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HYDRIDODINITROGEN AND HYDRIDO COMPLEXES OF IRON(II) WITH THE LINEAR TETRATERTIARY PHOSPHINE HEXAPHENYL-1,4,7,10-TETRAPHOSPHADECANE. CRYSTAL STRUCTURE OF THE COMPLEX $[FeH(N_2)((C_6H_5)_2PC_2H_4P(C_6H_5)C_2H_4P(C_6H_5)C_2H_4P(C_6H_5)_2)]Br \cdot C_2H_5OH$

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Summary

Treatment of the chromophore $[FeX(P_4)]^+$, where X = Br, I and P_4 is the tetradentate open-chain ligand hexaphenyl-1,4,7,10-tetraphosphadecane, with sodium tetrahydroborate under helium or nitrogen gave cationic hydrido- or hydrido-dinitrogen-iron(II) complexes of formula $[FeH(P_4)]X$ and $[FeH(N_2)(P_4)]X$. The structure of the $[FeH(N_2)(P_4)]Br \cdot C_2H_5OH$ complex was determined from three dimensional X-ray data collected by counter methods. The crystals are triclinic, space group $P\bar{1}$ with cell dimensions a = 15.392(8), b = 16.109(10), c = 9.914(5) Å, α = 69.57(8), β = 78.43(9), γ = 68.46(9)°. The structure was solved the heavy atom technique to a final conventional R factor of 0.053 over 1631 independent observed reflections. The structure consists of $[FeH(N_2)(P_4)]^+$ cations, bromide anions, and solvating C_2H_5OH molecules. The metal atom is octahedrally coordinated with the four phosphorus atoms of the ligand in the equatorial plane and with the hydrogen atom and one atom of the dinitrogen molecule in the axial positions.

Introduction

Following the discovery of transition metal compounds containing coordinated molecular nitrogen, the chemistry of nitrogen fixation has been extensively developed, particular interest being devoted to iron and molybdenum derivatives because of the role of these metals in nitrogenase [1]. In general, iron complexes with coordinated molecular nitrogen are stable if they contain tertiary phosphines and hydride ions as co-ligands; octahedral geometry has been attributed to these compounds [2], but no structural information has been reported.

TABLE 1

ANALYTICAL DATA AND PHYSICAL PROPERTIES OF THE COMPLEXES

Compound	Λ_M [a] (cm^2 ohm^{-1} mol^{-1})	Analysis Found(Calcd.)(%)							IR bands (cm^{-1}) [b]
		C	H	N	Fe	I	P	S	
$[FeH(P_4)]Br$	12(A)	62,3 (62,5)	5,5 (5.4)		6,9 (6,9)		15,3 (15,3)		ν(Fe—H)1900
$[FeH(P_4)]I$	11(A)	58,9 (59,0)	5,1 (5,1)		6.4 (6,5)	14.7 (14,8)			ν(Fe—H)1905
$[FeH(N_2)(P_4)]Br \cdot C_2H_5OH$	110(B)	59,7 (59,9)	5,7 (5,6)	3,2 (3,2)	6,4 (6,3)				$\nu(N_2)$2130
$[FeH(N_2)(P_4)]I \cdot C_2H_5OH$	107(B)	56,8 (56,9)	5,3 (5,3)	3,0 (3,0)	6,0 (6,0)		13,3 (13,3)		$\nu(N_2)$2130
$[FeH(CO)(P_4)]Br$	110(B)	61.7 (61,8)	5,2 (5,2)		6,6 (6,7)				ν(Fe—H)1890, ν(CO)1960
$[FeH(CO)(P_4)]I$	108(B)	55,7 (55,8)	4,9 (4,9)		6,2 (6,3)				ν(Fe—H)1895, ν(CO)1965
$[FeH(NCS)(P_4)] \cdot C_2H_5OH$		65,0 (65,0)	6,0 (5,9)	1,7 (1,7)	6,7 (6,7)			3,9 (3,9)	ν(Fe—H)1890, ν(NCS)2105

[a] Molar conductance of ca. 10^{-3} *M* solution in acetone (A) or methylene chloride (B) at 20°C. [b] Stretching vibrations (cm^{-1}) in Nujol mull in the 2000 cm^{-1} region.

We have now studied the reaction of iron(II) halides and the polydentate linear ligand hexaphenyl-1,4,7,10-tetraphosphadecane, $(C_6H_5)_2PC_2H_4P(C_6H_5)$-$C_2H_4P(C_6H_5)C_2H_4P(C_6H_5)_2$, P_4, with $NaBH_4$. Hydrido-iron(II) complexes with or without molecular nitrogen have been isolated according to whether or not nitrogen gas was present in the reaction vessel. The complexes were characterized by the usual physical measurements. A complete X-ray structure determination of the $[FeH(N_2)(P_4)]Br \cdot C_2H_5OH$ derivative has been carried out.

Experimental section

Reagent grade solvents were dried by usual procedures. The ligand hexaphenyl-1,4,7,10-tetraphosphadecane, P_4, was purchased from the Pressure Chemical Co., Pittsburgh, Pa., and was used without further purification.

