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## 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<sub>6</sub> **3**, synthesized from the 17-electron iron(III) hydride complex [Fe( $C_5Me_5$ )(dppe)H]PF<sub>6</sub> **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.<sup>1</sup> 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.<sup>2a-c</sup> 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(C5-Me<sub>5</sub>)(dppe)H]PF<sub>6</sub> 2, resulting from the one-electron oxidation of  $[Fe(C_5Me_5)(dppe)H]$  1.<sup>3</sup> 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<sup>III</sup> 19-electron adduct [Fe( $C_5$ - $Me_5$ )( $\eta^2$ -dppe)(CO)H]PF<sub>6</sub> **3**, isolated as a dark-green powder in 98% yield.<sup>†</sup> 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<sup>-1</sup>, 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) =  $0.304 \text{ mm s}^{-1}$  (vs. Fe). quadrupole splitting (QS) =  $0.715 \text{ mm s}^{-1}$ ] 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,  $IS = 0.260 \text{ mm s}^{-1}$  (vs. Fe),  $QS = 0.84 \text{ mm s}^{-1}$ , 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<sub>2</sub>Cl<sub>2</sub>-ClCH<sub>2</sub>CH<sub>2</sub>Cl 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.<sup>5</sup> 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: 1, 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<sub>2</sub>O, Et<sub>2</sub>O, 4 h, -80 °C; vi, ref. 10

<sup>†</sup> Selected spectroscopic data for new compounds: [Fe(C<sub>5</sub>Me<sub>5</sub>)-(dppe)(CO)H]PF<sub>6</sub> **3**. IR  $v_{CO}/cm^{-1}$  (Nujol) 1940s; Mössbauer (4.2 K) IS = 0.304 mm s<sup>-1</sup> (vs. Fe), QS = 0.715 mm s<sup>-1</sup>; ESR (77 K)  $g_1 = 2.0019, g_2 = 2.0367, g_3 = 2.0777, a_1 (^{31}P) = 17.70, a_1 (^{31}P) = 18.00, a_1 (^{31}P) = 17.10, a_1 (^{11}H) = 12.00, a_1 (^{11}H) = 6.20, a_1 (^{11}H) = 5.00 G$ , (1 G = 10<sup>-4</sup> T). [Fe( $\eta^4$ -C<sub>5</sub>Me<sub>5</sub>H)(dppe)CO] **4**. Satisfactory C, H, P analyses were obtained; IR  $v_{CO}/cm^{-1}$  (Nujol) 1880; Mössbauer (20°C, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  2.34 (m, CH<sub>2</sub>, 4H), 2.20 (b, 1H, C<sub>5</sub>Me<sub>5</sub>H), 1.89 (s, C<sub>5</sub>Me<sub>5</sub>H, 6H), 0.82 (s, C<sub>5</sub>Me<sub>5</sub>H, 6H), 0.26 (d, C<sub>5</sub>Me<sub>5</sub>H, <sup>3</sup>J<sub>PH</sub> 7 Hz, 3H); <sup>13</sup>C NMR (20°C, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  222.0 (t, CO, <sup>2</sup>J<sub>PC</sub> 16 Hz), 93.5, 63.1 (s, C<sub>5</sub>Me<sub>5</sub>H), 61.1 (d, C<sub>5</sub>Me<sub>5</sub>H, J<sub>CH</sub> 137 Hz); <sup>31</sup>P NMR (20°C, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  86.3 (s, dppe).



**Fig. 1.** ESR spectrum of  $[Fe(C_5Me_5)(\eta^2-dppe)(CO)H]BF_4$  3; (a) experimental spectrum of  $CH_2CI_2$ :  $(CICH_2)_2$  (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 <sup>31</sup>P and one <sup>1</sup>H 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<sub>5</sub>Me<sub>5</sub>)(dppe)(CO)H]PF<sub>6</sub> **3** as a 19-electron species, with the C<sub>5</sub>Me<sub>5</sub>, 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**.<sup>6</sup>‡

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<sub>2</sub>Cl<sub>2</sub> the orange solid complex [Fe( $\eta^4$ C<sub>5</sub>-Me<sub>5</sub>H)(dppe)CO] 4 is obtained in 92% yield after crystallisation from pentane (Scheme 1).<sup>†</sup> Although  $\eta^4$ -coordination of cyclopentadiene ligands is well-documented, the formation of compound 4 constitutes a rare example of  $\eta^5$ - $\eta^4$ -decoordination of the  $C_5Me_5$  ligand.<sup>7</sup> Moreover, the reduction of 3-d<sub>1</sub> 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<sup>0</sup> complex 4 with a stoichiometric amount of ferrocenium ion at -80 °C in CH<sub>2</sub>Cl<sub>2</sub>. 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

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

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<sub>4</sub>-Et<sub>2</sub>O complex in diethyl ether at  $-80^{\circ}$ 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 <sup>1</sup>H NMR spectra with the literature data.8 The one-electron reduction of 5, which has been previously reported, yields the hydride  $[Fe(C_5Me_5)(\eta^1-dppe)(CO)H]$  7 via the 19-electron species  $[Fe(C_5Me_5)(\eta^2-dppe)(CO)]$  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(1) intermediate 6 releases a phosphine ligand, the dppe is coordinated as an  $\eta^2$ chelating ligand in the iron(III) hydride 3. Moreover, an equilibrium between the 19-electron species 3 and a 17electron isomeric complex  $[Fe(C_5Me_5)(\eta^1-dppe)(CO)H]PF_6$ 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<sup>0</sup> 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.<sup>10</sup>

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