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Ancillary ligand control of reactivity. Protonation at hydride *vs.* cyanide in *trans*-$[FeH(CN)(R_2PCH_2CH_2PR_2)_2]$ (R = Et, Ph, *p*-tolyl) and X-ray crystal structure determination of *trans*-$[FeH(CNH)(R_2PCH_2CH_2PR_2)_2]BF_4$ (R = *p*-tolyl)

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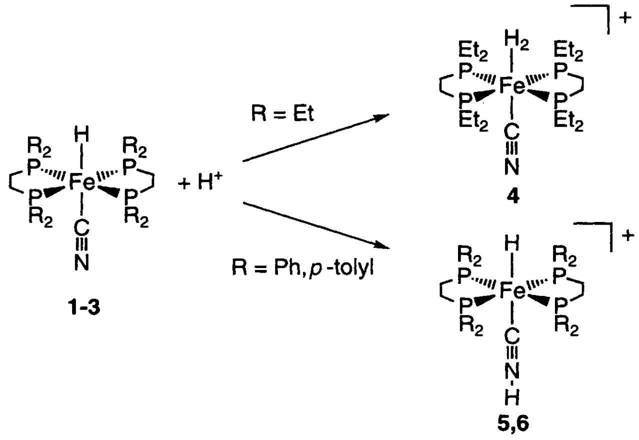
The ancillary ligands in *trans*-$[FeH(CN)L_2]$ control whether protonation occurs at hydride to produce a dihydrogen complex or at cyanide to produce a hydrogen isocyanide complex.

In a situation where more than one product is possible in a reaction involving a transition-metal complex, judicious selection of the ancillary ligands and reaction conditions can direct the reaction pathway toward the desired product. Just such a system is observed in the protonation of *trans*-$[FeH(CN)L_2]$ [L = depe (**1**), dppe (**2**), dtpe (**3**)].† The products of the protonation of **1–3** indicate that H^+ adds to the Fe–H bond in **1** while it adds to the cyanide nitrogen in **2** and **3** (Scheme 1). The potential for protonation to occur at cyanide *vs.* hydride at an iron centre may exist in [NiFe]-hydrogenases where cyanide coordination on iron at the active site has been proposed.[1,2] Tautomeric dihydrogen systems have been reported for $[Os(H_2)(\eta^2\text{-}S_2CH)(CO)(PPr^i_3)_2]BF_4$[3] and $[Os(H_2)(\eta^2\text{-quinS})(CO)(PPh_3)_2]BF_4$.[4]

Metathesis of chloride in *trans*-$[FeH(Cl)L_2]$ (L = depe,[5] dppe,[6] dtpe[7]) for cyanide produces the complexes *trans*-$[FeH(CN)L_2]$ [L = depe (**1**), dppe (**2**), dtpe (**3**)‡]. The hydridocyanide complexes **1–3** are characterized by ^1H and ^{31}P NMR spectra and FABMS. The FABMS of **1** gives evidence that **1** is protonated to give **4** in the gas phase.

Protonation of *trans*-$[FeH(CN)(depe)_2]$ **1** with 85% $[Et_2OH]BF_4$ in Et_2O under H_2 (1 atm) produces a yellow precipitate. The CD_2Cl_2 solution of this solid contains the dihydrogen compound *trans*-$[Fe(H_2)(CN)(depe)_2]BF_4$ **4**.§ This complex slowly decomposes to other species. In the ^1H NMR spectrum of this complex in CD_2Cl_2 a broad resonance is observed to high field (δ −14.05) due to the dihydrogen ligand. Measurement of the minimum spin–lattice relaxation time, T_1 = 15.2 ms (400 MHz, 229 K), allows the H–H separation to be calculated[8] at 0.85 or 1.07 Å for a fast or slow spinning dihydrogen ligand, respectively.



Scheme 1

The one-bond H–D coupling constant of 31.6 Hz was measured from the spectrum of the complex *trans*-$[Fe(HD)(CN)(depe)_2]BF_4$, **4′**, prepared by reacting **1** with $[Ph_3PD]BF_4$ in CD_2Cl_2. The coupling between the hydrogen and the four equivalent phosphorus nuclei is also observable in this system and a 1 : 1 : 1 triplet of quintets is observed, $^2J_{PH}$ = 5.8 Hz. By using an empirical correlation[9] between $^1J_{HD}$ and d_{HH} a separation of 0.89 Å is calculated. This is consistent with the result of the T_1 determination if the rotational frequency of the dihydrogen ligand is much greater than the spectrometer frequency (400 MHz). Complex **4** represents the first iron dihydrogen complex of the form *trans*-$[Fe(H_2)XL_2]^+$ to be prepared where X is not hydride.[10,11] The related complex *trans*-$[Ru(H_2)(CCPh)(dippe)_2]^+$ has been reported.[12]

