Bis[1,2-bis(dimethylphosphino)ethane]dihydrogenhydridoiron(II) Tetraphenylborate as a Model for the Function of Nitrogenases†

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The trihydride complex $[FeH_3(dmpe)_2]^+$ (dmpe = $Me_2PCH_2CH_2PMe_2$) is best represented as $[FeH(H_2)(dmpe)_2]^+$, with the H–H separation in the H_2 being *ca.* 0.81 Å. The H_2 can be replaced by N_2, CO, MeCN, MeNC and C_2H_4. The dinitrogen complex $[FeH(N_2)(dmpe)_2]^+$ may be deprotonated to yield the solution-stable, trigonal-bipyramidal species $[Fe(N_2)(dmpe)_2]$, which can be reprotonated by HCl to yield $[FeCl_2(dmpe)_2]$, N_2, H_2 and NH_3. The crystal structures of $[FeH(H_2)(dmpe)_2]BPh_4$ and $[FeH(N_2)(dmpe)_2]BPh_4$ have been determined.

Numerous studies on the function of molybdenum–iron nitrogenases have led to the conclusion that the active site, at which dinitrogen is bound and reduced, is hydridic.[1] Further, it is likely that if this is so, then the observations of H_2/D_2 scrambling during biological nitrogen fixation experiments have been taken to imply that the site should be at least trihydridic.[2] In many researches it has thus been considered that the grouping MoH_3 should be a basic model for the active site of nitrogenase. Notwithstanding, there is no definitive proof that a molybdenum atom does constitute the active site, and the recent structural studies[3] on *Azotobacter vinelandii* and *Clostridium pasteurianum* molybdenum–iron proteins certainly provide no further evidence to support this idea. At the same time, and noting that iron is the transition metal common to all three kinds of nitrogenase,[4] we have provided[5] preliminary evidence that iron(II) and iron(0) can mediate the conversion of co-ordinated dinitrogen to ammonia. This paper describes those researches in detail. Some aspects of this work have been discussed briefly in preliminary communications.[5,6]

Results and Discussion

We decided to investigate the properties of the iron trihydride $[FeH_3(dmpe)_2]^+$ (dmpe = $Me_2PCH_2CH_2PMe_2$) as a reactant with dinitrogen. This material is generated in solution from $[FeH_2(dmpe)_2]$ and methanol,[7] and had not been isolated in the solid state. We were able to obtain the trihydride as the tetraphenylborate salt by reaction of $[FeCl_2(dmpe)_2]$ with $NaBH_4$ in methanol in the presence of $NaBPh_4$. The ^1H NMR (see Fig. 1) and $^{31}P\text{-}\{^1H\}$ spectra at a range of temperatures clearly show that the compound exhibits a *trans*-phosphine stereochemistry, with the complex formally a (dihydrogen)hydridoiron compound at 223 K. At room temperature in solution the hydrogen atoms are exchanging, though equivalence was not achieved within the temperature range of our experiments.

We determined the relaxation time T_1 for the dihydrogen and hydride ligands as a function of temperature by the standard 180°-*t*-90° inversion-recovery method.[8] The minimum values in solution in CD_2Cl_2 are 7.5 ms at 180 K for the dihydrogen signal and 59.9 ms at 255 K for the hydride signal, both measured at 270 MHz. The value of 7.5 ms is fully consistent with a dihydrogen complex in which the relaxation mechanism is purely dipole–dipole.[9] Application of the usual theory to the data yields an H–H separation of 0.81 Å.[10] This value is certainly within the range expected for dihydrogen complexes.[11] Related estimates[10] are 0.86 Å for $[FeH(H_2)(dppe)_2]^+$ (dppe = $Ph_2PCH_2CH_2PPh_2$) and 0.91 Å for $[FeH(H_2)(depe)_2]^+$ (depe = $Et_2PCH_2CH_2PEt_2$), though the latter is unreliable because the corresponding value of T_1 was not shown to be a minimum value.

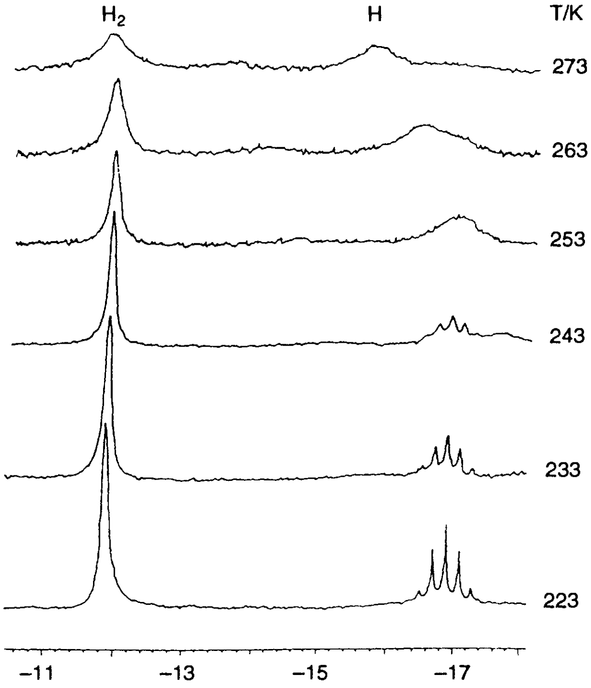

Fig. 1 Variable-temperature ^1H NMR spectra for $[FeH(H_2)(dmpe)_2]^+$ in the hydride region, showing development of signals assigned to hydride and dihydrogen ligands [solvent $(CD_3)_2CO$]

We undertook an X-ray structural analysis of $[FeH(H_2)(dmpe)_2]BPh_4$. The result is shown in Fig. 2, and selected bond lengths and angles and atomic coordinates are shown in Tables 1 and 2, respectively. We were not able to resolve the

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

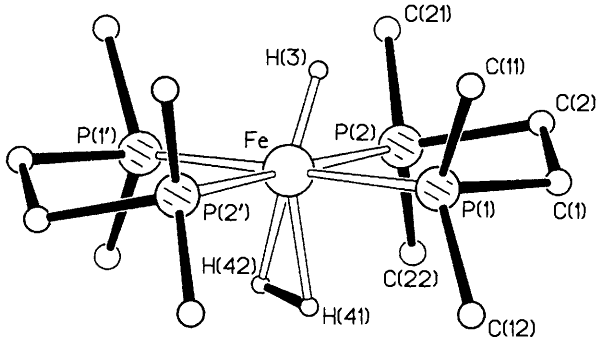


Fig. 2 Diagrammatic perspective view of the $[FeH(H_2)(dmpe)_2]^+$ cation. The hydride and dihydrogen ligands are disordered in a centrosymmetrical arrangement

Table 1 Selected molecular dimensions (bond lengths in Å, angles in °) in *trans*-$[FeH(H_2)(dmpe)_2]BPh_4$ with estimated standard deviations (e.s.d.s) in parentheses*

(*a*) About the Fe atom

Fe–P(1)	2.182(2)	Fe–H(3)	1.30(10)
Fe–P(2)	2.196(2)	Fe–H(41)	1.70(6)
		Fe–H(42)	1.63(10)
P(1)–Fe–P(2)	85.9(1)	P(2)–Fe–H(41)	87(3)
P(1)–Fe–H(3)	86(5)	P(2)–Fe–H(42)	83(6)
P(1)–Fe–H(41)	82(8)	H(3)–Fe–H(41)	151(6)
P(1)–Fe–H(42)	111(3)	H(3)–Fe–H(42)	144(8)
P(2)–Fe–H(3)	67(6)	H(41)–Fe–H(42)	30(4)

(*b*) Torsion angle in the dmpe ligand

P(1)–C(1)–C(2)–P(2)	−36.4(11)

(*c*) In the dihydrogen ligand

H(41)–H(42)	0.86(12)

* The hydride and dihydrogen ligands were refined with geometrical constraints.

electron density corresponding to the H^- and H_2 ligands, the data suggesting equal densities on either side of the FeP_4 plane in the centrosymmetric system. This is presumably due to disorder, whereby the stacking of the FeP_4 units is not affected by these small ligands whose influence does not extend outside the volume delineated by the phosphines. However, we fitted H and H_2 as best we could, constraining the Fe–H and H–H bond lengths as described in the Experimental section; refinement then gave the bond lengths shown. Otherwise, the structure is consistent with all our spectral data.

This structure raises the problem of how the dihydrogen and hydride are able to scramble across the FeP_4 plane. The system is clearly quite labile, and it may be that one of the dmpe molecules is becoming temporarily detached from the iron at one end, allowing the hydrogen atoms to become equivalent. There is certainly a precedent in iron chemistry for this to happen.[12]

The dihydrogen in $[FeH(H_2)(dmpe)_2]^+$ is labile, and can be replaced by a range of other species. We have shown in studies to be reported elsewhere[13] that the rate-determining step in such reactions is the unimolecular loss of H_2, which suggests another possible mechanism for the exchange of H^- and H_2, though a less likely one. $[FeH(H_2)(dmpe)_2]^+$ reacts with CO at 1 atm (*ca.* 10^5 Pa) pressure in thf giving a yellow solution from which *trans*-$[FeH(CO)(dmpe)_2]BPh_4$ was obtained in quantitative yield. The IR, ^1H NMR and ^{31}P-{^1H} NMR spectra are consistent with this. The same complex was also obtained from the reaction of $[FeCl_2(dmpe)_2]$ and $NaBH_4$ in ethanol under CO, followed by addition of $NaBPh_4$.

