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Syntheses and properties of isocyanide complexes of iron, *trans*-$[FeH(CNR)(Ph_2PCH_2CH_2PPh_2)_2][A]$ ($A = BF_4$ or PF_6)

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Abstract

The complexes *trans*-$[FeH(CNR)(dppe)_2][A]$ (R = Me, Et, ${}^tBu$, C_6H_4OMe-4, C_6H_4Me-4, C_6H_5, or $C_6H_4NO_2$-4; $A = PF_6$ or BF_4; dppe = $Ph_2PCH_2CH_2PPh_2$) have been prepared either by treatment of a tetrahydrofuran solution of *trans*-$[FeHCl(dppe)_2]$ under argon with the appropriate isocyanide, in the presence of Tl[A], or upon N_2 replacement in *trans*-$[FeH(N_2)(dppe)_2][A]$ by CNR. The dinitrogen complexes were obtained by reaction of *trans*-$[FeHCl(dppe)_2]$ in THF with Tl[A] under N_2.

Introduction

The dinitrogen-binding ability of some iron(II) and iron(0) phosphine-ligated centres has been known since the seventies, particularly in complexes of the types $[FeH_2(N_2)(PR_3)_3]$(R = alkyl or aryl) [1], $[FeH(N_2)L_2][BPh_4]$ [L = dppe ($Ph_2PCH_2CH_2PPh_2$) or depe ($Et_2PCH_2CH_2PEt_2$)] [2], $[FeH(N_2)L][BF_4]$ [L = $P(CH_2CH_2PPh_2)_3$ or $N(CH_2CH_2PPh_2)_3$] [2] and $[Fe(N_2)(dppe)_2]$ [3]. More recently, dinitrogen complexes with chelating N,O-containing ligands have also been reported [4], $Na_2[Fe(Y)N_2]$ [Y = (1,2-ethanediyldinitrilo)tetraacetate or *trans*-(1,2-cyclohexanediyldinitrilo)tetraacetate].

However, the N_2 ligand usually does not exhibit appreciable chemical reactivity, except in $[Fe(N_2)(Me_2PCH_2CH_2PMe_2)_2]$, as recently reported [5a], and in some less well-defined, dinuclear systems [5b]. Moreover, the suggestion that Mo is the active metal in the iron-molybdenum cofactor of nitrogenase has gained indirect support [6], and the coordination chemistry of N_2 at iron centres has not been explored.

Nevertheless, an alternative nitrogenase has been discovered containing V instead of Mo [7a] and, more recently, a further nitrogenase, without Mo or V, and with Fe only, has also been recognized [7b]. This has revived interest in the field of chemical nitrogen fixation, and extensive synthetic, Mössbauer [8], X-ray structural [9] and chemical [5a] studies of various diphosphine complexes of iron(II) have

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been described. Here we report our investigation of the binding and activation of alternative substrates of nitrogenase at iron centres which can ligate N_2.

We have previously prepared series of isocyanide complexes with d^6 N_2-binding sites, for example *trans*-[M(CNR)$_2$(dppe)$_2$](M = Mo or W) [10a], [M(CNR)$_x$L$_{6-x}$](x = 2–4, L = PMe$_2$Ph or PMePh$_2$) [10b] and *trans*-[ReCl(CNR)(dppe)$_2$] [11], and studied their reactivity towards protic attack to give aminocarbyne compounds, such as *trans*-[M(CNHMe)(CNMe)(dppe)$_2$]$^+$ [12] and *trans*-[ReCl(CNHR)(dppe)$_2$]$^+$ [13], Now we report the extension of this work to the Fe^{II} site, *trans*-{FeH(dppe)$_2$}$^+$, which also [2] ligates N_2, and we compare the electronic properties and chemical behaviour of the derived isocyanide complexes with those exhibited by the afore-mentioned Group VI or VII transition-metal species.