Physical measurements

Magnetic, conductometric and spectrophotometric (both visible and infrared) measurements were carried out using the methods previously described [3].

Preparation of the complexes

$[FeH(P_4)]X$, X = Br, I. To a solution of the appropriate anhydrous iron(II) salt (1 mmol) in absolute ethanol (20 ml) was added a solution of the ligand (1 mmol) in methylene chloride (30 ml). To the resulting green solution was added the stoichiometric amount of a solution of sodium tetrahydroborate in absolute ethanol (20 ml) under helium. The resulting orange mixture was stirred for 1 h, then the sodium halide was filtered off, and the product isolated by slow evaporation of the solvent under helium. The crystals were filtered off and washed with absolute ethanol and light petroleum.

$[FeH(N_2)(P_4)]X \cdot C_2H_5OH$, X = Br, I. These complexes were prepared by the procedure described above for the hydrido compounds but with use of nitrogen instead of helium. These compounds can be prepared also by bubbling nitrogen through methylene chloride and ethanol solutions of hydrido complexes $[FeH(P_4)]X$. The complexes crystallize with a molecule of ethanol. $\nu(OH) = 3320\ cm^{-1}$ (bromo derivative), $3380\ cm^{-1}$ (iodo derivative).

$[FeH(CO)(P_4)]X$, X = Br, I. These derivatives can be prepared in the same manner as the analogous dinitrogen complexes by carring out the reaction under carbon monoxide or by bubbling carbon monoxide through methylene chloride solutions of the complexes $[FeH(N_2)(P_4)]X$.

$[FeH(NCS)(P_4)]$. A solution of potassium thiocyanate (2 mmol) in absolute ethanol (20 ml) was added to a solution of anhydrous iron(II) bromide (1 mmol) in absolute ethanol (20 ml) under nitrogen. The solution was stirred for 30 minutes, and the potassium bromide then filtered off. The solution was then treated as described above.

Analytical data and physical properties of the complexes are listed in Table 1.

Collection of X-ray data

The crystal used for data collection was an irregular prism of dimensions

0.04 × 0.10 × 0.40 mm. The crystals belong to the triclinic system and the choice of $P\bar{1}$ was later confirmed by the successful refinement of the structure. Unit cell parameters were determined by least squares refinement of the setting angles of 20 reflections carefully centered on a Philips PW 1100 computer-controlled diffractometer. The cell dimensions are a = 15.392(8), b = 16.109(10), c = 9.914(5) Å, α = 69.57(8), β = 78.43(9), γ = 68.46(9)°. The observed density of 1.36 g cm^{-3} measured by flotation agrees with the value of 1.371 g cm^{-3} calculated for two formula units $[FeH(N_2)(P_4)]Br \cdot C_2H_5OH$ per unit cell.

Data collection was carried out using Mo-K_α (0.7107 Å) radiation monochromatized by a graphite crystal at a take off angle of 3.5°. Reflections within $2\theta \leqslant 40°$ were collected using the ω—2θ scan technique, the scan width being calculated according to the formula of Alexander and Smith [4]. Scan range = $A + B \tan \theta$ with A = 0.64 and B = 0.69. The scan speed was 0.05° per second, and stationary background measurements were taken before and after each scan for a time equal to half the scan time. The intensities of three standard reflections measured every two hours showed no systematic trend. After correction for background, the intensities were assigned standard deviations calculated as described elsewhere [5], using the value of 0.04 for the instability factor K. From the 3958 reflections collected, 1631 having $I \geqslant 3\sigma(I)$ were considered observed and included in the following calculations. The intensities were corrected for Lorentz polarization effects, but no absorption correction was applied; the linear absorption coefficient μ beiing 14.6 cm^{-1}.

Solution and refinement

Calculations were carried out on a SEL 32/70 computer using the SHELX-76 programme [6]. Atomic scattering factors and anomalous dispersion corrections were taken from ref. 7. The structure was solved by the heavy atom technique. Successive Fourier syntheses revealed all the remaining non-hydrogen atoms including those belonging to the solvating C_2H_5OH molecule, whose presence was already known from analytical and infrared data.

Full matrix least squares refinements were carried out the function minimized being $\Sigma w(|F_0| - |F_c|)^2$ where $w = 1/\sigma^2(F_0)$. The agreement factors R and R_w are defined as $\Sigma||F_0| - |F_c||/\Sigma|F_0|$ and $[\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2}$, respectively. Anisotropic thermal parameters were used only for the heavier atoms and the carbon atoms of the phenyl rings were treated as rigid groups of D_{6h} symmetry with C—C = 1.395 Å and individual thermal parameters. The hydrogen atoms were introduced in the calculated positions but not refined (C—H = 0.96 Å). Since an attempt to refine the ethanol molecule gave poor bond distances and angles, the solvent atoms were introduced in the following calculations as a fixed contribution, with positional parameters from the Fourier maps.