Table 2 Final atomic coordinates (fractional × 10^4) for *trans*-$[FeH(H_2)(dmpe)_2]BPh_4$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Fe	2500	2500	0
C(11)	2371(8)	5822(8)	−552(5)
C(12)	883(8)	4414(13)	−823(5)
P(1)	1854(1)	4419(2)	−303.0(8)
C(1)	1564(8)	5222(10)	307(4)
C(2)	2058(9)	4874(9)	872(4)
P(2)	2378(1)	3064(2)	879.8(7)
C(21)	3243(4)	3131(12)	1510(3)
C(22)	1700(6)	2091(11)	1193(4)
H(3)	3075(57)	3292(127)	295(53)
H(41)	1553(31)	1871(84)	−137(40)
H(42)	1880(54)	1267(96)	57(68)
B(5)	0	1922(8)	2500
C(51)	805(3)	2891(6)	2578(2)
C(52)	801(4)	4169(7)	2314(3)
C(53)	1484(5)	4955(7)	2358(3)
C(54)	2215(5)	4455(8)	2663(3)
C(55)	2256(4)	3179(8)	2923(3)
C(56)	1564(3)	2409(6)	2880(2)
C(61)	−30(3)	995(6)	1911(2)
C(62)	−387(3)	1468(6)	1344(3)
C(63)	−360(4)	746(8)	840(3)
C(64)	35(4)	−500(9)	884(3)
C(65)	398(4)	−991(7)	1428(4)
C(66)	368(3)	−263(7)	1933(3)

The hydride and dihydrogen ligands were refined with geometrical constraints.

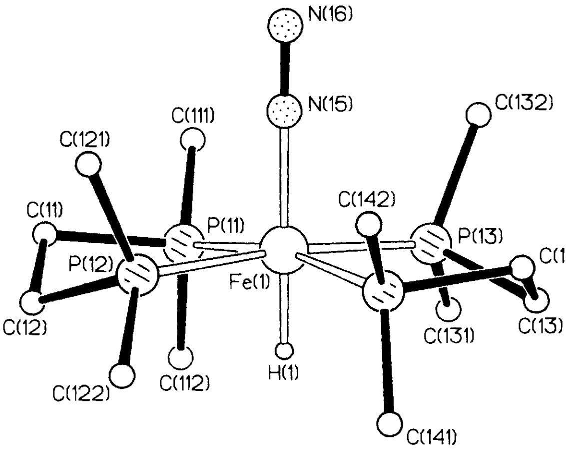


Fig. 3 One of the two independent, virtually identical cations in the crystals of $[FeH(N_2)(dmpe)_2]BPh_4$

Similarly, the complex $[FeH(H_2)(dmpe)_2]^+$ reacts with N_2, MeNC, MeCN and C_2H_4 (= L) to yield complexes $[Fe(H)L(dmpe)_2]^+$. Selected spectral and analytical data are included in Table 3. These complexes are very similar to some complexes $[Fe(H)L(depe)_2]^+$ reported a while ago.[14]

We determined the structure of $[FeH(N_2)(dmpe)_2]BPh_4$ by X-ray crystallographic analysis. It is represented in Fig. 3 and selected bond lengths and angles and atomic coordinates are in Tables 4 and 5 respectively. The structure is entirely consistent with the spectroscopic data. There are two independent $[FeH(N_2)(dmpe)_2]^+$ moieties in the unit cell, with virtually identical conformations and the same dimensions except for the dinitrogen molecules. A similar situation has been observed in the crystal of $[CoH(N_2)(PPh_3)_3]$.[15] The mean N–N bond length is 1.145(3) Å, which is not unusual for terminally end-on bonded dinitrogen,[16] and certainly does not suggest any form of 'activation'. The iron atom is octahedrally co-ordinated and displaced out of the equatorial plane towards the dinitrogen

Table 3 Characterisation data for the new complexes

			Analysis^a (%)					
Complex	Colour	Yield (%)	C	H	N	$^{31}P-\{^1H\}$ NMR^b	^1H NMR^b	IR/cm$^{-1\,c}$
$[FeH(H_2)(dmpe)_2]BPh_4$	Yellow	70–80	63.8 (63.7)	7.9 (8.1)	0 (0.0)	−68.9 (s)	−17.4 (q, $^2J_{PH}$ = 50.5, FeH), −11.6 (br, s, FeH_2)	1856, ν(Fe–H)
$[FeD(D_2)(dmpe)_2]BPh_4$						—	−16.9 (q, $^2J_{PD}$ = 8.0, FeD), −11.8 (br, s, FeD_2)	1341, ν(Fe–D)
$[FeH(N_2)(dmpe)_2]BPh_4$	Orange	≈100	61.0 (61.4)	7.5 (7.5)	4.1 (4.0)	—75.7 (s)^d	−19.4 (q, $^2J_{PH}$ = 51.0, FeH)	2106, ν(N_2) 1841, ν(Fe–H)
$[FeH(^{15}N_2)(dmpe)_2]BPh_4$	Orange	≈100	—	—	—	−64.4 (m, N_α) −49.3 (m, N_β),^{e} $^1J_{NN}$ = 4, $^2J_{NP}$ ≈ 2	—	2023, ν($^{15}N_2$)
$[FeH(CO)(dmpe)_2]BPh_4$	Pale yellow	≈100	63.0 (63.1)	7.4 (7.5)	0 (0.0)	−73.8 (s)	−11.9 (q, $^2J_{PH}$ = 49.4, FeH)	1926, ν(CO) 1806, ν(Fe–H)
$[FeH(CNMe)(dmpe)_2]BPh_4$	Pale yellow	≈100	62.9 (63.6)	7.6 (7.8)	1.9 (1.9)	−69.5 (s)	−14.9 (q, $^2J_{PH}$ = 49.0, FeH), 3.24 (s, $CNCH_3$)	2101, ν(CN) 1800, ν(Fe–H)
$[FeH(C_2H_4)(dmpe)_2]BPh_4$	Orange	≈100	64.5 (64.8)	8.1 (8.1)	0 (0.0)	−72.2 (s)	−13.11 (q, $^2J_{PH}$ = 59.1, FeH), 1.82 (br, s, C_2H_4, overlapping P–CH_2)	1875, ν(Fe–H)
$[FeH(NCMe)(dmpe)_2]BPh_4$	Orange	≈100	63.1 (63.6)	7.8 (7.8)	1.9 (1.9)	−71.1 (s)	−24.0 (q, $^2J_{PH}$ = 49.4, FeH), 2.17 (s, CH_3CN)	2231, ν(CN) 1824, ν(Fe–H)
$[Fe(O_2CH)(dmpe)_2]BPh_4$	Red-orange	63–100	61.1 (61.7)	7.6 (7.4)	0 (0.0)	−67.3 (t, P_A), −78.5 (t, P_B), $^2J_{PP}$ 38.1	f	1345, $\nu_{asym}(CO_2)$
$[Fe(S_2CH)(dmpe)_2]BPh_4$	Purple	65–100	58.5 (59.0)	7.0 (7.0)	0 (0.0)	−76.1 (t, P_A), −80.3 (t, P_B), $^2J_{PP}$ 37.4	f	1268, $\nu_{asym}(CS_2)$

^{a} Calculated values in parentheses. ^{b} Shifts in ppm, coupling constants in Hz. ^{c} In Nujol, unless otherwise stated. ^{d} Becomes a doublet in absence of ^1H decoupling. ^{e} ^{15}N NMR data. ^{f} Signals only from dmpe.