Results and discussion

Syntheses

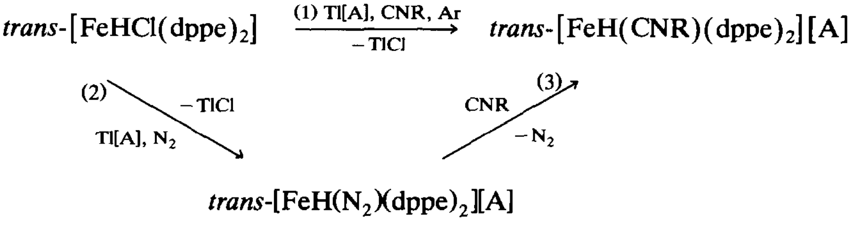
Treatment of a tetrahydrofuran (THF) solution of *trans*-[FeHCl(dppe)$_2$] under argon with the appropriate isocyanide (in a molar ratio of 3 : 1), in the presence of Tl[A] (A = PF$_6$ or BF$_4$) in a slight excess, gives the isocyanide complexes *trans*-[FeH(CNR)(dppe)$_2$][A] (**1**; R = Me, Et, ^{t}Bu, C_6H_4OMe-4, C_6H_4Me-4, C_6H_5, or $C_6H_4NO_2$-4; A = PF$_6$ or BF$_4$) (reaction 1, Scheme 1).

If the reaction with Tl[A] is carried out under dinitrogen in the absence of isocyanide the dinitrogen complex *trans*-[FeH(N$_2$)(dppe)$_2$][A] (**2**, A = BF$_4$ or PF$_6$) is obtained (reaction 2, Scheme 1).

These reactions may be compared to the synthesis of *trans*-[Re(CNR)$_2$(dppe)$_2$][BF$_4$] [14] upon N_2- and chloride-replacement in the presence of Tl[BF$_4$] in *trans*-[ReCl(N$_2$)(dppe)$_2$].

The isocyanide complexes **1** can also be prepared by treatment of a THF solution of the dinitrogen compound **2** with the appropriate isocyanide (reaction 3, Scheme 1).

Reactions 1 and 2 conceivably occur via the known 5-coordinate blue species [FeH(dppe)$_2$]$^+$, which is the product obtained from this reaction in benzene in the absence of a substrate and which in THF forms the red hexa-coordinate [FeH(THF)(dppe)$_2$]$^+$ with a labile THF ligand [15a]. These reactions are closely related to those reported for the syntheses of *trans*-[FeH(L)(dppe)$_2$]Y (L = CO, N_2, NCMe, NCPh, NH_3, pyridine, THF, or Me$_2$CO; Y = BPh$_4$ or ClO$_4$) by treatment of [FeHCl(dppe)$_2$] with Na, Y, and L [15b], and for the preparation [16] of the related complexes *trans*-[FeH(L)(depe)$_2$][BPh$_4$] [L = CO, N_2, CN^{t}Bu,



Scheme 1. Syntheses of the isocyanide complexes *trans*-[FeH(CNR)(dppe)$_2$][A] (**1**; R = alkyl or aryl; A = PF$_6$ or BF$_4$)

Table 1

Physical data for complexes *trans*-[FeHL(dppe)$_2$][A] [L = CNR (1) or N$_2$]

