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Dicationic iron(II) complexes with dihydrogen *trans* to π-acid ligands: *trans*-$[Fe(\eta^2\text{-}H_2)(L)(dppe)_2]^{2+}$ (L = CO or CNH). Is there Fe–H_2 π-back bonding?†

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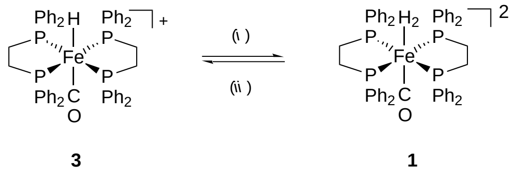
The new, electron-deficient iron(II) dihydrogen complexes *trans*-$[Fe(\eta^2\text{-}H_2)(L)(dppe)_2]^{2+}$ (L = CO or CNH) were surprisingly stable with respect to the loss of H_2 even though there is little Fe–H_2 π-back bonding.

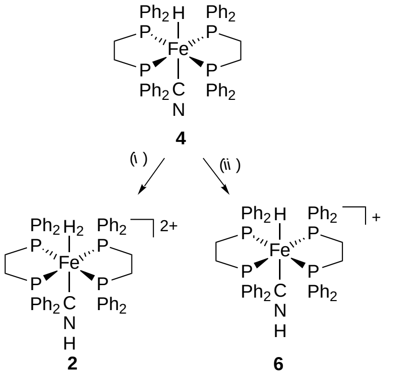
The factors that contribute to the stability of transition-metal dihydrogen complexes with respect to loss of H_2 are not yet well understood. For example counter ions of cationic η^2-H_2 complexes can often substitute for the H_2 ligand[1,2] but there is an exception where H_2 displaces a chloride ligand.[3] An overabundance of π-acid ancillary ligands such as CO is thought to destabilise the M–H_2 interaction by reducing $d\pi(M) \longrightarrow \sigma^*(H_2)$ back bonding.[4,5] A high N–N stretching frequency (greater than 2160 cm^{-1}) and a positive $M(d^5)/M(d^6)$ redox potential [greater than *ca.* 1 V *versus* normal hydrogen electrode (NHE)] of a dinitrogen complex *trans*-$[M(N_2)(CO)L_4]$ have been proposed as indicators of lack of π-back bonding and therefore instability of the corresponding dihydrogen complex, $[M(\eta^2\text{-}H_2)(CO)L_4]$.[5] The instability of dihydrogen complexes of strong main-group Lewis acids, such as CH_3^+ (ref. 6) and BBr_3,[7] support the idea that dπ electrons are needed for a stable bonding interaction. However the work of Heinekey and Luther[8] suggests that dihydrogen complexes are stabilised by a positive charge relative to neutral complexes even though this would reduce the dπ electron energy. In support of this view, we report here the observation of the exceptional complexes *trans*-$[Fe(\eta^2\text{-}H_2)(CO)(dppe)_2]^{2+}$ **1** and *trans*-$[Fe(\eta^2\text{-}H_2)(CNH)(dppe)_2]^{2+}$ **2**, which are stable to η^2-H_2 loss at 25 °C and yet have very little $d\pi(Fe) \longrightarrow \sigma^*(\eta^2\text{-}H_2)$ back bonding. Osmium forms more stable dihydrogen complexes than iron[1] and dicationic osmium dihydrogen complexes have been recently reported, including: *trans*-$[Os(\eta^2\text{-}H_2)(CO)(dppp)_2][BF_4][OTf]$,[9] *cis*-$[Os(\eta^2\text{-}H_2)(CO)(bipy)_2][OTf]_2$,[8] *trans*-$[Os(\eta^2\text{-}H_2)(NCMe)(dppe)_2][BF_4]_2$,[10] $[Os(\eta^2\text{-}H_2)(PPr^i_3)_2(NCMe)_3][BF_4]_2$[11] and *trans*-$[Os(\eta^2\text{-}H_2)(L)(en)_2]^{2+}$[12] and $[Os(\eta^2\text{-}H_2)(L)(NH_3)_4]^{2+}$[13] (L is not a strong π acceptor).

