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**Preliminary communication**

**Complexes of tertiary phosphines with iron(II) and dinitrogen, dihydrogen, and other small molecules**

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**Abstract**

The treatment of  $[\text{FeCl}_2(\text{diphosphine})_2]$  with sodium borohydride in ethanol produces the hydrides  $[\text{FeH}_3(\text{diphosphine})_2]^+$  in high yield. These complexes react with a variety of small molecules including  $\text{N}_2$  to give further complexes.  $\text{CO}_2$  and  $\text{CS}_2$  insert into the iron hydride bond to yield formato- and dithioformato-complexes, respectively, and carboxymethyl acetylene and phenyl acetylene yield a cyclic alkenyl complex and an acetylide, respectively.

Iron(II) trihydrides (or iron(II) dihydrogen monohydrides) have been reported for several tertiary phosphines. They are prepared by a variety of more or less complex methods [1–3]. We have discovered that they are accessible in high yield by the simple sodium borohydride reduction of the corresponding dichloro(tertiary phosphine) complex in alcohols, under Ar rather than  $\text{N}_2$  to avoid subsequent formation of a dinitrogen complex. In this fashion we have prepared  $[\text{FeH}_3(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]^+$ ,  $[\text{FeH}_3(\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2)_2]^+$ , and  $[\text{FeH}_3(\text{PMe}_2\text{Ph})_4]^+$ .

The spectral properties are consistent with those already reported, but the summary discussion presented here will be concerned only with reactions of  $[\text{FeH}_3(\text{dmpe})_2]^+$  ( $\text{dmpe} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ ),  $\nu(\text{FeH}) = 1856 \text{ cm}^{-1}$ , isolated for the first time as a characterised solid.

Exposure of  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2]^+$ , which has previously been observed by NMR spectroscopy in alcoholic solutions of the dihydride  $[\text{FeH}_2(\text{dmpe})_2]$  [4], to dinitrogen produced *trans*- $[\text{FeH}(\text{N}_2)(\text{dmpe})_2][\text{BPh}_4]$  ( $\nu(^{14}\text{N}_2) = 2094$ ,  $\nu(^{15}\text{N}_2) = 2024 \text{ cm}^{-1}$ ). The polyhydride abstracts dinitrogen from  $[\text{M}(\text{N}_2)_2(\text{dppe})_2]$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ) and even  $[\text{W}(\text{N}_2)_2(\text{depe})_2]$ . The reaction between  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  and X ( $\text{X} = \text{CO}$ ,  $\text{CNMe}$  or  $\text{C}_2\text{H}_4$ ) yields the corresponding products  $[\text{FeH}(\text{X})(\text{dmpe})_2][\text{BPh}_4]$ . Other small molecules displace the dihydrogen ligand, as detailed in Scheme 1.



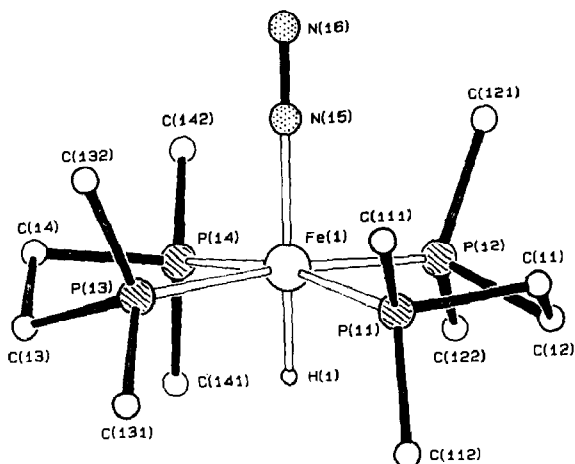


Fig. 1. One of the two independent (virtually identical) cations in crystals of  $[\text{FeH}(\text{N}_2)(\text{dmpe})_2][\text{BPh}_4]$ . Mean bond dimensions:  $\text{Fe}-\text{H} = 1.32(2)$ ,  $\text{Fe}-\text{N} = 1.818(11)$ ,  $\text{Fe}-\text{P} = 2.205(6)$ ,  $\text{N}-\text{N} = 1.13(3)$ ,  $\text{NFeP} = 94.4(6)$ ,  $\text{FeNN} = 178.3(9)^\circ$ .

