Phosphido Bridged Iron Carbonyl Hydrides: Synthesis and *X*-Ray Structure of $(\mu\text{-H})_2Fe_3(CO)_8(\mu\text{-PPh}_2)_2$

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Reaction of the carbonyl anion $Fe_4(CO)_{13}{}^{2-}$ with strong acid in the presence of diphenylphosphine affords the trinuclear phosphido bridged cluster $(\mu\text{-H})_2Fe_3(CO)_8(\mu\text{-PPh}_2)_2$ (**1**) which has been fully characterised by *X*-ray diffraction; ready intramolecular elimination of benzene from (**1**) at room temperature in the presence of CO yields the phosphinidene complex $Fe_3(CO)_9(\mu_3\text{-PPh})_2$ (**2**).

The chemistry of phosphido (PR_2) bridged bi- and polynuclear compounds has recently come under intense scrutiny.[1] This interest can be traced to the belief that the μ-PR_2 group, as a strongly bound yet flexible ligand, may help maintain the nuclearity of a polymetallic framework during catalytic or stoicheiometric transformations. Somewhat surprisingly in view of the importance of metal hydrides in catalysis, relatively few mixed hydrido–phosphido clusters have been characterised and their chemistry is, as yet, virtually unexplored.[2] In this communication we describe a facile route to the novel cluster $(\mu\text{-H})_2Fe_3(CO)_8(\mu\text{-PPh}_2)_2$ (**1**), a rare example of a bisphosphido bridged dihydride.[2c] The synthetic strategy, protonation of an anion and dihydrogen elimination in the presence of diphenylphosphine may have wider implications for the generation of hydrido bridged phosphides.

Protonation by excess of trifluoroacetic acid of a slurry of $[(Ph_3P)_2N]_2[Fe_4(CO)_{13}]$[3] (1.8 mmol) in THF (THF = tetrahydrofuran) at 273 K in the presence of Ph_2PH (5.4 mmol) rapidly gave a dark brown solution which turned dark green on warming to room temperature. Chromatography on Florisil [eluant heptane–toluene 50:50 (v/v)] afforded dark green (**1**) (60%) and a yellow complex identified as $(Ph_2PH)Fe(CO)_4$.[4] In the absence of CF_3CO_2H, the anion $Fe_4(CO)_{13}{}^{2-}$ does not react with Ph_2PH even in refluxing THF. These observations are consistent with the overall stoicheiometry given in equation (1).

$$(\mu\text{-H})_2Fe_3(CO)_8(\mu\text{-PPh}_2)_2$$

(1)

$$Fe_3(CO)_9(\mu_3\text{-PPh})_2$$

(2)

$$Fe_4(CO)_{13}{}^{2-} \xrightarrow{2H^+} H_2Fe_4(CO)_{13} \xrightarrow[273\text{ K THF}]{3Ph_2PH} (\mathbf{1}) + (Ph_2PH)Fe(CO)_4 + H_2 + CO \quad (1)$$

Spectroscopic data [i.r. ν(CO) C_7H_{16} 2059m, 2019s, 1983w, and 1970m cm^{-1}; ^1H n.m.r., 297 K (C_6D_6) δ −20.7 (t, 2H, $^2J_{P\text{-}H}$ 41.8 Hz); ^{31}P n.m.r. (^1H coupled) 297 K (C_6D_6) δ +203.2 p.p.m. (t)] suggested a symmetric structure for (**1**) with equivalent μ-H and μ-PPh_2 ligands. The molecular structure† (Figure 1) consists of a triangular core of iron atoms with two short Fe–Fe bonds [Fe(1)–Fe(2) 2.6670(8), Fe(2)–Fe(3) 2.6588(8) Å] each bridged by hydrido and phosphido groups. The third unbridged bond [Fe(1)–Fe(3) 2.8264(8) Å] is one of the longest yet reported.[2,5] The two phosphido (and hydrido) ligands are located above and below the trimetal plane such that the molecule possesses an approximate C_2 axis bisecting the angle C(4)–Fe(2)–C(5). Neglecting the Fe–Fe bonds the stereochemistry at the unique metal atom Fe(2) is thus pseudo-octahedral with two *trans* phosphorus atoms and the carbonyl groups C(4)–O(4) and C(5)–O(5) coplanar with the *cis* hydrides H(1) and H(2). This *trans* diaxial configuration of two μ-PPh_2 groups appears to be a recurring feature of $M_3(\mu\text{-PPh}_2)_2$ clusters.[2c,d,6]