The complexes *trans*-$[Fe(\eta^2\text{-}H_2)(L)(dppe)_2]^{2+}$ (L = CO **1**,‡ CNH **2**§) are prepared as solutions in CH_2Cl_2 or CD_2Cl_2 by addition of an excess of HOTf to a solution of *trans*-$[Fe(H)(CO)(dppe)_2][BF_4]$ **3**¶ or *trans*-$[Fe(H)(CN)(dppe)_2]$ **4** (Schemes 1 and 2). The ^{31}P NMR spectra of complexes **1** and **2** show that they have a *trans* stereochemistry or that they are fluxional. The NH group in **2** is detected as a 1 : 1 : 1 triplet at δ 8.79 in the ^1H NMR spectrum. The ^1H NMR spectra of **1** and **2** exhibit a broad upfield resonance for η^2-H_2 at δ −6.8 and −9.08, respectively, with characteristically short spin–lattice relaxation times (T_1). The minimum T_1 values are 11.1 ms at 253 K and 300 MHz for **1**, and 21.5 ms at 262 K and 500 MHz for **2**. The H–H separations can be calculated from the T_1 (minimum) values to be 0.85 Å for **1** and 0.87 Å for **2** by use of an equation appropriate for high frequency (⩾500 MHz) 90° reorientations or spinning of the η^2-H_2 ligand that also takes into account dipolar contributions from the dppe ligands.[16] Longer distances calculated on the basis of restricted internal motion of η^2-H_2[16] are not consistent with distances calculated from *J*(HD) (see below). It has been suggested that the fast spinning regime is only appropriate in complexes with four identical ligands *cis* to H_2,[17] while more recently it has been reported that about half of the known dihydrogen compounds are best modelled as fast spinning and not all of them have four identical ligands *cis* to H_2.[18]

Another method for estimating the H–H separation in metal dihydrogen compounds involves measuring *J*(HD) for the analogous HD complexes. Addition of excess $[^2H_1]$triflic acid to complexes **3** or **4** produces the desired deuteriated complexes *trans*-$[Fe(\eta^2\text{-}HD)(CO)(dppe)_2]^{2+}$, **1-*d***‖ or *trans*-$[Fe(\eta^2\text{-}HD)$-



Scheme 1 (*i*) Excess HOTf, CH_2Cl_2; (*ii*) Et_2O, CH_2Cl_2



Scheme 2 (*i*) 2 HOTf or excess $[Et_2OH][BF_4]$; (*ii*) HOTf or $[PPh_3H]$-$[OTf]$

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† Abbreviations used: dppe = 1,2-bis(diphenylphosphino)ethane; OTf^- = triflate, $CF_3SO_3^-$; dppp = 1,2-bis(diphenylphosphino)propane; bipy = 2,2′-bipyridyl; en = ethane-1,2-diamine.

‡ Selected data for **1**. HOTf (35 mg, 0.2 mmol) was added to a yellow solution of *trans*-$[Fe(H)(CO)(dppe)_2][BF_4]$ **3** (20 mg, 0.02 mmol) in CH_2Cl_2 (0.6 cm^3) to give a yellow solution of **1** and a small amount of gas evolution (presumably H_2) and of an amorphous white precipitate. $\tilde{\nu}_{max}/cm^{-1}$ (CH_2Cl_2) 2006 (CO). δ_P(121 MHz, CD_2Cl_2) 67.4 (s). δ_H(300 MHz, CD_2Cl_2) −6.8 [br s, T_1/ms (minimum, 253 K, 300 MHz) 11.1, η^2-H_2].