Table 4 Selected molecular dimensions (bond lengths in Å, angles in °) in *trans*-$[FeH(N_2)(dmpe)_2]BPh_4$ with e.s.d.s in parentheses

(*a*) In the co-ordination spheres of the iron atoms

Fe(1)–P(11)	2.199(1)	Fe(2)–P(21)	2.216(2)
Fe(1)–P(12)	2.217(2)	Fe(2)–P(22)	2.215(1)
Fe(1)–P(13)	2.220(2)	Fe(2)–P(23)	2.173(2)
Fe(1)–P(14)	2.205(1)	Fe(2)–P(24)	2.189(1)
Fe(1)–H(1)	1.33(4)	Fe(2)–H(2)	1.30(4)
Fe(1)–N(15)	1.826(5)	Fe(2)–N(25)	1.802(7)
P(11)–Fe(1)–P(12)	85.4(1)	P(21)–Fe(2)–P(22)	85.1(1)
P(11)–Fe(1)–P(13)	94.0(1)	P(21)–Fe(2)–P(23)	93.4(1)
P(12)–Fe(1)–P(13)	173.6(1)	P(22)–Fe(2)–P(23)	174.3(1)
P(11)–Fe(1)–P(14)	167.9(1)	P(21)–Fe(2)–P(24)	168.8(1)
P(12)–Fe(1)–P(14)	93.5(1)	P(22)–Fe(2)–P(24)	94.4(1)
P(13)–Fe(1)–P(14)	85.7(1)	P(23)–Fe(2)–P(24)	86.0(1)
P(11)–Fe(1)–N(15)	96.3(1)	P(21)–Fe(2)–N(25)	94.4(2)
P(12)–Fe(1)–N(15)	93.0(2)	P(22)–Fe(2)–N(25)	93.0(2)
P(13)–Fe(1)–N(15)	93.3(2)	P(23)–Fe(2)–N(25)	92.5(2)
P(14)–Fe(1)–N(15)	95.9(1)	P(24)–Fe(2)–N(25)	96.8(2)
H(1)–Fe(1)–P(11)	84.5(12)	H(2)–Fe(2)–P(21)	86.2(16)
H(1)–Fe(1)–P(12)	86.7(18)	H(2)–Fe(2)–P(22)	92.1(15)
H(1)–Fe(1)–P(13)	87.0(18)	H(2)–Fe(2)–P(23)	82.3(15)
H(1)–Fe(1)–P(14)	83.3(12)	H(2)–Fe(2)–P(24)	82.6(16)
H(1)–Fe(1)–N(15)	179.1(13)	H(2)–Fe(2)–N(25)	174.9(15)

(*b*) In the dinitrogen ligands

N(15)–N(16)	1.112(9)	N(25)–N(26)	1.178(13)
Fe(1)–N(15)–N(16)	179.4(6)	Fe(2)–N(25)–N(26)	177.5(5)

(*c*) Torsion angles in the diphosphine ligands

P(11)–C(11)–C(12)–P(12)	48.3(6)
P(13)–C(13)–C(14)–P(14)	48.8(6)
P(22)–C(22)–C(21)–P(21)	51.7(5)
P(24)–C(24)–C(23)–P(23)	43.3(9)

molecule by *ca.* 0.18 Å. The Fe–H separation [1.32(2) Å] is shorter than in $[FeH(N_2)\{(Ph_2PCH_2CH_2PPhCH_2)_2\}]Br\cdot EtOH$ [1.53(9) Å][17] and in $[FeH_2(N_2)(PEtPh_2)_3]$ (1.43 Å, mean value)[11] but it is also shorter than the sum of the iron and hydrogen covalent radii (1.53 Å).[18] The Fe–P separations [2.204(5) Å, mean] are slightly longer than in the $[FeH(H_2)(dmpe)_2]^+$ precursor [2.189(7) Å, mean], which is presumably a consequence of the greater oxidising (electron-withdrawing) power of N_2 as compared to H_2.

The complex $[FeH(H_2)(dmpe)_2]BPh_4$ reacts with CX_2 (X = O or S) in tetrahydrofuran (thf) to give a red (X = O) and a violet (X = S) product, analysing for $FeHCX_2(dmpe)_2BPh_4$ (Table 3). The same materials are obtainable from $[FeCl_2(dmpe)_2]$ and $NaBH_4$ in ethanol with CX_2, after addition of $NaBPh_4$. The IR spectra show no band assignable to ν(Fe–H) and for X = O there is a band at 1550 cm^{-1} assignable to ν(C=O) which could be due to co-ordinated CO_2, though this is unlikely. The $^{31}P-\{^1H\}$ NMR spectra are A_2B_2 type, and consequently we believe that CX_2 has inserted into the iron–hydride bond yielding *cis*-$[Fe(X_2CH)(dmpe)_2]BPh_4$, a formato or thioformato complex for X = O or S, respectively where X_2CH is bidentate.

Insertion of CX_2 into metal–hydride bonds to form formato and thioformato complexes was very well established many years ago,[19] and examples are $[Co(O_2CH)(PPh_3)_3]$, $[Fe(O_2CH)_2(PEtPh_2)_2]$ and $[Fe(S_2CH)_2(Et_2PCH_2CH_2PEt_2)_2]$. However, although the IR characteristics of the formato group of our compounds are quite consistent with the literature data, there may be complications. The complex $[Fe(O_2CH)(dmpe)_2]BPh_4$ is a single iron species, as shown by the Mössbauer spectrum in the solid state (δ = 0.26, Δ = 1.33, $\Gamma_{\frac{1}{2}}$ = 0.21 mm s^{-1}), but the $^{31}P-\{^1H\}$ NMR spectrum in acetone solution hints at complications. The two A_2B_2 triplets are consistently of different intensities, and there is another smaller triplet evident at δ −78.4, $^2J_{PP}$ = 35.4 Hz. This suggests the presence of another cisoid form, conceivably with monodentate formate. This requires further investigation. There is no evidence of a similar phenomenon in solutions of the dithioformato complex.

The apparent ease with which $[FeH(H_2)(dmpe)_2]^+$ reacts with N_2 encouraged us to investigate reactions between it and dinitrogen complexes in order to synthesise species

Table 5 Final atomic coordinates (fractional × 10^4) for *trans*-$[FeH(N_2)(dmpe)_2]BPh_4$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe(1)	1 667.0(4)	4 087.1(4)	7 507.2(4)	Fe(2)	2 861.1(4)	386.7(4)	2 572.9(4)
C(111)	−314(3)	2 918(5)	5 436(4)	C(211)	4 814(5)	320(5)	2 156(6)
C(112)	1 334(5)	4 150(5)	5 493(4)	C(212)	5 042(6)	534(7)	3 916(6)
P(11)	962.4(8)	3 443.5(9)	6 053.1(8)	P(21)	4 396.7(9)	748(1)	2 963(1)
C(11)	1 266(5)	2 445(5)	5 661(4)	C(21)	5 024(4)	2 019(4)	3 365(5)
C(12)	2 297(5)	2 729(5)	6 266(3)	C(22)	4 611(4)	2 466(4)	3 922(4)
P(12)	2 485.6(9)	3 218.2(9)	7 399.2(9)	P(22)	3 308(1)	1 912.4(9)	3 246(1)
C(121)	2 139(6)	2 191(4)	7 639(5)	C(221)	3 104(6)	2 590(5)	2 595(6)
C(122)	3 771(4)	3 681(5)	8 017(5)	C(222)	2 904(6)	2 323(6)	4 087(5)
C(131)	750(5)	5 646(4)	6 859(4)	C(231)	2 827(9)	−1 776(6)	2 376(8)
C(132)	−201(5)	4 624(6)	7 573(6)	C(232)	2 675(8)	−1 465(7)	865(5)
P(13)	966.6(9)	5 073.2(9)	7 599.9(8)	P(23)	2 445(1)	−1 084(1)	1 806(1)
C(13)	1 694(5)	6 077(4)	8 660(3)	C(23)	1 163(5)	−1 677(6)	1 305(9)
C(14)	2 085(5)	5 732(4)	9 350(4)	C(24)	719(5)	−1 092(5)	1 073(6)
P(14)	2 602.8(9)	4 943.1(9)	8 930.8(8)	P(24)	1 338.9(9)	73(1)	1 958(1)
C(141)	3 791(4)	5 770(4)	9 277(4)	C(241)	716(6)	4(10)	2 620(7)
C(142)	2 811(6)	4 382(5)	9 688(4)	C(242)	869(5)	732(6)	1 391(6)
N(15)	796(3)	3 238(3)	7 646(3)	N(25)	2 905(4)	195(4)	3 542(4)
N(16)	261(4)	2 725(4)	7 730(5)	N(26)	2 911(6)	36(7)	4 156(5)
H(1)	2 310(22)	4 707(23)	7 419(20)	H(2)	2 802(23)	444(23)	1 834(22)
B(3)	7 955(3)	839(3)	2 146(3)	B(4)	6 388(3)	4 229(3)	7 196(3)
C(31a)	8 936(3)	1 580(3)	2 223(3)	C(41a)	5 666(3)	4 743(3)	6 968(3)
C(32a)	8 936(3)	1 771(3)	1 501(3)	C(42a)	5 131(3)	4 633(3)	6 123(3)
C(33a)	9 710(4)	2 414(4)	1 527(4)	C(43a)	4 454(3)	4 998(3)	5 915(4)
C(34a)	10 537(4)	2 918(3)	2 299(4)	C(44a)	4 299(4)	5 503(4)	6 575(4)
C(35a)	10 584(3)	2 757(3)	3 024(3)	C(45a)	4 805(4)	5 635(4)	7 416(4)
C(36a)	9 797(3)	2 108(3)	2 993(3)	C(46a)	5 475(3)	5 260(3)	7 607(3)
C(31b)	8 142(3)	671(3)	3 046(3)	C(41b)	7 381(3)	4 895(3)	8 098(2)
C(32b)	7 613(3)	743(3)	3 514(3)	C(42b)	7 739(3)	5 863(3)	8 523(3)
C(33b)	7 755(3)	526(3)	4 244(3)	C(43b)	8 635(4)	6 386(4)	9 253(3)
C(34b)	8 454(4)	234(3)	4 545(3)	C(44b)	9 191(4)	5 961(5)	9 587(3)
C(35b)	8 998(4)	146(3)	4 114(3)	C(45b)	8 875(3)	5 010(4)	9 178(3)
C(36b)	8 848(3)	350(3)	3 386(3)	C(46b)	7 997(3)	4 500(3)	8 459(3)
C(31c)	7 554(3)	−213(3)	1 357(3)	C(41c)	5 754(3)	3 303(3)	7 274(3)
C(32c)	8 022(4)	−502(4)	893(3)	C(42c)	5 878(3)	3 194(3)	8 042(3)
C(33c)	7 667(5)	−1 407(5)	265(4)	C(43c)	5 274(3)	2 423(3)	8 077(3)
C(34c)	6 821(5)	−2 052(4)	70(4)	C(44c)	4 515(3)	1 733(3)	7 322(4)
C(35c)	6 330(4)	−1 803(4)	513(4)	C(45c)	4 356(3)	1 807(3)	6 538(3)
C(36c)	6 694(3)	−904(3)	1 140(3)	C(46c)	4 963(3)	2 571(3)	6 519(3)
C(31d)	7 195(3)	1 313(3)	1 912(3)	C(41d)	6 750(3)	3 951(3)	6 435(3)
C(32d)	6 449(3)	995(3)	1 083(3)	C(42d)	6 813(3)	3 108(3)	6 102(3)
C(33d)	5 838(4)	1 424(4)	890(4)	C(43d)	7 215(3)	2 931(4)	5 520(3)
C(34d)	5 959(4)	2 212(5)	1 534(5)	C(44d)	7 550(3)	3 612(5)	5 256(3)
C(35d)	6 700(4)	2 575(4)	2 364(4)	C(45d)	7 511(3)	4 459(5)	5 572(3)
C(36d)	7 306(3)	2 130(3)	2 550(3)	C(46d)	7 122(3)	4 616(3)	6 153(3)