L, A	Colour	Infrared (cm^{-1}) [a] ν(C≡N)	Analysis [Found (calcd.) (%)]		
			C	H	N
CNMe, PF$_6$ [b]	Yellow	2140	59.8 (60.5)	5.0 (4.9)	1.5 (1.3)
CNMe, BF$_4$ [b]	Yellow	2140	63.0 (63.9)	5.0 (5.2)	1.3 (1.4)
CNEt, PF$_6$	Yellow	2140	62.2 (62.7)	5.2 (5.2)	1.3 (1.3)
CN^{t}Bu, PF$_6$ [c]	Yellow	2100	61.7 (62.2)	5.0 (5.3)	1.2 (1.3)
CNC$_6$H$_4$OMe-4, PF$_6$ [d]	Brownish orange	2070	57.5 (57.2)	5.0 (4.6)	1.6 (1.1)
CNC$_6$H$_4$OMe-4, BF$_4$ [d]	Brownish orange	2070	59.4 (59.9)	5.2 (4.9)	1.2 (1.1)
CNC$_6$H$_4$Me-4, PF$_6$	Yellow	2030	64.9 (64.6)	5.2 (5.1)	1.1 (1.3)
CNC$_6$H$_5$, PF$_6$	Yellow	2040	63.8 (64.3)	5.4 (4.9)	1.1 (1.3)
CNC$_6$H$_4$NO$_2$-4, PF$_6$ [b]	Red	2010	59.8 (60.1)	4.9 (4.5)	2.5 (2.4)
N$_2$, BF$_4$ [b]	Yellow	[e]	62.1 (62.4)	5.4 (4.9)	2.5 (2.8)

[a] In KBr pellets; strong ν(CN) bands. [b] With 0.5 CH$_2$Cl$_2$ of crystallisation. [c] With H$_2$O of crystallisation. [d] With 2CH$_2$Cl$_2$ of crystallisation. [e] ν(N≡N) = 2130 cm^{-1} (strong band).

CNC$_6$H$_4$OMe-4, NCMe, NCPh, P(OMe)$_3$, or P(OPh)$_3$; depe = Et$_2$PCH$_2$CH$_2$PEt$_2$] from reaction of [FeHCl(depe)$_2$] with L in the presence of NaBPh$_4$.

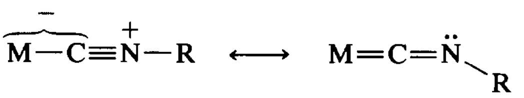
Properties

Complexes **1** are isolated as red (R = C$_6$H$_4$NO$_2$-4), orange (R = C$_6$H$_4$OMe-4) or yellow (in all the other cases) solids which are stable in air at room temperature for considerable periods.

Their IR spectra (Table 1) exhibit strong bands in the 2140–2020 cm^{-1} region assigned to ν(CN), whereas the strong bands at 835 or ca. 1050 cm^{-1} are due to the [PF$_6$]$^-$ and [BF$_4$]$^-$ counter-ion, respectively; for (**1**, R = C$_6$H$_4$NO$_2$-4), the medium intensity bands at 1582 and 1510 cm^{-1} are due to the NO$_2$ substituent. Weak and broad bands at ca. 1840 or 1825 cm^{-1} are observed for (**1**, R = Me and Et, respectively) and they are tentatively assigned to ν(FeH) by analogy with *trans*-[FeHCl(dppe)$_2$] which exhibits this stretching mode as a weak band at 1955 cm^{-1}. However, no band which could be attributed to ν(FeH) has been detected for the other complexes **1**; such an absence also occurs for related dinitrogen or isocyanide complexes of Fe^{II} with depe [16] or hexaphenyl-1,4,7,10-tetraphosphadecane [17].

Although ν(CN) occurs in complexes **1** at a wavenumber which is slightly lower than that exhibited by the corresponding free isocyanide (*e.g.*, 2140 *vs.* 2150 cm^{-1} for ligating or free CNMe, respectively), thus suggesting considerable π-electron donor ability of the Fe^{II} centre, the ν(CN) lowering upon coordination of the isocyanide at this centre is much less than those reported for the d^6 Mo, W or Re centres, namely *trans*-[Mo(CNMe)$_2$(dppe)$_2$] where ν(CN) = 1862 cm^{-1} and the isocyanide is known to present a bent geometry at the N atom [10]. This IR behaviour parallels that observed for N$_2$ at those centres where, for example, ν(N$_2$) = 1970 cm^{-1} for *trans*-[Mo(N$_2$)$_2$(dppe)$_2$], whereas, at *trans*-[FeH(N$_2$)(dppe)$_2$]$^+$, it occurs at a much higher frequency, 2130 cm^{-1}.