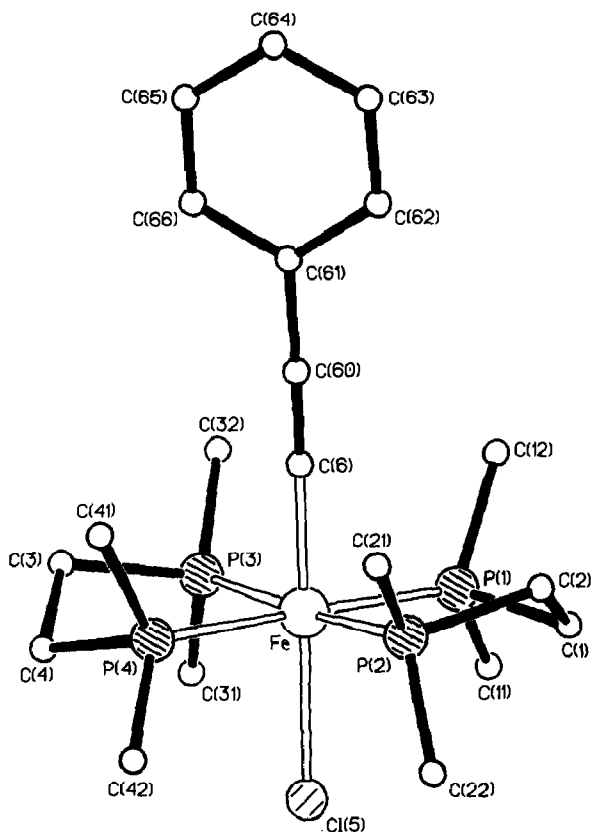


Fig. 2. Molecular structure of  $[\text{FeCl}(\text{C}\equiv\text{CPh})(\text{dmpe})_2]^+$ :  $\text{Fe}-\text{Cl} = 2.389(1)$ ,  $\text{Fe}-\text{C} = 1.897(3)$ , mean  $\text{Fe}-\text{P} = 2.218(2)$ ,  $\text{C}\equiv\text{C} = 1.192(3)$  Å, mean  $\text{CFeP} = 89.3(8)$ ,  $\text{FeCC} = 178.4(2)$ ,  $\text{CFeCl} = 179.1(1)^\circ$ .

affording a green complex which we formulate as a vinylidene derivative, *trans*-[Fe(=C=CHPh)(Cl)(dmpe)<sub>2</sub>]<sup>+</sup>, though it may be an adduct of phenyl acetylene.

However, HC≡CCOOMe reacts with [FeCl<sub>2</sub>(dmpe)<sub>2</sub>] and NaBH<sub>4</sub> in a different fashion. In this case, the alkenyl complex *cis*-[Fe(CH=CHCOOMe)(dmpe)<sub>2</sub>][BPh<sub>4</sub>] is obtained, as inferred from spectroscopic and analytical data. Its formation is explained in terms of insertion of the acetylene into the metal hydride bond of [FeH(H<sub>2</sub>)(dmpe)<sub>2</sub>]<sup>+</sup> generated in situ in the reaction mixture. All these reactions are summarised in Scheme 1.

Reactions with molecules relevant to nitrogen fixation, such as hydrazines and diazonium salts, have yielded complexes whose full characterisation is currently underway.

## References and notes

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- 5 <sup>1</sup>H(CD<sub>3</sub>COCD<sub>3</sub>): δ(Fe-H): -19.35 ppm, quintet, <sup>2</sup>J(PH) = 51 Hz. <sup>31</sup>P{<sup>1</sup>H} (acetone/CD<sub>3</sub>COCD<sub>3</sub>): -75.68 ppm, singlet. <sup>31</sup>P-proton coupled: -75.68 ppm, doublet, <sup>2</sup>J(PH) = 51 Hz. References: <sup>1</sup>H: SiMe<sub>4</sub>; <sup>31</sup>P: P(OMe)<sub>3</sub>.
- 6 Crystal data for [FeH(N<sub>2</sub>)(dmpe)<sub>2</sub>][BPh<sub>4</sub>]: C<sub>36</sub>H<sub>53</sub>BFeN<sub>2</sub>P<sub>4</sub>, *M* = 704.4. Triclinic, space group *P* $\bar{1}$  (no. 2), *a* 16.3464(9), *b* 16.315(2), *c* 17.617(1) Å, α 106.086(7)°, β 109.721(5)°, γ 106.136(7)°; *V* 3874.7(7) Å<sup>3</sup>; *Z* = 4; *D*<sub>c</sub> 1.207 g cm<sup>-3</sup>; *F*(000) 1496; μ(Mo-K<sub>α</sub>) 5.8 cm<sup>-1</sup>; λ(Mo-K<sub>α</sub>) 0.71069 Å. Diffractometer data; structure determination by heavy atom method; hydride ligands located and refined satisfactorily; full matrix least-squares refinement to *R* = 0.070, *R*<sub>g</sub> = 0.067 for 10082 reflections (all data with θ < 22.5), weighted *w* = σ<sub>F</sub><sup>-2</sup> [10].
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- 9 Crystal data for [FeCl(C≡CPh)(dmpe)<sub>2</sub>]: C<sub>20</sub>H<sub>37</sub>ClFeP<sub>4</sub>, *M* = 492.7. Monoclinic, space group *P*2<sub>1</sub>/*n* (equiv. to no. 14), *a* 30.731(2), *b* 8.861(1), *c* 9.059(1) Å, β 96.423(6)°; *V* 2451.5 Å<sup>3</sup>; *Z* = 4; *D*<sub>c</sub> 1.335 g cm<sup>-3</sup>; *F*(000) = 1040; μ(Mo-K<sub>α</sub>) = 9.9 cm<sup>-1</sup>. Analysis as in [6]. *R* = *R*<sub>g</sub> = 0.032 for 3172 reflections (i.e. those with θ < 23° and *I* > σ<sub>*I*</sub>), weighted *w* = σ<sub>F</sub><sup>-2</sup> [10].
- 10 G.M. Sheldrick, SHELX, Program for crystal structure determination, University of Cambridge, 1976, modified 1977.