§ Selected data for **2**. *trans*-$[Fe(H)(CN)(dppe)_2]$ **4**[15] (13 mg, 0.015 mmol) was dissolved in CH_2Cl_2 or CD_2Cl_2 (1 cm^3) and cold (0 °C) HOTf (15 mg, 0.1 mmol) was added. The initial orange colour of the solution faded to the yellow colour of **2** immediately and a small amount of H_2 (δ_H 4.6) was liberated. $\tilde{\nu}_{max}/cm^{-1}$ (CH_2Cl_2) 2059 (CN). δ_P(121 MHz, CD_2Cl_2) 70.4 (s). δ_H(500 MHz, CD_2Cl_2) −9.08 [br s, T_1/ms (minimum, 262 K, 500 MHz) 21.5, η^2-H_2], 8.79 [br 1 : 1 : 1 t, *J*(NH) 75 Hz, CNH].

¶ Selected data for **3**. *trans*-$[Fe(\eta^2\text{-}H_2)(H)(dppe)_2][BF_4]$ **5**[14] (950 mg, 1.0 mmol) was dissolved in CH_2Cl_2 (30 cm^3) and CO gas was bubbled through the solution for 2 h. Evaporation of the solvent and washing with diethyl ether gave the product as a yellow powder (> 90%). $\tilde{\nu}_{max}/cm^{-1}$ (CH_2Cl_2) 1947 (CO). δ_P(121 MHz, CD_2Cl_2) 84.8 (s). δ_H(300 MHz, CD_2Cl_2) −7.8 [qnt, *J*(PH) 47.1 Hz, FeH].

‖ Selected data for **1-*d***. Preparation was as for **1** with the exception that DOTf was used. δ_H(300 MHz, CD_2Cl_2) −6.8 [1 : 1 : 1 t qnt, *J*(HD) 33.1, *J*(PH) 3.3 Hz, FeHD].

Table 1 Properties of the isoelectronic dihydrogen carbonyl complexes *trans*-$[M(\eta^2\text{-}H_2)(CO)(dppe)_2]^{n+}$

M	*n*	δ_H/ppm	δ_P/ppm	$\tilde{\nu}$(CO)/cm^{-1}	*J*(HD)/Hz	T_1(minimum)/ms	*d*(HH)/Å	Ref.
Mo	0	−4.70[a]	b	1815[c]	34	20[d]	0.88[e]	23, 25
Mn	1	−7.23[f]	85.4[f]	1896[g]	32	b	0.89[e]	24
Fe	2	−6.8[f]	67.4[f]	2006[g]	33.1	11.1[h]	0.86[i]	This work

[a] In $[^2H_8]$toluene. [b] Not reported. [c] Nujol mull. [d] At 200 MHz, 203 K. [e] By solid-state NMR spectroscopy. [f] In CD_2Cl_2. [g] In CH_2Cl_2. [h] At 300 MHz, 253 K. [i] By solution NMR spectroscopy.

$(CND)(dppe)_2]^{2+}$ **2-*d*$_2$**.** These complexes have *J*(HD) coupling constants of 33.1 Hz for **1-*d*** and 32.5 Hz for **2-*d*$_2$**, the highest values yet reported for iron dihydrogen complexes. The H−H separation is calculated to be 0.87 Å for **1** and 0.88 Å for **2** from *J*(HD) by an empirical correlation.[19] These values are in good agreement with the values for fast rotation calculated from T_1(minimum), indicating that there is little barrier to H_2 rotation.

There is an increase in ν(CO) of 59 cm^{-1} on changing from hydride to dihydrogen ligands between *trans*-$[Fe(H)(CO)(dppe)_2][BF_4]$ **3** and *trans*-$[Fe(\eta^2\text{-}H_2)(CO)(dppe)_2][BF_4][OTF]$ **1**. There is an increase in ν(CN) of 7 cm^{-1} between *trans*-$[FeH(CNH)(dppe)_2][OTf]$ **6**†† and *trans*-$[Fe(\eta^2\text{-}H_2)(CNH)(dppe)_2][OTf]_2$ **2**. This is likely due to a combination of an electrostatic effect[20] and of the reduction in the π-back donation from the iron to the carbonyl or hydrogenisocyanide.