Therefore, the electronic structure of the ligating isocyanide at iron(II) should be represented intermediate between the two following forms, but closer to the first, whereas at molybdenum the structure is closer to the second.



$$\mathrm{\overset{-}{M{-}C}{\equiv}\overset{+}{N}{-}R} \longleftrightarrow \mathrm{M{=}C{=}\ddot{N}{-}R}$$

These results are consistent with the expected lower electronrichness of the Fe^{II} compared to the Mo^0 or Re^I centre, the first having weaker π-electron release and stronger σ-acceptor character. A similar rationale explains the lower ν(CN) or ν(N$_2$) frequencies (by *ca.* 40–50 cm^{-1}) exhibited by *trans*-[FeHL(depe)$_2$]$^+$ (L=CN^{t}Bu, CNC$_6$H$_4$OMe-4 or N$_2$) [16] compared with the dppe complexes **1** of our study. In compounds **1**, the aryl isocyanide complexes display ν(CN) frequencies lower than those of the alkyl isocyanide complexes, consistent with the expected stronger π-acceptor character of the former.

In the ^{1}H NMR spectra of complexes **1** [(CD$_3$)$_2$CO, 298 K] (Table 2), the hydride resonance occurs as a quintet (^2J(PH) = 46.4–46.9 Hz, at δ −8.6 to −11.5 ppm) due to coupling to the 4 equivalent P nuclei, whereas in the ^{31}P{^{1}H} NMR spectra's a is observed singlet at δ −48.0 to −51.9 ppm rel. P(OMe)$_3$, indicating a *trans* geometry of those compounds. Moreover, in the ^{31}P–^{1}H-undecoupled spectrum, a broad doublet is observed with the expected coupling constant, in agreement with the ^{31}P coupling to the hydride ^{1}H.

In comparison with [FeHCl(dppe)$_2$] (δ(Fe*H*) −26.8 ppm, ^2J(PH) = 49.1 Hz), a substantial shift to lower field is observed in the ^{1}H NMR spectra for the hydride resonances of **1**, in which isocyanide is a weaker net-electron donor.

In the ^{1}H NMR spectrum of **1** (R = C$_6$H$_4$NO$_2$-4), the phenyl proton resonances of the isocyanide give rise to two AB doublets (^3J(HH) = 9.1 Hz) at δ 8.16 and 6.79 ppm; the lower field pair can be assigned to the phenyl ring protons in *ortho*-positions relative to the nitro group, by analogy with the spectrum quoted [18] for [Co(CNC$_6$H$_4$NO$_4$-4)$_2${PPh(OEt)$_2$}$_3$][ClO$_4$]. For **1** (R = C$_6$H$_4$OMe-4 or C$_6$H$_4$Me-4), the lower field half of the AB-type resonance of the isocyanide phenyl ring protons is buried under the dppe-phenyl complex multiplets.

We have also examined the reactivity of complexes **1** towards electrophiles and nucleophiles, but no reaction was detected either with mineral acids or with alcohols (MeOH or EtOH) or amines (such as MeNH$_2$) (in a ten- to twenty-fold molar excess).

Final comments

This work has extended to an Fe^{II} hydride the syntheses of isocyanide complexes at a centre capable of binding dinitrogen.