containing Fe–N–N–metal systems, since such bridging species might conceivably be involved in nitrogenase function. The first dinitrogen complex we investigated was $[Mo(N_2)_2(dppe)_2]$,[20] because there is a precedent for such a system {*e.g.*, $[Mo(C_6H_5Me)(PPh_3)_2N_2Fe(C_5H_5)(dmpe)]^+$},[21] though apparently not with an 'activated' N_2 as in the bis(dinitrogen) complex.

In a 2:1 mixture of $[FeH(H_2)(dmpe)_2]BPh_4$ and $[Mo(N_2)_2(dppe)_2]$ in thf under Ar exchange of H_2 and N_2 occurs, and $[FeH(N_2)(dmpe)_2]BPh_4$ and $[MoH_4(dppe)_2]$[22] were obtained quantitatively as judged by IR spectroscopy, and the individual products were recovered in 70% yield.

This is an extraordinary observation. Judged by the values of $\nu(N_2)$, 2106 cm^{-1} for the iron complex and 1977 cm^{-1} for the molybdenum complex,[20] it is quite unexpected. It must therefore be driven by the relative metal–hydrogen bond energies, and we know little about these. However, $[MoH_4(dppe)_2]$ is apparently a tetrahydride rather than some form of dihydrogen complex.[22,23]

We are currently undertaking a kinetic study of this reaction.[13] However, the mechanism is clearly not simple, and it must involve several stages, presumably involving intermediates such as $[MoH_2(N_2)(dppe)_2]$. Both the H_2 in $[FeH(H_2)(dmpe)_2]^+$ and the N_2 in $[Mo(N_2)_2(dppe)_2]$ are thermally labile at room temperature so either or both may be involved in the rate-determining step. The first-order rate constant for loss of N_2 from $[Mo(N_2)_2(dppe)_2]$ is 2.8×10^{-4} s^{-1} at 27 °C[24] and we are currently[13] undertaking a detailed kinetic study of the substitution reactions of $[FeH(H_2)(dmpe)_2]^+$.

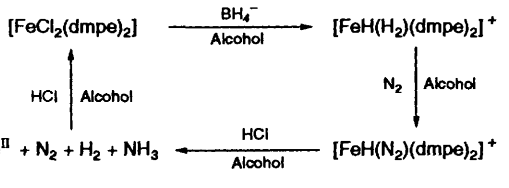
This reaction is not unique. It was observed in 1972[25] that $[Mo(N_2)_2(dppe)_2]$ and $[FeH_4(PEtPh_2)_3]$ yield $[FeH_2(N_2)(PEtPh_2)_3]$ and $[MoH_2(dppe)_2]$ (probably actually the tetrahydride), but the reaction was not clean. We have observed that $[FeH(H_2)(dmpe)_2]^+$ can abstract dinitrogen from both $[W(N_2)_2(dppe)_2]$[26] and $[W(N_2)_2(depe)_2]$,[27] though the reactions are not clean and no tungsten-containing products were isolated. However, the N_2 in such tungsten complexes is not thermally labile, though photolabile,[24] and so the overall reaction probably differs from that involving molybdenum. No reaction was observed between $[FeH(H_2)(dmpe)_2]^+$ and $[ReCl(N_2)(PMe_2Ph)_4]$,[28] but the rhenium-dinitrogen complex [$\nu(N_2)$ 1920 cm^{-1}] apparently binds N_2 very strongly, although $[ReCl(H_2)(PMe_2Ph)_4]$ is known.[29]

The possibility that iron may be at the active site in all three kinds of nitrogenase and that molybdenum and vanadium may function as dinitrogen traps,[5] later passing the N_2 to iron, is

Table 6 Ammonia production

Compound or system	Solvent/acid	Concentration[a] of recovered NH_3 (mmol)	Yield[b] of NH_3 (%)
$[FeH(N_2)(dmpe)_2]BPh_4$	thf–HCl	0	0
$[FeH(N_2)(dmpe)_2]BPh_4$	thf–H_2SO_4	1.4	3.6
$[FeH(N_2)(dmpe)_2]BPh_4$ + LiPh (5 mol equivalent)	thf–H_2SO_4	1.0	2.6
$[Fe(N_2)(dmpe)_2]$	thf–H_2SO_4	3.4	8.6
$[Fe(N_2)(dmpe)_2]$	thf–HCl	4.8	12
$[Fe(N_2)(dmpe)_2]$	Et_2O–HCl	3.8	9.6
$[Fe(N_2)(dmpe)_2]$[c] + $MgCl_2$ (10 mol equivalents)	thf–HCl	2.6	6.6

[a] Concentration of solution after base distillation and making up to 25 cm^3 starting from 1 mmol Fe complex. These values are corrected for blanks consisting of $[FeH(H_2)(dmpe)_2]BPh_4$ treated as necessary with base and/or acid in the appropriate solvent under argon. Under such circumstances background concentrations of *ca.* 0.15 mmol ammonia were obtained. [b] Yield expressed as (mol NH_3 per mol $[FeH(N_2)(dmpe)_2]BPh_4$) × 100. [c] In only this case was any hydrazine observed, yield 0.4% based on initial iron complex.



Scheme 1

neither supported nor disfavoured by the recently published structures of molybdenum–iron nitrogenases. The structures[3] do little to suggest where the active site might be, beyond showing that molybdenum is present as six-co-ordinate molybdenum(IV), and that the structure contains plenty of 'unsaturated' iron. However, there has been no iron–dinitrogen chemistry which yields ammonia under conditions which might approximate to the iron environment of nitrogenase, *viz.*, hydroxylic-type solvents, relatively mild reducing agents, low acidities, about neutral. Iron can mediate the reduction of dinitrogen to ammonia, but to date[30] this has always involved non-hydroxylic solvents such as ethers, and reducing agents such as organolithium reagents.