Addition of 1 equiv. of 85% $[Et_2OH]BF_4$ to *trans*-$[FeH(CN)(dppe)_2]$ **2** or *trans*-$[FeH(CN)(dtpe)_2]$ **3** in Et_2O under H_2 (1 atm) results in yellow precipitates which in CD_2Cl_2 solution contain the coordinated hydrogen isocyanide complexes *trans*-$[FeH(CNH)(dppe)_2]BF_4$ **5**,¶ or *trans*-$[FeH(CNH)(dtpe)_2]BF_4$ **6**,‖ respectively. A quintet resonance is observed to high field for the hydride ligands in the ^1H NMR spectrum of each compound. A broad doublet resonance with $^2J_{HC}$ = 98 Hz for the hydrogen isocyanide ligand is observed in the proton-coupled ^{13}C NMR spectrum of *trans*-$[FeH(^{13}CNH)(dppe)_2]BF_4$ **5′**. The magnitude of $^2J_{HC}$ confirms the assignment of the ligand as CNH as a much larger one-bond coupling would be anticipated for an NCH ligand.[13]

In order to unequivocally determine the coordination mode of the hydrogen isocyanide ligand a single-crystal X-ray diffraction study of **6** was performed.** The coordination sphere about the iron (Fig. 1) is occupied by a square plane of P atoms and a C atom from the CNH ligand *trans* to the hydride ligand which was located and refined with an isotropic thermal parameter. The molecule has twofold crystallographic symmetry. The BF_4^- appears to be positioned in order to hydrogen bond with the NH, but the hydrogen was not located due to disorder. The F···N separation of 2.9 Å is less than the sum of the van der Waals radii of 3.1 Å. The coordination mode was determined to be Fe–CNH based on an analysis of the thermal ellipsoids and comparison with the other known hydrogen isocyanide structures. A search of the Cambridge Structural Database[14] revealed that the M–C separations in hydrogen isocyanide complexes[15,16] are ≤2.0 Å while the M–N separations in hydrogen cyanide[17–21] (formonitrile) complexes are >2.3 Å. The Fe–C separation in **6** is 1.842(6) Å and the HFeCN unit is linear as required by symmetry.

The change in the site of protonation in these complexes can be explained by considering the differences in acidities between the hydrogen isocyanide complex **5** and the hypothetical complex *trans*-$[FeH(CNH)(depe)_2]^+$ **7** (ΔpK_a^{CNH}), and between the dihydrogen complex **4** and the hypothetical complex *trans*-$[Fe(H_2)(CN)(dppe)_2]^+$ **8** (ΔpK_a^{H2}). The change in the

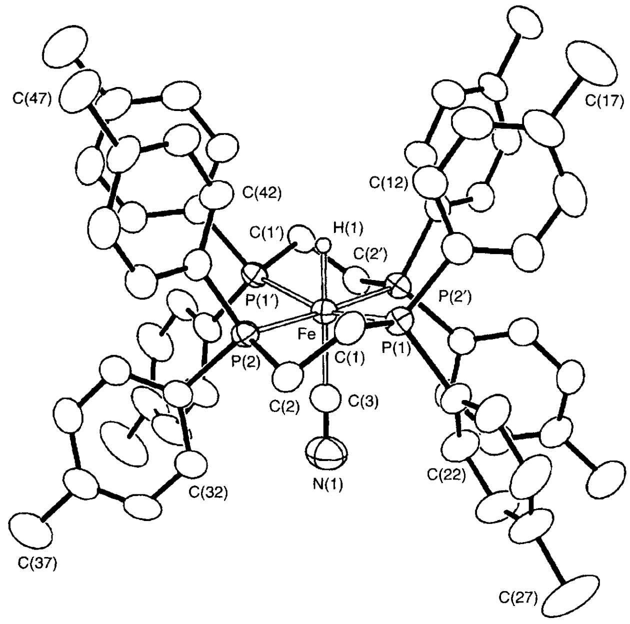


Fig. 1 ORTEP diagram of the cation of **6**. Thermal ellipsoids represent the 50% probability surface. Selected bond lengths (Å) and angles (°): Fe–H(1) 1.39(6), Fe–C(3) 1.842(6), C(3)–N(1) 1.183(8), Fe–P(1) 2.2557(10), Fe–P(2) 2.335(9), H(1)–Fe–C(3) 180.0, Fe–C(3)–N(1) 180.0.

acidity of the dihydrogen ligand by changing ancillary ligands from depe to dppe is predicted to be 7 pK_a units [ΔpK_a^{H2} = pK_a^{H2}(**4**) − pK_a^{H2}(**8**)].†† The effect is large because the acidic proton in **4** or **8** is located three bonds away from the site where the change of substituent on phosphine occurs.[22] The change in acidities of the hydrogen isocyanide ligands in **5** or **7** is expected to be much smaller because the acidic proton is five bonds removed from the substituent change. The change of ancillary ligand from depe to dppe lowers the pK_a of the hypothetical dihydrogen compound **8** below that of the hydrogen isocyanide complex **5**.