However, in comparison with the electron-rich Re^I, Mo^0 or W^0 centres, the {FeH(dppe)$_2$}$^+$ site has a much lower π-electron releasing ability and the iso-

Table 2

Selected ^{1}H and ^{31}P{^{1}H} NMR data [a] for complexes *trans*-[FeH(CNR)(dppe)$_2$][A] (**1**, A = PF_6 or BF_4)

R	^{1}H NMR [b]			^{31}P{^{1}H} NMR δ [c]
	δ [b]	Relative intensity	Assignment	
Me	3.20 s	3	$\mathrm{CNC}H_3$	−48.04 s [e]
	−11.03 qt [d]	1	$\mathrm{Fe}H$	
Et	3.58 q [f]	2	$\mathrm{C}H_2\mathrm{CH}_3$	−48.53 s
	1.03 t [f]	3	$\mathrm{CH_2C}H_3$	
	−11.03 qt [d]	1	$\mathrm{Fe}H$	
^{t}Bu	1.10 s	9	$\mathrm{C}(\mathrm{C}H_3)_3$	−50.42 s
	−11.48 qt [g]	1	$\mathrm{Fe}H$	
C_6H_4OMe-4	6.86 d [h]	2	$\mathrm{CNC_6}H_4\mathrm{OMe}$ (2H_B)	−49.37 s
	3.87 s	3	$\mathrm{CNC_6H_4OC}H_3$	
	−9.87 qt [i]	1	$\mathrm{Fe}H$	
C_6H_4Me-4	6.48 d [j], br	2	$\mathrm{CNC_6}H_4\mathrm{Me}$ (2H_B)	−51.84 s
	2.32 s	3	$\mathrm{CNC_6H_4}Me$	
	−10.04 qt [h]	1	$\mathrm{Fe}H$	
C_6H_5	6.83–6.78 m	2	$\mathrm{CNC_6}H_5$ (2) [m]	−49.55 s [l]
	−9.57 qt [k]	1	$\mathrm{Fe}H$	
$C_6H_4NO_2$-4	8.16 d [n]	2	$\mathrm{CNC_6}H_4\mathrm{NO_2}$ (2H_A *ortho* to NO_2)	−50.42 s
	6.79 d [n]	2	$\mathrm{CNC_6}H_4\mathrm{NO_2}$ (2H_B *ortho* to CN)	
	−8.57 qt [i]	1	$\mathrm{Fe}H$	

[a] In $(CD_3)_2CO$; s, singlet; d, doublet; t, triplet; q, quartet; qt, quintet; m, multiplet; br, broad. [b] Dppe resonances generally in ranges δ = 8.0–6.9 (aromatic) and 3.0–2.1 (methylene). [c] δ Values in ppm relative to trimethylphosphite. [d] ^2J(PH) 46.4 Hz. [e] Broad doublet [^2J(PH) ≈ 46 Hz] in the ^{31}P–^{1}H-undecoupled spectrum. [f] ^3J(HH) 7.8 Hz. [g] ^2J(PH) 46.7 Hz. [h] ^3J(HH) 4.0 Hz (higher field half of an AB-type resonance—see text). [i] ^2J(PH) 46.9 Hz. [j] ^3J(HH) 8.2 Hz (higher field half of an AB type resonance). [k] ^2J(PH) 46.8 Hz. [l] Broad doublet [^2J(PH) ≈ 48 Hz] in the ^{31}P–^{1}H-undecoupled spectrum. [m] Other phenyl resonances obscured by dppe aromatic resonances. [n] Lower and higher field halves of an AB-type resonance (see text), ^3J(HH) 9.1 Hz.

cyanides bound to iron are much weaker π-acceptors and stronger σ-donors, and are probably bound linearly. Accordingly, and in contrast to the known susceptibility of the isocyanides bound to those electron-rich sites [12,13] to electrophilic attack at the N atom, these ligands are not activated towards electrophilic attack at the iron site. Moreover, isocyanide activation towards nucleophilic attack by reagents such as amines or alcohols has not been observed in complexes **1**, although such reactivity has been well documented [19] in cases where the ligating isocyanide behaves mainly as a σ-donor and exhibits ν(CN) values well above those of the free isocyanide.