Since $[FeH(H_2)(dmpe)_2]^+$ can be reversibly deprotonated[6] by base to yield $[FeH_2(dmpe)_2]$ we reasoned that $[FeH(N_2)(dmpe)_2]^+$ might similarly be deprotonated, yielding $[Fe(N_2)(dmpe)_2]$. The important point is that such a deprotonation is also formally a reduction from iron(II) to iron(0), the two electrons from the Fe–H bond now being non-bonding and potentially available for reducing substrates. We found that $[FeH(N_2)(dmpe)_2]^+$ reacts with bases such as $KOBu^t$ in thf to yield an orange solution. The solutions show a band assignable to $\nu(N_2)$ at 1975 cm^{-1} [1917 cm^{-1} for $\nu(^{15}N_2)$] compared to 2106 cm^{-1} in the starting complex. This is consistent with the formation of $[Fe(N_2)(dmpe)_2]$, analogous to $[Fe(N_2)(dppe)_2]$[31] and $[Fe(N_2)(Me_2PCH_2CH_2CH_2PMe_2)_2]$.[32] Ethereal solutions of $[Fe(N_2)(dmpe)_2]$ are stable under N_2, but we could not isolate it as a solid. Removal of solvent *in vacuo* resulted in loss of N_2, and left an oil, which apparently picked up some N_2 upon exposure to this gas. The ^{31}P-$\{^1H\}$ NMR spectrum of a solution of $[Fe(N_2)(dmpe)_2]$ in thf–C_6D_6 is of a typical A_2B_2 spin system, suggesting a trigonal-bipyramidal structure with N_2 in the equatorial plane. The residue after removal of N_2 is thus probably $[Fe(dmpe)_2]$ which has an extensive chemistry which was investigated some years ago[33a] in a very different context.†

The complex $[Fe(N_2)(dmpe)_2]$ reacts with CO in thf to give a material which shows two bands assignable to $\nu(CO)$, at 1880 and 1915 cm^{-1}. These are assignable to $[Fe(CO)_3(dmpe)]$.[33a,34] However, after short reaction times we isolated a pyrophoric solid which shows $\nu(CO)$ (thf) at 1830 cm^{-1} and which has a broad singlet in the ^{31}P-$\{^1H\}$ NMR spectrum centred at δ −77.5 at −50 °C. The same material is accessible from $[FeH(CO)(dmpe)_2]^+$ and $KOBu^t$, and it seems to have been synthesised previously[33] from $[FeH(C_{10}H_7)(dmpe)_2]$ and CO, as judged from IR and NMR spectra. It seems to be $[Fe(CO)(dmpe)_2]$. We also obtained evidence for a CS_2 adduct (see Experimental section).

When we investigated the protonation of $[Fe(N_2)(dmpe)_2]$ it quickly became evident that the $[FeH(N_2)(dmpe)_2]^+$ was not the only product. With an excess of ethereal HCl, and after base distillation of the product, we isolated ammonia in variable amounts, in the range 0.06–0.12 mmol NH_3 per mol initial $[FeH(N_2)(dmpe)_2]^+$. In fact, the indophenol test[35] showed that ammonia was produced before base distillation. In contrast, the reaction of $[FeH(N_2)(dmpe)_2]^+$ and ethereal HCl produced $[FeCl_2(dmpe)_2]$ and no ammonia, so that the ammonia presumably arises by protonation of $[Fe(N_2)(dmpe)_2]$. The ultimate iron-containing product with ethereal HCl proved to be $[FeCl_2(dmpe)_2]$, by spectral comparison with an authentic sample. About 80% of the iron could be accounted for as $[FeCl_2(dmpe)_2]$, which itself reacts slowly with HCl to give red materials.

We are currently optimising the yield of ammonia as a function of acid, solvent and temperature. Our initial data are shown in Table 6. We are also attempting to vary the ligand system, and have so far obtained comparable amounts of ammonia by a similar route from $[FeH(N_2)(depe)_2]^+$ [14] and $[FeH(N_2)\{(Ph_2PCH_2CH_2PCH_2)_2\}]^+$.[17] If we assume that overall two electrons are available to reduce each molecule of N_2 (from $Fe^0 \longrightarrow Fe^{II}$) then our current yields are of the order of 18%. However, there are evidently at least three reactions occurring in the reprotonation system: direct liberation of N_2, yielding $[Fe(dmpe)_2]$ and its decomposition products; protonation of co-ordinated N_2, yielding ammonia and N_2; and protonation at iron giving $[FeH(N_2)(dmpe)_2]^+$ and eventually $[FeCl_2(dmpe)_2]$, and H_2, which was also detected. The direct liberation of N_2 made it impossible to obtain a nitrogen balance.

We draw the following conclusions from the results reported here.

(*i*) Iron is capable of mediating the conversion of dinitrogen to ammonia by a route which involves concomitant oxidation of iron(0) to iron(II). The iron(0) does not require extreme reducing conditions to produce it, merely a sufficient change in the pH (or its equivalent) of the medium. Although we have yet to uncover the mechanistic details of this conversion, this suggests on chemical grounds alone that iron, the only transition element common to all three kinds of nitrogenase,[4] may always be at the active site rather than molybdenum or vanadium.

(*ii*) It is possible to envisage a cyclic system operating in

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† *Note added at proof:* the isolation and crystal structure of $[Fe(N_2)(depe)_2]$ have now been described;[33b] the geometry is the same as that inferred for $[Fe(N_2)(dmpe)_2]$.

alcoholic solution based upon this chemistry (Scheme 1). We do not know that the dmpe would remain bidentate throughout the cycle, but certainly the isolation of $[\text{FeCl}_2(\text{dmpe})_2]$ shows that the system is sufficiently robust to survive. We are currently attempting to carry out this cycle in one pot. To date we have only carried through the separate steps independently, and yields have not been optimised.

(*iii*) This cycle suggests that nitrogenases themselves could function in a way not recognised hitherto. If the nitrogenase provides a constant electron flux to the active site, and there is, as seems likely, a chemical cycle of some kind involved in the binding and reduction of N_2, then that cycle could be turned simply by systematically changing the pH in the vicinity of the site. Considering the cycle sketched above, and starting at $[\text{FeCl}_2(\text{dmpe})_2]$, the arrival of electrons at the site when access of protons is restricted is equivalent to the formation of H^-. These reagents would convert the dichloride to the dihydrogenhydride. The binding of N_2 (under the same conditions of proton access) would make the remaining hydride more protic itself than hitherto. It would then leave the site causing reduction. Finally, enhanced access of protons would reoxidise the site and produce ammonia. The cycle is thus turned by cycling the H^+ concentration and not by pulsing the electron flux. This could be a relatively easy option for an enzyme system to modulate the cycle.

(*iv*) Finally, when looking for 'models' for nitrogenase function, we have hitherto satisfied ourselves that a system could mediate the conversion of N_2 to NH_3 and have paid far less attention to other substrates reacting at the same site. Of the three supposedly key elements in nitrogenases, our molybdenum models are based on Mo^{0}[36] (likely in an enzyme?) or Mo^{IV}[37] (N_2 bridging two molybdenum atoms, apparently impossible[3] for nitrogenase), vanadium on $\text{V}^{-\text{I}}$[38] (even less likely) or V^{II}[39] (bridging, and apparently also excluded on structural grounds[3]) and iron (Fe^{II} or Fe^{0}, as discussed above). All three elements certainly qualify as candidates for the active site on chemical grounds, though not equally so. Nevertheless, we are now in a position to refine our models. Nitrogenases reduce a large range of substrates other than N_2 and we need to study how these substrates are treated by our putative models, bearing in mind that in nitrogenases themselves these other substrates may not all be reduced at the 'active site'. Finally, we now have a range of complexes containing the M(diphosphine)_2 core based upon Mo, or V or Fe, as well as on other elements which can bind and activate N_2. It is already clear from these that simple correlations between, say, $\nu(N_2)$, N_2 lability and N_2 activation are not adequate. However, we should now be able to begin to disentangle, with empirical data, the factors which make for N_2 activation and which provoke substrate reductions parallel to those carried out by nitrogenases. This should then enable us to refine our functional models for nitrogenases to give more realistic examples than the phosphine complexes currently available. Such studies are in hand.

Experimental

All operations were carried out under dry dinitrogen or argon following standard Schlenk techniques. All the solvents were distilled under N_2 from an appropriate drying agent prior to use. When N_2 exclusion was required, the solvent was saturated with argon by bubbling through immediately before use.

Infrared spectra were recorded on a Perkin Elmer 882 instrument in Nujol mulls or in solution. The UV measurements were obtained using a Perkin Elmer Lambda 5 spectrometer. NMR spectra were taken on JEOL GSX-270 equipment, in appropriate deuteriated solvents, using as references SiMe_4 for ^1H, P(OMe)_3 for $^{31}\text{P-}\{^1\text{H}\}$, and MeNO_2 for ^{15}N measurements. Analyses were by Mr. C. J. Macdonald of this Laboratory, using a Perkin Elmer 2400 CHN elemental analyser. Mössbauer spectra were recorded by Dr. D. J. Evans on an E.S. Technology MS-105 Mössbauer spectrometer with a 25 mCi ^{57}Co source in a rhodium matrix. Spectra were recorded at 77 K and referenced against iron foil at 298 K.

1,2-Bis(dimethylphosphino)ethane and 1,2-bis(diethylphosphino)ethane were prepared by literature methods.[40] $[\text{FeCl}_2(\text{dmpe})_2]$,[41] $[\text{Mo(N}_2)_2(\text{dppe})_2]$,[20] $[\text{W(N}_2)_2(\text{dppe})_2]$[26] and $[\text{W(N}_2)_2(\text{depe})_2]$[27] were also prepared by published methods. Sodium tetraphenylborate, NaBH_4 and NaBD_4 were purchased from Aldrich Chemical Co. Carbon disulfide was purchased from BDH Chemicals Co. and used without purification.