Complexes **1** and **2** are highly acidic but stable with respect to H_2 loss. The filtered solution of **1** is stable under vacuum at 20 °C until excess HOTf is evaporated; then the complex reverts back to complex **3**. A solution of complex **2** can be evaporated under vacuum to give a film, which when redissolved in CD_2Cl_2 still only contains **2** according to NMR spectroscopy.

Complex **1** in CD_2Cl_2 is deprotonated by dry Et_2O or tetrahydrofuran (thf) (the pK_a of protonated ether[21] is reported to be −2.4) to give **3** (Scheme 1). Complex **3** is not protonated by excess $[Et_2OH][BF_4]$ while complex **4** is protonated by an excess of $[Et_2OH][BF_4]$ to give **2** and other products (Scheme 2) and is therefore less acidic than **1**. Complex **4** is protonated by 1 equivalent of $[PPh_3H][OTf]$ (aqueous pK_a *ca.* 2) to give **6**, but a ten-fold excess of this acid does not produce **2**. This suggests that **2** has an aqueous pK_a below 0.

In a survey of neutral chromium dihydrogen complexes with η^2-H_2 *trans* to CO, it was noted that the unstable ones had corresponding dinitrogen complexes with redox potentials $E°(d^5/d^6)$ greater than 0.5 V *vs.* NHE.[5] For *trans*-$[Fe(N_2)(CO)(dppe)_2]^{2+}$ **7**, the dinitrogen complex corresponding to complex **1**, the redox potential is predicted from an empirical relation[5,22] to be 3 V. This is well above the proposed limiting value of 0.5 V for the stability of the η^2-H_2 complexes under consideration here. This indicates that there will be little π-back bonding in **1** or **7** and that the 0.5 V limit is not correct for dicationic species.

Complex **1** is the third member of the series of complexes *trans*-$[M(\eta^2\text{-}H_2)(CO)(dppe)_2]^{n+}$ (M = Mo,[23] $n = 0$; M = Mn,[24] $n = 1$) with a d^6 metal centre. Selected properties of these complexes are provided in Table 1. There is an increase in ν(CO) on going from Mo to Mn to Fe. This progression reflects the increase in Lewis acidity of the metal centres and supports σ donation from η^2-H_2 to the metal, rather than π-back bonding from the metal to σ*(H_2), as the mode of M−H_2 stabilisation. The molybdenum complex is unstable under vacuum[22] while the iron complex is stable.

In conclusion, stable dicationic η^2-H_2 iron(II) complexes can be prepared with *trans* π-acid ligands. The short H−H separations indicate that the H_2 molecule is not greatly activated by π donation into σ*(H_2) and that the M−H_2 σ interaction is strong. There is recent theoretical support for the idea that the dσ interaction increases as dπ electrons become unavailable for π bonding.[26] These complexes illustrate that a strong σ interaction with the metal is sufficient to allow for stable H_2 complexes and yet cause little elongation of the H_2 bond.

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** Selected data for **2-*d*$_2$**. Preparation was as for **2** with the exception that DOTf was used. δ_H(300 MHz, CD_2Cl_2) −9.03 [1 : 1 : 1 t m, *J*(HD) 32.5 Hz, FeHD].

†† Selected data for **6**. CH_2Cl_2 (1 cm^3) was added to a mixture of $[PPh_3H][OTf]$ (15 mg, 0.036 mmol) and *trans*-$[FeH(CN)(dppe)_2]$[15] (31 mg, 0.032 mmol). Evaporation of the solvent and washing with diethyl ether gave the product as a yellow powder (> 90%). $\tilde{\nu}_{max}$/cm^{-1} (Nujol) 2052 (CN), 1802 (FeH). δ_P(121 MHz, CD_2Cl_2) 87.4 (s). δ_H(300 MHz, CD_2Cl_2) 9.81 [br 1 : 1 : 1 t, *J*(NH) 80, CNH], −10.96 [qnt, *J*(PH) 45.6 Hz, FeH] (Found: C, 62.8; H, 5.13; N, 1.74. Calc. for $C_{54}H_{50}F_3FeNO_3P_4S$: C, 62.98; H, 4.89; N, 1.36%).