidation, is irreversible since the subsequent reduction of **3** gives **4**.

The observation of the equilibrium between **2** and its CO adduct **3** is unique, involving isolated 17- and 19-electron species, and is of considerable relevance to efforts aimed at providing a better understanding of the ligand substitution reactions of 17-electron systems *via* an associative mechanism.[10]

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‡ Note that a *trans* structure was also observed for the related compound [Fe(C_5Me_5)(dppe)$(H)_2$]BF_4.[3]