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*dihydrogenhydridoiron*(II) *Tetraphenylborate*.—A slurry of $[\text{FeCl}_2(\text{dmpe})_2]$ (1.04 g, 2.43 mmol) in N_2-free ethanol (*ca.* 25 cm^3) under argon was treated with NaBH_4 in ethanol (0.09 g, *ca.* 2.5 mmol in 10 cm^3 of EtOH). A sequence of colour changes was observed. The final red-orange cloudy solution was stirred for 15 min under argon, then NaBPh_4 (0.9 g, *ca.* 2.6 mmol) in ethanol (10 cm^3) was added, precipitating a solid. The mixture was stirred for *ca.* 1 h and then filtered. The pale yellow solid was washed with EtOH in order to remove all NaCl formed, and then with ether and dried *in vacuo*. This product, obtained in 70–80% yield, is pure enough for synthetic purposes. Yellow crystals can be obtained by dissolving the product in thf, filtering through Celite, layering with ethanol or hexane and cooling to −20 °C.

The *trans*-bis[1,2-bis(diethylphosphino)ethane]dihydrogenhydridoiron(II) tetraphenylborate can also be prepared by this method, starting from $[\text{FeCl}_2(\text{depe})_2]$.

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*deuteridodideuteriumiron*(II) *Tetraphenylborate*.—This complex, prepared for comparative purposes, was synthesised in the same way as the dihydrogenhydrido complex, but using NaBD_4 and CH_3OD instead of NaBH_4 and EtOH. IR: ν(Fe–D) at 1341 cm^{-1}. No ν(Fe–H) was observed. ^2H NMR: δ(D) −1688 (qnt, $^2J_{\text{DP}} = 8$ Hz), $\delta(\text{D}_2)$ −11.84 (br s) (at −75 °C in thf).

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*dinitrogenhydridoiron*(II) *Tetraphenylborate*.—This complex can be prepared using the procedure described above, but under dinitrogen rather than argon. The crude product is usually a mixture of dihydrogen and dinitrogen complexes, and must be recrystallised from thf or acetone under dinitrogen. Yield: 75%.

Alternatively, this product can be prepared by reaction of $[\text{FeH(H}_2)(\text{dmpe})]\text{BPh}_4$ with dinitrogen in thf, in essentially quantitative yield.

The ^{15}N-labelled dinitrogenhydrido-complex $[\text{FeH}(^{15}\text{N}_2)(\text{dmpe})_2]\text{BPh}_4$ was prepared as follows: $[\text{FeH(H}_2)(\text{dmpe})_2]\text{BPh}_4$ (1.3 g, 1.9 mmol) was dissolved under N_2 in thf (60 cm^3) in a 250 cm^3 flask equipped with a magnetic stirring bar and a greaseless tap. The solution was frozen in liquid nitrogen, and then evacuated on the high-vacuum line, $^{15}\text{N}_2$ was pumped in using a Töpler pump. The frozen mixture was allowed to thaw, and it was stirred in the closed flask under $^{15}\text{N}_2$ for 1.5 h at *ca.* 40 °C. After this the flask was frozen again and unreacted $^{15}\text{N}_2$ was recovered using the Töpler pump. The following manipulations were performed under argon, rather than N_2, in order to avoid $^{15}\text{N}_2$–$^{14}\text{N}_2$ exchange. Filtration through Celite and solvent removal yielded an orange solid, which was washed with ether and dried *in vacuo*.

Preparations of trans-$[\text{FeH(L)(dmpe)}_2]\text{BPh}_4$ *Derivatives*.—These were synthesised, either by stirring $[\text{FeH(H}_2)(\text{dmpe})_2]\text{BPh}_4$ in thf in an atmosphere of L (L = CO, N_2 or C_2H_4), reaction with L in thf under argon (L = CNMe), or stirring in L under argon (L = MeCN). Typical reaction time was 1 h, and yields were quantitative. They can also be prepared by the reaction of $[\text{FeCl}_2(\text{dmpe})_2]$ with NaBH_4 in ethanol, under an atmosphere of L or in the presence of L under argon, followed by precipitation with NaBPh_4, although the products obtained in this way are frequently contaminated with $[\text{FeH(H}_2)(\text{dmpe})_2]\text{BPh}_4$.

cis-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*formato*-O,O′-*iron*-(II) *Tetraphenylborate*.—The complex [FeCl$_2$(dmpe)$_2$] (0.55 g, 1.3 mmol) was dissolved under CO$_2$ in absolute EtOH (20 cm^3) and NaBH$_4$ (0.05 g, *ca.* 1.3 mmol) in ethanol (5 cm^3) was added dropwise *via* syringe. A red-brown solution was obtained. After stirring for *ca.* 10 min, NaBPh$_4$ (0.44 g, *ca.* 1.3 mmol) in EtOH (5 cm^3) was added. A red-orange precipitate formed immediately. It was stirred for 30 min. The product was filtered off, washed with ethanol and hexane and dried *in vacuo*. The product was recrystallised from thf–ethanol as red-orange microcrystals.

The same product was obtained by reaction of [FeH(H$_2$)(dmpe)$_2$]BPh$_4$ with CO$_2$ in thf, in essentially quantitative yield.

cis-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*dithioformato*-S,S′-*iron*(II) *Tetraphenylborate*.—Method (*a*): the complex [FeCl$_2$(dmpe)$_2$] (0.42 g, 1 mmol) in ethanol (20 cm^3) under argon was treated with an excess of CS$_2$ (0.6 cm^3). A dark blue solution was obtained. Addition of 1 equivalent of NaBH$_4$ (0.04 g) in ethanol produced colour changes and eventually a dark brown, sticky solution. Then NaBPh$_4$ in ethanol (0.38 g, *ca.* 1 mmol) was added and a purple precipitate was obtained after stirring for *ca.* 2 h. It was filtered off, washed with ethanol and hexane and dried *in vacuo*. It was recrystallised from thf–ethanol.

Method (*b*): over a slurry containing [FeH(H$_2$)(dmpe)$_2$]BPh$_4$ (0.57 g, 0.84 mmol) in thf (30 cm^3) under argon, CS$_2$ (1 cm^3) was added *via* syringe. There was a change from yellow to purple. The mixture was stirred for 3 h, then it was filtered through Celite, and the solvent removed *in vacuo*, affording a violet solid, which was washed with ethanol and ether and dried *in vacuo*. Yield: quantitative. The complex was recrystallised as above.

Crystal Structure Analysis of trans-[FeH(N$_2$)(dmpe)$_2$]BPh$_4$.—*Crystal data*. $C_{12}H_{33}FeN_2P_4 \cdot C_{24}H_{30}B$, M = 704.4, triclinic, space group $P\bar{1}$ (no. 2), $a = 16.3464(9)$, $b = 16.3150(18)$, $c = 17.6169(11)$ Å, $\alpha = 106.086(7)$, $\beta = 109.721(5)$, $\gamma = 106.136(7)°$, $U = 3874.7(7)$ Å^3, $Z = 4$, $D_c = 1.207$ g cm^{-3}, $F(000) = 1496$, μ(Mo-Kα) = 5.76 cm^{-1}, λ(Mo–K$\bar{\alpha}$) = 0.71069 Å.

The crystals, obtained from acetone, were large, orange-red prisms, up to 7 mm on an edge. A small fragment of one crystal (size *ca.* 0.20 × 0.45 × 0.60 mm) was mounted on a glass fibre. After preliminary photographic examination, the crystal was transferred to an Enraf-Nonius CAD4 diffractometer (with monochromated radiation) where accurate cell dimensions were obtained from goniometer settings of 25 reflections with θ *ca.* 14–15°, each centred in four orientations. Diffraction intensities were then measured for all ($\pm h$, $+k$, $\pm l$) reflections to $\theta_{max} = 22.5°$. During processing, these data were corrected for Lorentz and polarisation effects, slight crystal deterioration, and to ensure no negative nett intensities (using Bayesian statistical methods). An absorption correction was not considered necessary.

10082 Unique data were entered into the SHELX program system[42] and the positions of the two independent iron atoms found by the heavy-atom method. Subsequent electron density and Fourier difference syntheses yielded the positions of all non-hydrogen atoms. Refinement of the 952 atomic parameters in two large blocks by least-squares methods was completed with $R = 0.070$, $R_g = 0.067$[42] for all data, weighted $w = \sigma_F^{-2}$.

In the final cycles of refinement all non-hydrogen atoms were allowed anisotropic thermal parameters. Hydrogen atoms on the dmpe ligands and in the anions were placed in ideal positions and were allowed freely-refined isotropic thermal parameters. The hydridic hydrogens, H(1) and H(2), were located and refined independently. Scattering factors for neutral atoms were taken from ref. 43. All computer programs used in this analysis are noted in ref. 44 and were run on a MicroVAX-II computer in this Laboratory.

Crystal Structure Analysis of trans-[FeH(H$_2$)(dmpe)$_2$]BPh$_4$.—*Crystal data*. $C_{12}H_{35}FeP_4 \cdot C_{24}H_{20}B$, $M = 678.4$, monoclinic, space group $C2/c$ (no. 15), $a = 17.326(1)$, $b = 9.640(1)$, $c = 23.444(2)$ Å, $\beta = 105.230(6)°$, $U = 3778.3$ Å^3, $Z = 4$, $D_c = 1.192$ g cm^{-3}, $F(000) = 1448$, μ(Mo-Kα) = 5.9 cm^{-1}, λ(Mo-K$\bar{\alpha}$) = 0.71069 Å.