Although (**1**) reacts readily with CO this reaction results in irreversible transformation of the phosphido bridges. When solutions of (**1**) are treated with CO gas (1 atm, 297 K) and the reaction monitored by ^{31}P n.m.r. spectroscopy, the resonance due to (**1**) is replaced by a singlet at δ +279.4 p.p.m. characteristic of $Fe_3(CO)_9(\mu\text{-PPh})_2$ (**2**). The identity of (**2**) was further confirmed by comparison of its i.r. spectrum with an authentic sample.[1c,7] Thus intramolecular reductive elimination of benzene from (**1**) affording the phosphinidene complex (**2**) is a remarkably ready process. Although aryl eliminations from phosphine or phosphido compounds are known[8] such reactions generally require high temperatures. These observations have obvious significance for the possible use of phosphido bridged clusters in catalytic reductions.

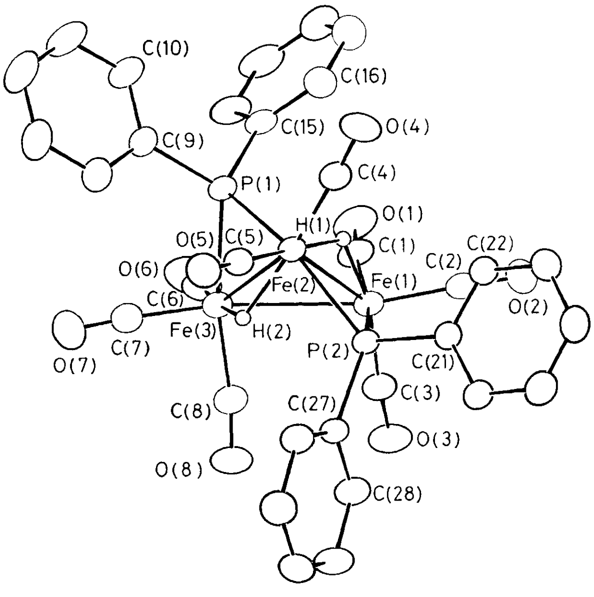

Figure 1. A perspective view of the molecular structure of $(\mu_2\text{-H})_2Fe_3(\mu_2\text{-PPh}_2)_2(CO)_8$ (**1**), showing the atomic numbering scheme. Important bond lengths and angles: Fe(1)–Fe(2) 2.6670(8), Fe(2)–Fe(3) 2.6588(8), Fe(1)–Fe(3) 2.8264(8), Fe(2)–P(1) 2.201(1), Fe(3)–P(1) 2.262(1), Fe(1)–P(2) 2.258(1), Fe(2)–P(2) 2.207(1), Fe(2)–H(1) 1.54(4), Fe(3)–H(2) 1.55(4), Fe(1)–H(1) 1.59(4), and Fe(2)–H(2) 1.69(4) Å; Fe(2)–P(1)–Fe(3) 73.1(1), Fe(2)–P(2)–Fe(1) 73.4(1), P(1)–Fe(2)–P(2) 143.6(1), P(1)–Fe(2)–H(2) 82(1), P(1)–Fe(2)–H(1) 79(1), P(2)–Fe(2)–H(2) 76(1), P(2)–Fe(2)–H(1) 78(1), C(4)–Fe(2)–C(5) 90.9(1), P(1)–Fe(2)–C(4) 98.5(1), P(2)–Fe(2)–C(4) 106.9(1), P(1)–Fe(2)–C(5) 103.7(1), and P(2)–Fe(2)–C(5) 101.5(1)°.

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† *Crystal data*: $C_{32}H_{22}Fe_3P_2O_8\cdot 0.5C_7H_8$; $M = 810.09$, triclinic, space group $P\bar{1}$, (cell constants at 295 ± 1 K), $a = 10.918(2)$, $b = 11.898(2)$, $c = 14.705(3)$ Å, $\alpha = 75.02(1)$, $\beta = 84.72(1)$, $\gamma = 70.84(1)°$, $U = 1743.0(5)$ Å^3, $Z = 2$, $D_m = 1.52$, $D_c = 1.543$ g cm^{-3}, $F(000) = 822$, $\mu(\text{Mo-}K_\alpha) = 14.07$ cm^{-1}. The structure was solved by Patterson and Fourier methods using 4243 observed reflections [$I \geq 3\sigma(I)$] from 6151 reflections measured ($2\theta \leq 50°$) on a Syntex $P2_1$ diffractometer. The structure was refined by full matrix least squares techniques to final agreement factors of $R = 0.034$, $R_w = 0.039$. All non-solvent hydrogen atoms were located and included in the final cycles of refinement. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.