The chemical behaviour appears to agree with the following trend: electrophilic or nucleophilic attack is observed only for sufficiently low (negative) or high (positive) CN frequency shifts upon coordination. The $\{FeH(dppe)_2\}^+$ centre appears to have electron donor/acceptor properties intermediate between those exhibited by the metal sites which are able to induce electrophilic or nucleophilic attack at isocyanides.

Experimental

All reactions were carried out by standard inert-gas flow and vacuum techniques. Solvents were purified by standard techniques. IR spectra were recorded with Perkin Elmer 683 or 457 spectrometers. NMR spectra were recorded using JEOL EC 100 or VARIAN Unity 300 machines.

[FeHCl(dppe)$_2$] was prepared by a literature method [15a], as were CNMe [20], CNEt [21], CN^{t}Bu [21] and the aryl isocyanides [22].

Syntheses of trans-*[FeH(CNR)(dppe)$_2$][A] (1, A = PF$_6$ or BF$_4$)*

(a) From trans-*[FeHCl(dppe)$_2$].* Since the method is general, only the synthesis of **1** (R = Me, A = BF$_4$) is given, as an example.

Methyl isocyanide (0.16 cm^3, 3.3 mmol) and Tl[BF$_4$] (0.48 g, 1.6 mmol) were added to a solution of *trans*-[FeHCl(dppe)$_2$] (0.98 g, 1.1 mmol) in THF (50 cm^3) under argon, and the mixture was stirred at room temperature for 1 h. The yellow precipitate was filtered off, thoroughly washed with portions of distilled water (total of 50 cm^3) to remove the thallium salts (TlCl and the excess of Tl[BF$_4$]), then with EtOH and, finally, with Et$_2$O; the yellow residue of complex **1** (R = Me, A = BF$_4$) was then dried *in vacuo*. A further crop of this product was obtained upon concentration of the mother-liquor and addition of EtOH (or MeOH), followed by removal (by filtration) of the precipitated yellow solid, which was then washed with distilled water, EtOH and Et$_2$O, before being dried *in vacuo*. The product was recrystallized from CH$_2$Cl$_2$/Et$_2$O. The total yield was above 80%, as well as for the other alkyl isocyanide complexes **1**; however, considerably lower yields (which can be < 10%), particularly for **1**, R = C$_6$H$_5$, C$_6$H$_4$Me-4 or C$_6$H$_4$Cl-4, were commonly obtained when a smaller excess of the isocyanide (below a 2 molar ratio relative to the metal) was used.

(b) From trans-*[FeH(N$_2$)(dppe)$_2$][A] (A = PF$_6$ or BF$_4$).* This method has the disadvantage of requiring the prior synthesis of a dinitrogen complex. It is general, and a typical procedure for the preparation of **1** (R = Me, A = PF$_6$) was carried out as follows.

Methyl isocyanide (0.050 cm^3, 1.0 mmol) was added to a solution of *trans*-[FeH(N$_2$)(dppe)$_2$][PF$_6$] (0.31 g, 0.30 mmol, prepared as indicated below) in THF (35 cm^3) and the mixture was stirred under argon for ca. 1.5 h. The isolation of the isocyanide complex product was carried out as in (a), but with omission of water as a wash.

Syntheses of trans-*[FeH(N$_2$)(dppe)$_2$][A] (A = PF$_6$ or BF$_4$)*

Dinitrogen was bubbled through a solution of *trans*-[FeHCl(dppe)$_2$] (0.65 g, 0.73 mmol) in THF (30 cm^3) to which TlBF$_4$ (0.32 g, 1.1 mmol) (or TlPF$_6$, 0.75 g, 2.1 mmol) was then added. The suspension was stirred for ca. 1 h and a yellow solid was filtered off, thoroughly washed with distilled water (total of 50 cm^3) and EtOH and then dried *in vacuo*. A further crop was obtained from the mother-liquor, upon concentration and addition EtOH, which gave a precipitate which was filtered off, washed with distilled water and EtOH and dried *in vacuo*. The total yield was ca. 30%.

Acknowledgements

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