One clear yellow square prism recrystallised from acetone of *ca.* 0.10 × 0.10 × 0.19 mm was mounted on a glass fibre, photographed and then transferred to our diffractometer where accurate cell dimensions, from centred reflections with θ *ca.* 10.5°, were refined as described above. Intensity data were collected to $\theta_{max} = 20°$, beyond which there was little to be observed. Intensity control reflections indicated steady deterioration by 23% over the period of measurement, and corrections for this, and for Lorentz–polarisation effects, absorption (from ψ-scan measurements) and to eliminate negative intensities (by Bayesian statistics) were applied.

Of 1767 independent reflections input into the SHELX program system, 1168 had $I \geqslant 2\sigma_I$ and were used in structure determination by heavy-atom methods. A Patterson map suggested that the Fe atom lies on a special position. Subsequent location of ligand and anion atoms confirmed that it lies at the centre of symmetry at ($\frac{1}{4}$, $\frac{1}{4}$, 0). Hydrogen atoms on the dmpe and in the anion were included in idealised positions. In the refinement by full-matrix least-squares methods, all non-hydrogen atoms were allowed anisotropic thermal parameters. The hydride and dihydrogen ligands were found disordered in the centrosymmetrical arrangement. Unrestrained refinement of these hydrogen ligands was not satisfactory, and in the final cycles the three Fe–H and the dihydrogen H–H distances were restrained towards previously determined values.[45] Refinement of the 241 atomic parameters was concluded with $R = 0.062$, $R_g = 0.044$[42] for 1507 reflections with $I > \sigma_I$, weighted $w = \sigma_F^{-2}$. The thermal parameters in the cation were much higher than in the [BPh$_4$]$^-$ anion and indicative of the disorder in the cation.

Scattering values, computer programs and equipment were as described for the previous analysis.

Exchange of Dinitrogen between [FeH(H$_2$)(dmpe)$_2$]BPh$_4$ *and* [Mo(N$_2$)$_2$(dppe)$_2$].—The complexes [FeH(H$_2$)(dmpe)$_2$]BPh$_4$ (0.3 g, 0.42 mmol) and [Mo(N$_2$)$_2$(dppe)$_2$] (0.15 g, 0.16 mmol) in thf (20 cm^3) were stirred under argon at room temperature. The reaction was monitored by IR spectroscopy, which showed the disappearance of ν(N$_2$) in the molybdenum complex and the growth of a new band at 2106 cm^{-1} assignable to ν(N$_2$) in [FeH(N$_2$)(dmpe)$_2$]$^+$.

After 18 h, the solvent was removed *in vacuo*. The residue was extracted with toluene (2 × 10 cm^3) and the extract filtered and concentrated. Addition of MeOH precipitated a lemon-yellow microcrystalline solid, which was filtered off and dried. IR and NMR spectroscopy showed it to be [MoH$_4$(dppe)$_2$].

The residue insoluble in toluene was recrystallised from acetone, affording *trans*-[FeH(N$_2$)(dmpe)$_2$]BPh$_4$.

Both [MoH$_4$(dppe)$_2$] and [FeH(N$_2$)(dmpe)$_2$]BPh$_4$ were collected in *ca.* 70% yield.

The same procedure was followed for the reaction of [FeD(D$_2$)(dmpe)$_2$]BPh$_4$ and [Mo(N$_2$)$_2$(dppe)$_2$]. The products were [MoD$_4$(dppe)$_2$] and [FeD(N$_2$)(dmpe)$_2$]BPh$_4$.

Hydrogen-2 NMR data for [MoD$_4$(dppe)$_2$]: −3.65 (qnt, $^2J_{DP} = 4.4$ Hz) (thf). A deuterium signal was also observed at δ 7.73, possibly due to deuteriation in the phosphine aromatic rings (approximately one deuterium per two phenyl rings).

Bis[1,2-*bis*(*dimethylphosphino*)*ethane*]*dinitrogeniron*(0).—A solution containing [FeH(N$_2$)(dmpe)$_2$]BPh$_4$ (0.75 g, *ca.* 1.1 mmol) in thf was treated with solid KOBu^t (0.14 g, *ca.* 1.4 mmol, slight excess). An immediate darkening of the solution was observed. The reaction was monitored by solution IR spectroscopy. The band at 2106 cm^{-1} gradually disappeared and a strong band appeared at 1975 cm^{-1}.

After stirring for 1.5 h at room temperature, the solution was filtered through Celite under dinitrogen, in order to remove solid $KBPh_4$, or taken to dryness, extracted with Et_2O or thf and filtered through Celite. These solutions contain $[Fe(N_2)(dmpe)_2]$.

IR spectrum: $\nu(N_2)$ 1975 cm^{-1}; $\nu(^{15}N_2)$ 1917 cm^{-1}. $^{31}P-\{^1H\}$ NMR spectrum: A_2B_2 spin system. $\delta(P_A)$ -64.02 (t), $\delta(P_B)$ -74.17 (t), $^2J_{PP} = 26$ Hz.

Bis[1,2-*bis*(*dimethylphosphino*)*ethane*]*carbonyliron*(0).—Carbon monoxide was bubbled for several minutes through an ethereal solution containing $[Fe(N_2)(dmpe)_2]$, prepared as described above. Addition of hexane precipitated a pale orange pyrophoric solid.

IR spectrum: $\nu(CO)$ 1830 cm^{-1} (thf solution); 1818 cm^{-1} (Nujol mull). $^{31}P-\{^1H\}$ NMR spectrum: δ -77.5 (br s, $\Delta_{\frac{1}{2}}$ 57 Hz) (thf–C_6D_6). When solutions of $[Fe(CO)(dmpe)_2]$ in thf are allowed to stand under CO, new $\nu(CO)$ bands appear at 1880 and 1915 cm^{-1}, which have been assigned to $[Fe(CO)_3(dmpe)]$.[33]

The monocarbonyl was also obtained following a procedure similar to that for the preparation of $[Fe(N_2)(dmpe)_2]$, but using $[FeH(CO)(dmpe)_2]BPh_4$ instead of $[FeH(N_2)(dmpe)_2]BPh_4$.

Bis[1,2-*bis*(*dimethylphosphino*)*ethane*](*carbon disulfide*)*iron*(0).—An ethereal solution of $[Fe(N_2)(dmpe)_2]$ was treated with carbon disulfide (1 cm^3, excess). A dark red colour developed immediately, and a precipitate formed. The mixture was stirred for 1 h and then it was filtered, washed with hexane, and dried *in vacuo*. The IR spectrum displayed $\nu(C{=}S)$ at 1050 and 1080 cm^{-1}. A medium, broad band at 1803 cm^{-1} was always present, assigned to $\nu(Fe{-}H)$ in a co-product of the reaction.

$^{31}P-\{^1H\}$ NMR spectrum: $[Fe(CS_2)(dmpe)_2]$, ABCD spin system, $\delta(P_A)$ -83.2, $\delta(P_B)$ -82.2, $\delta(P_C)$ -95.1, $\delta(P_D)$ -68.6, $^2J_{AB} = 0$, $^2J_{AC} = 24.5$, $^2J_{AD} = 57.9$, $^2J_{BC} = 38.4$, $^2J_{BD} = 46.3$, $^2J_{CD} = 19.7$ Hz (thf–C_6D_6). A strong singlet was also present at δ -71, which splits to a doublet when the spectrum is recorded in the proton-coupled mode.

Protonation of $[Fe(N_2)(dmpe)_2]$.—The complex $[FeH(N_2)(dmpe)_2]BPh_4$ (1 mmol) in thf under dinitrogen was treated with 1.1 mmol of KOBu^t, in order to generate $[Fe(N_2)(dmpe)_2]$. The mixture was stirred for 1 h and filtered through Celite, or taken to dryness, extracted with Et_2O, and then filtered through Celite. To the resulting ethereal or thf solution containing $[Fe(N_2)(dmpe)_2]$, an excess of acid was added (concentrated H_2SO_4 or HCl–Et_2O, generated from Me_3SiCl and MeOH in Et_2O). The mixture was stirred at room temperature for 3 h and the solvent then removed *in vacuo*. Aqueous KOH (15 cm^3 of a 40% solution) was added under argon, and the resulting solution was distilled. The first 10 cm^3 of distillate were collected in 15 cm^3 of 0.5 mol dm^{-3} H_2SO_4 aqueous solution. The final solution was made up to 25 or 50 cm^3 using 0.5 mol dm^{-3} H_2SO_4. Ammonia[35] and hydrazine tests[46] were carried out on this solution, with results shown in Table 6. The measurements were made against a blank containing the solution obtained by base distillation of the residue of the reaction of $[FeH(H_2)(dmpe)_2]BPh_4$ plus KOBu^t and HCl in thf under argon.