In conclusion the site of protonation of *trans*-[FeH(CN)L_2] can be directed to hydride (producing a dihydrogen ligand) or to cyanide (producing a hydrogen isocyanide ligand) by controlling the nature of the ancillary ligands.

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Footnotes

† Abbreviations used: quinS = 8-quinolinethiolate, depe = 1,2-bis(diethylphosphino)ethane, dppe = 1,2-bis(diphenylphosphino)ethane, dtpe = 1,2-bis(di-*p*-tolylphosphino)ethane, dippe = 1,2-bis(diisopropylphosphino)ethane.

‡ The characterisation of these complexes will be reported elsewhere.

§ *trans*-[Fe(H_2)(CN)(depe)$_2$]BF_4 **4**. Addition of 1 equiv. of acid {85% [Et_2OH]BF_4 in Et_2O or [Ph_3PH]BF_4 in CD_2Cl_2} to **1** produced **4** as revealed by NMR. ^1H NMR (CD_2Cl_2): δ −14.05 [br s, FeH_2, T_1 (min, 400 MHz) 15.2 ms]. *trans*-[Fe(HD)(CN)(depe)$_2$]BF_4 **4′**. 1 equiv. of [Ph_3PD]BF_4 was added to **1** in CD_2Cl_2. ^1H NMR (CD_2Cl_2): δ −14.08 (1 : 1 : 1 t of qnt, FeHD, $^1J_{DH}$ 31.6 Hz, $^2J_{PH}$ 5.8 Hz). *trans*-[Fe(H_2)(^{13}CN)(depe)$_2$]BF_4 **4″**. Preparation is as above for **4** except [FeH(^{13}CN)(depe)$_2$] was employed. $^{31}P\{^1H\}$-NMR (CD_2Cl_2): δ 77.7 (d, $^2J_{CP}$ 17 Hz). ^{13}C NMR (CD_2Cl_2): δ 145.6 (m, FeCN.

¶ *trans*-[FeH(CNH)(dppe)$_2$]BF_4 **5**. Protonation of **2** (100 mg, 0.11 mmol) in Et_2O (8 ml) under H_2 with 1.1 equiv. of 85% [Et_2OH]BF_4 (20 μl, 0.12 mmol) in diethyl ether produced **5**. ^1H NMR (CD_2Cl_2): δ −10.7 (qnt, FeH, $^2J_{PH}$ 49 Hz). FABMS *m/z* 880 (calc. 880). *trans*-[FeH(CNH)(dppe)$_2$]BF_4 **5′**. Preparation is as for **5** except [FeH(^{13}CN)(dppe)$_2$] was used. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 88.0 (d, $^2J_{CP}$ 16 Hz). ^{13}C NMR (CD_2Cl_2): δ 179.4 (br d, $^2J_{HC}$ 98 Hz, CNH).

‖ *trans*-[FeH(CNH)(dtpe)$_2$]BF_4 **6**. Protonation of **3** with 1 equiv. of 85% [Et_2OH]BF_4 in Et_2O under H_2 produced **6**. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 86.5 (s). ^1H NMR (CD_2Cl_2): δ −10.78 (qnt, FeH, $^2J_{PH}$ 47 Hz). FABMS *m/z* 992 (calc. 992).

** Complex **6** crystallises in the orthorhombic space group *Pbcn* with unit-cell parameters a = 25.700(4), b = 12.453(2), c = 19.151(3) Å, Z = 4. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/134.

†† It is assumed that the complexes *trans*-[Fe(H_2)(CN)L_2]$^+$ require the same energy of hydrogen abstraction to produce *trans*- [FeH(CN)L_2]$^+$ and H·.[23] The difference in reduction potential of *trans*-[FeH(CN)L_2]$^+$ for L = depe *vs.* dppe is expected to be $\Delta E_{1/2} = -0.4$ V.[23,24] Therefore $\Delta pK_a = -16.9\ \Delta E_{1/2} = 7$.[23]

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