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Preliminary communication

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

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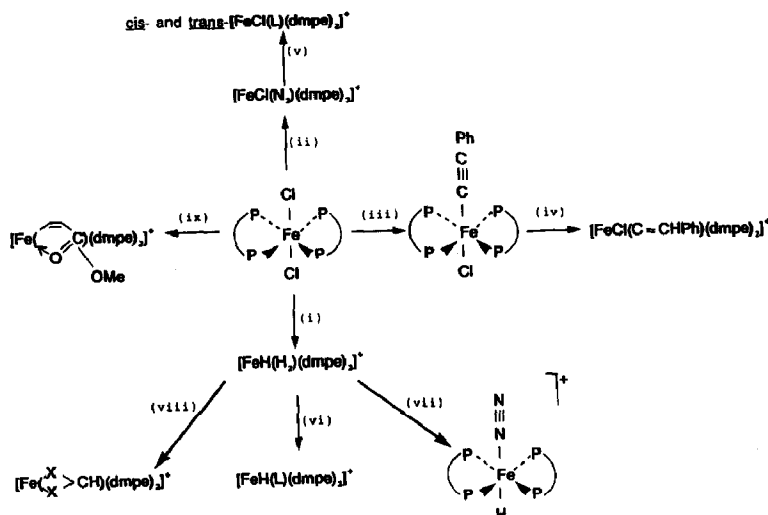
Abstract

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 N_2 to give further complexes. CO_2 and 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 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 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 ($\text{X} = \text{CO}$, CNMe or C_2H_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.



Scheme 1. Reactions of $[\text{FeCl}_2(\text{diphosphine})_2]$. Reagents: (i) EtOH, Ar, NaBH_4 ; (ii) EtOH, N_2 ; (iii) EtOH, NaBH_4 , $\text{PhC}\equiv\text{CH}$; (iv) EtOH, HCl ; (v) acetone, $\text{L} = \text{CO}$ or MeNC ; (vi) acetone, $\text{L} = \text{CO}$, MeNC or C_2H_4 ; (vii) acetone, N_2 ; (viii) THF, CX_2 ($\text{X} = \text{O}$ or S); (ix) EtOH, HCCCCOOMe , NaBH_4 .

The hydridodinitrogen complex $[\text{FeH}(\text{N}_2)(\text{dmpe})_2][\text{BPh}_4]$ ($\nu(\text{N}_2) = 2094$, $\nu(\text{FeH}) = 1841 \text{ cm}^{-1}$) was synthesised in high yield by reaction of $[\text{FeCl}_2(\text{dmpe})_2]$ with NaBH_4 in ethanol under dinitrogen, followed by addition of NaBPh_4 . A *trans* stereochemistry is suggested by the $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra [5*]. This has been confirmed by an X-ray structure determination [6*], which gave bond values (Fig. 1) within the normal ranges. This is only the second example of a crystal structure determination of a dinitrogen complex of iron [7].

Despite the high value of $\nu(\text{N}_2)$ in this complex and the normal values for Fe–N and N–N distances, the dinitrogen ligand is strongly bound and is displaced only slowly by CO or CNMe, affording mixtures of the dinitrogen complex and the corresponding $[\text{FeH}(\text{L})(\text{dmpe})_2][\text{BPh}_4]$ ($\text{L} = \text{CO}$ or CNMe).

The green, octahedral adduct *trans*- $[\text{FeCl}_2(\text{dmpe})_2]$ [8] dissolves in tetrahydrofuran to give a green non-conducting solution. However, in alcohols under dinitrogen it affords reddish solutions, from which the new dinitrogen complex $[\text{FeCl}(\text{N}_2)(\text{dmpe})_2]^+$ ($\nu(\text{N}_2) = 2105 \text{ cm}^{-1}$) was isolated as its $[\text{BPh}_4]^-$ salt. A sharp singlet in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum suggests a *trans* stereochemistry. The dinitrogen ligand is readily displaced from this complex by CO or CNMe, yielding mixtures of *cis*- and *trans*- $[\text{FeCl}(\text{X})(\text{dmpe})_2]^+$ ($\text{X} = \text{CO}$ or CNMe) which have been characterised by IR and NMR spectroscopy and analysis.

The reaction of $[\text{FeCl}_2(\text{dmpe})_2]$ with 1 mol equivalent of borohydride in the presence of phenylacetylene produced an acetylide complex, *trans*- $[\text{FeCl}(\text{C}\equiv\text{CPh})(\text{dmpe})_2]$ ($\nu(\text{C}\equiv\text{C}) = 2044 \text{ cm}^{-1}$) of structure determined by X-ray analysis (Fig. 2) [9*]. Presumably the borohydride abstracts the acidic proton in $\text{HC}\equiv\text{CPh}$ and the resulting acetylide anion gives a metathesis reaction with the iron complex. The acetylide ligand in $[\text{FeCl}(\text{C}\equiv\text{CPh})(\text{dmpe})_2]$ is readily and reversibly protonated,

* Reference number with asterisk indicates a note in the list of references.