Gas Evolution Measurements.—To $[FeH(N_2)(dmpe)_2]BPh_4$ (1 mmol) in a 250 cm^3 flask provided with a magnetic stirring bar and a greaseless tap under dinitrogen, thf was added. An addition tube containing *ca.* 1 mole equivalent of solid KOBu^t was attached. The system was evacuated and then frozen in liquid nitrogen. Several freeze-thaw cycles were carried out in order to ensure the complete degassification of the mixture, and the KOBu^t was then mixed in under vacuum. The mixture was stirred for 1 h and frozen, and the permanent gases evolved were measured using a Töpler pump (0.37 mmol of dinitrogen, as confirmed by mass spectrometry).

The mixture was again frozen, and the addition tube was quickly replaced in a countercurrent of dinitrogen by another containing concentrated H_2SO_4 (1.0 cm^3). The system was evacuated again and degassed using several freeze-thaw cycles, and finally the acid was added to the solution and the mixture stirred for 1 h. The gases evolved were measured. The remaining 0.63 mmol of dinitrogen was released as gas, together with approximately 1 mmol of dihydrogen, as inferred from mass spectrometry and gas chromatography. No ammonia or hydrazine was detected after base distillation of the residue from the protonation.

Acknowledgements

This work was carried out with partial support to M. J.-T. under EEC contract SC2*410.

References

1 See, D. J. Lowe and R. N. F. Thorneley, *Biochem. J.*, 1984, **224**, 895.

2 J. Chatt in *Nitrogen Fixation*, eds. W. D. P. Stewart and J. R. Gallon, Academic Press, New York, 1980, p. 1.

3 J. Kim and D. C. Rees, *Nature* (*London*), 1992, **360**, 553; M. M. Georgiadis, H. Komiya, P. Chakrabarti, D. Woo, J. J. Kornuc and D. C. Rees, *Science*, 1992, **257**, 1653; J. Bolin, A. E. Ronco, T. V. Morgan, L. E. Mortenson and N.-M. Xuong, *Proc. Natl. Acad. Sci., U.S.A.*, 1993, **90**, 1078.

4 See, R. R. Eady, *Adv. Inorg. Chem.*, 1991, **36**, 77.

5 G. J. Leigh and M. Jimenez-Tenorio, *J. Am. Chem. Soc.*, 1991, **113**, 5862.

6 A. Hills, D. L. Hughes, M. Jimenez-Tenorio and G. J. Leigh, *J. Organomet. Chem.*, 1990, **391**, C41.

7 M. V. Baker, L. D. Field and D. J. Young, *J. Chem. Soc., Chem. Commun.*, 1988, 546.

8 R. Freeman, *A Handbook of Nuclear Magnetic Resonance*, Longman, Harlow, 1987.

9 J. A. Pople, W. G. Schneider and H. J. Bernstein, *High Resolution NMR*, McGraw-Hill, New York, 1959.

10 R. H. Crabtree and D. G. Hamilton, *J. Am. Chem. Soc.*, 1986, **108**, 4032; M. T. Bautista, K. A. Earl, P. A. Maltby, R. H. Morris, C. T. Schweitzer and A. Sella, *J. Am. Chem. Soc.*, 1988, **110**, 7031; P. G. Jessop and R. H. Morris, *Coord. Chem. Rev.*, 1992, **121**, 155.

11 L. S. van der Slays, J. Eckert, O. Eisendein, J. H. Hall, J. C. Huffman, S. A. Jackson, T. H. Koetzle, G. J. Kulas, P. J. Vergamini and K. G. Coulton, *J. Am. Chem. Soc.*, 1990, **112**, 4831.

12 C. Bianchini, A. Meli, M. Peruzzini, P. Frediani, C. Bohana, M. A. Esteuelas and L. A. Oro, *Organometallics*, 1992, **11**, 138; R. A. Henderson, *J. Chem. Soc., Dalton Trans.*, 1988, 515.

13 M. G. Basallotte, M. Jimenez-Tenorio and G. J. Leigh, unpublished work.

14 G. M. Bancroft, M. J. Mays and B. E. Prater, *J. Chem. Soc. A*, 1970, 956; G. M. Bancroft, M. J. Mays, B. E. Prater and F. P. Stefanini, *J. Chem. Soc. A*, 1970, 2146.

15 B. R. Davis, N. C. Payne and J. A. Ibers, *J. Am. Chem. Soc.*, 1969, **91**, 1210.

16 G. J. Leigh, *Acc. Chem. Res.*, 1992, **25**, 177.

17 G. A. Ghillardi, S. Midollini, L. Sacconi and P. Stoppioni, *J. Organomet. Chem.*, 1981, **205**, 193.

18 *Lange's Handbook of Chemistry*, 13th edn., ed. J. A. Dean, McGraw-Hill, New York, 1985.

19 L. Pu, A. Yamamoto and S. Ikeda, *J. Am. Chem. Soc.*, 1968, **90**, 3896; V. D. Bianco, S. Dorozo and M. Rossi, *J. Organomet. Chem.*, 1972, **35**, 337; C. Bianchini, P. Innocenti, A. Meli, A. Orlandini and G. Scapacci, *J. Organomet. Chem.*, 1982, **233**, 233.

20 M. W. Anker, J. Chatt, G. J. Leigh and A. G. Wedd, *J. Chem. Soc., Dalton Trans.*, 1975, 2369.

21 M. L. H. Green and W. E. Silverthorn, *J. Chem. Soc., Dalton Trans.*, 1973, 301.

22 P. Meakin, L. J. Guggenberger, W. G. Peet, E. L. Muetterties and J. P. Jesson, *J. Am. Chem. Soc.*, 1973, **95**, 1467.

23 J. P. Jesson, in *Transition Metal Hydrides*, Marcel-Dekker, New York, 1971, ch. 4.

24 J. Chatt, R. A. Head, G. J. Leigh and C. J. Pickett, *J. Chem. Soc., Dalton Trans.*, 1978, 1638.

25 M. Aresta and A. Sacco, *Gazz. Chim. Ital.*, 1972, **102**, 755.

26 J. Chatt, B. Bell and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1972, 2492.

27 W. Hussain, G. J. Leigh, H. Mohd.-Ali, C. J. Pickett and D. A. Rankin, *J. Chem. Soc., Dalton Trans.*, 1984, 1703.

28 J. Chatt, J. R. Dilworth and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1973, 612.

29 F. A. Cotton and R. L. Luck, *J. Chem. Soc., Chem. Commun.*, 1988, 1277.

30 See, for example, T. A. Bazenova, M. Gruselle, G. Le Ng, A. E. Shilov and A. K. Shilova, *Kinet. Katal.*, 1982, **23**, 246.

31 R. A. Cable, M. Green, R. E. Mackenzie, P. L. Timms and T. W. Turney, *J. Chem. Soc., Chem. Commun.*, 1976, 270.

32 H. H. Karsch, *Chem. Ber.*, 1984, **117**, 3123.

33 (*a*) S. D. Ittel, C. A. Tolman, A. D. English and J. P. Jesson, *J. Am. Chem. Soc.*, 1978, **100**, 4080; (*b*) S. Komiya, M. Akita, A. Yoza, N. Kasuga, A. Fukuoka and Y. Kai, *J. Chem. Soc., Chem. Commun.*, 1993, 787.

34 M. Akhtar, P. D. Ellis, A. G. Macdiarmid and J. D. Odom, *Inorg. Chem.*, 1972, **71**, 2917.

35 M. W. Weatherburn, *Anal. Chem.*, 1967, **39**, 971; A. L. Chaney and E. P. Marbach, *Clin. Chem.*, 1962, **8**, 130.

36 R. A. Henderson, *J. Chem. Soc., Dalton Trans.*, 1982, 917.

37 R. R. Schrock, R. M. Kolodzieh, A. H. Liu, W. M. Davis and M. G. Vale, *J. Am. Chem. Soc.*, 1990, **112**, 4338.

38 C. Woitha and D. Rehder, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1438.

39 G. J. Leigh, R. Prieto-Alcón and J. R. Sanders, *J. Chem. Soc., Chem. Commun.*, 1991, 920.

40 R. J. Burt, J. Chatt, W. Hussain and G. J. Leigh, *J. Organomet. Chem.*, 1979, **182**, 203.

41 G. S. Girolami, G. Wilkinson, A. M. R. Galas, M. Thornton-Pett and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1985, 1339.

42 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.

43 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 99 and 149.

44 S. N. Anderson, R. L. Richards and D. L. Hughes, *J. Chem. Soc., Dalton Trans.*, 1986, 245.

45 J. S. Ricci, T. F. Koetzle, M. T. Bautista, T. M. Hofstede, R. H. Morris and J. F. Sawyer, *J. Am. Chem. Soc.*, 1989, **111**, 8823.

46 G. W. Watt and J. D. Chrisp, *Anal. Chem.*, 1952, **24**, 2006.

Received 19*th May* 1993; *Paper* 3/02853D