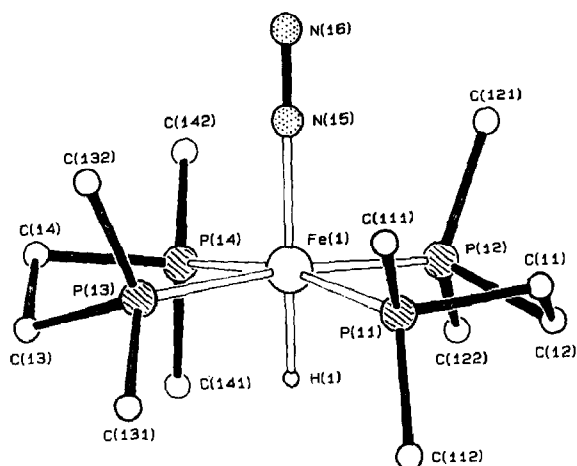


Fig. 1. One of the two independent (virtually identical) cations in crystals of $[\text{FeH}(\text{N}_2)(\text{dmpe})_2][\text{BPh}_4]$. Mean bond dimensions: $\text{Fe}-\text{H}=1.32(2)$, $\text{Fe}-\text{N}=1.818(11)$, $\text{Fe}-\text{P}=2.205(6)$, $\text{N}-\text{N}=1.13(3)$, $\text{NFeP}=94.4(6)$,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

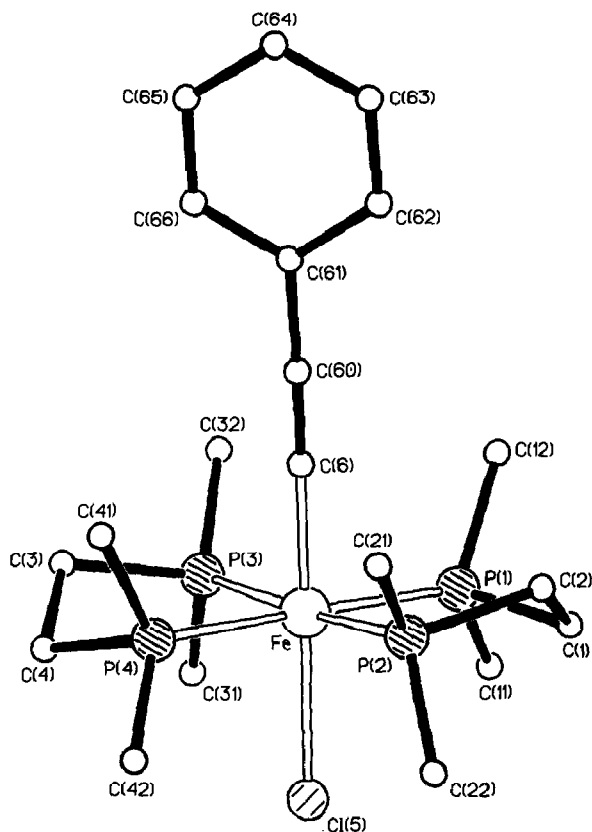


Fig. 2. Molecular structure of $[\text{FeCl}(\text{C}\equiv\text{CPh})(\text{dmpe})_2]$: $\text{Fe}-\text{Cl}=2.389(1)$, $\text{Fe}-\text{C}=1.897(3)$, mean $\text{Fe}-\text{P}=2.218(2)$, $\text{C}\equiv\text{C}=1.192(3)$ Å, mean $\text{CFeP}=89.3(8)$, $\text{FeCC}=178.4(2)$, $\text{CFeCl}=179.1(1)^\circ$.

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

However, HC≡CCOOMe reacts with [FeCl₂(dmpe)₂] and NaBH₄ in a different fashion. In this case, the alkenyl complex *cis*-[Fe(CH=CHCOOMe)(dmpe)₂][BPh₄] 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(H₂)(dmpe)₂]⁺ 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 ¹H(CD₃COCD₃): δ(Fe-H): -19.35 ppm, quintet, ²J(PH) = 51 Hz. ³¹P{¹H} (acetone/CD₃COCD₃): -75.68 ppm, singlet. ³¹P-proton coupled: -75.68 ppm, doublet, ²J(PH) = 51 Hz. References: ¹H: SiMe₄; ³¹P: P(OMe)₃.
- 6 Crystal data for [FeH(N₂)(dmpe)₂][BPh₄]: C₃₆H₅₃BFeN₂P₄, *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) Å³; *Z* = 4; *D*_c 1.207 g cm⁻³; *F*(000) 1496; μ(Mo-*K*_α) 5.8 cm⁻¹; λ(Mo-*K*_α) 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*_g = 0.067 for 10082 reflections (all data with θ < 22.5), weighted *w* = σ_F⁻² [10].
- 7 G.A. Ghillardi, S. Midollini, L. Sacconi and P. Stoppioni, *J. Organomet. Chem.*, 205 (1981) 193.
- 8 G.S. Girolami, G. Wilkinson, A.M.R. Galas, M. Thornton-Pett and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1985) 1339.
- 9 Crystal data for [FeCl(C≡CPh)(dmpe)₂]: C₂₀H₃₇ClFeP₄, *M* = 492.7. Monoclinic, space group *P*2₁/*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 Å³; *Z* = 4; *D*_c 1.335 g cm⁻³; *F*(000) = 1040; μ(Mo-*K*_α) = 9.9 cm⁻¹. Analysis as in [6]. *R* = *R*_g = 0.032 for 3172 reflections (i.e. those with θ < 23° and *I* > σ_I), weighted *w* = σ_F⁻² [10].
- 10 G.M. Sheldrick, SHELX, Program for crystal structure determination, University of Cambridge, 1976, modified 1977.