A ΔF map calculated at the R factor of 0.056 showed four peaks whose intensity was about 0.5 $e/Å^3$. The first three peaks were in the region of the solvent molecule and the fourth, 1.45 Å from the metal atom and *trans* to the nitrogen molecule, was attributed to the hydrido ligand. Even a Fourier map [8] calculated at this stage showed the hydrido ligand at a distance of 1.68 Å. The hydride ligand was successfully refined, the largest shift over error in the last cycle being 0.03. The final agreement factors R and R_w are 0.053 and 0.51 respectively.

TABLE 2

POSITIONAL AND THERMAL PARAMETERS FOR $[FeH(N_2)(P_4)]Br \cdot C_2H_5OH$ [a]

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br	6813(1)	221(1)	7907(2)	722(16)	499(14)	610(15)	−158(11)	−11(12)	−191(12)
Fe	3660(2)	2692(2)	2550(2)	265(15)	334(16)	275(16)	−82(13)	0(12)	−110(12)
P(1)	3286(3)	2378(3)	4934(4)	331(29)	360(29)	273(29)	−101(23)	−51(23)	−82(23)
P(2)	5113(3)	1843(3)	3106(5)	291(28)	328(28)	314(29)	−64(24)	−19(23)	−83(23)
P(3)	4173(3)	2309(3)	542(4)	334(29)	348(30)	294(29)	−87(24)	−3(23)	−121(24)
P(4)	2242(3)	3268(3)	1714(4)	305(29)	353(29)	273(29)	−65(23)	−56(23)	−58(23)
N(1)	3818(9)	3851(11)	2151(14)	278(91)	592(117)	215(90)	−145(92)	−19(68)	−105(92)
N(2)	3918(12)	4517(11)	1894(19)	755(129)	414(114)	839(139)	−234(110)	−194(98)	−89(105)
C(1)	4379(9)	1818(10)	5847(15)	286(42)					
C(2)	5047(10)	1170(10)	5005(15)	352(43)					
C(3)	5675(11)	1019(11)	2015(17)	476(48)					
C(4)	5001(11)	1119(10)	973(17)	495(50)					
C(5)	3201(10)	2278(10)	−218(16)	362(44)					
C(6)	2368(10)	3125(10)	−103(16)	384(45)					
H	3401(64)	1798(67)	2935(100)	131(304)					
O	1570	8740	3080	1500					
C(43)	830	8950	1900	2000					
C(44)	1410	8430	1340	2000					

[a] The form of the thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ all quantities are multiplied by 10^4.

TABLE 3

THERMAL AND DERIVED POSITIONAL PARAMETERS OF GROUP ATOMS FOR $[FeH(N_2)(P_4)]Br \cdot C_2H_5OH$ [a]

Atom	X	Y	Z	$U(Å^2)$
C(7)	2660(5)	3357(7)	5671(10)	266(40)
C(8)	3135(5)	3958(7)	5619(10)	328(44)
C(9)	2653(5)	4782(7)	5983(10)	478(49)
C(10)	1694(5)	5005(7)	6401(10)	405(46)
C(11)	1219(5)	4404(7)	6453(10)	533(51)
C(12)	1701(5)	3580(7)	6089(10)	401(46)
C(13)	2675(7)	1509(7)	5890(8)	310(42)
C(14)	2548(7)	955(7)	5183(8)	384(46)
C(15)	2140(7)	262(7)	5944(8)	510(51)
C(16)	1860(7)	122(7)	7412(8)	590(55)
C(17)	1988(7)	676(7)	8119(8)	538(52)
C(18)	2395(7)	1369(7)	7358(8)	395(46)
C(19)	5997(8)	2397(7)	2899(9)	386(45)
C(20)	6546(8)	2188(7)	4010(9)	531(51)
C(21)	7272(8)	2562(7)	3752(9)	597(54)
C(22)	7448(8)	3145(7)	2383(9)	750(62)
C(23)	6899(8)	3354(7)	1272(9)	610(55)
C(24)	6174(8)	2980(7)	1530(9)	508(50)
C(25)	4709(7)	3039(5)	−977(12)	389(45)
C(26)	5506(7)	2653(5)	−1799(12)	539(52)
C(27)	5885(7)	3237(5)	−2972(12)	774(64)
C(28)	5468(7)	4207(5)	−3323(12)	618(56)
C(29)	4672(7)	4592(5)	−2501(12)	557(52)
C(30)	4292(7)	4008(5)	−1328(12)	341(43)
C(31)	1599(7)	4527(7)	1401(10)	296(41)
C(32)	1067(7)	5048(7)	217(10)	405(46)
C(33)	601(7)	6003(7)	−15(10)	510(51)
C(34)	666(7)	6439(7)	938(10)	626(56)
C(35)	1198(7)	5918(7)	2122(10)	588(54)
C(36)	1664(7)	4962(7)	2354(10)	421(46)
C(37)	1312(7)	2752(6)	2659(11)	355(44)
C(38)	673(7)	3101(6)	3702(11)	468(49)
C(39)	6(7)	2672(6)	4460(11)	561(53)
C(40)	−22(7)	1894(6)	4174(11)	569(53)
C(41)	617(7)	1545(6)	3131(11)	573(54)
C(42)	1284(7)	1974(6)	2373(11)	479(49)

[a] All quantities are multiplied by 10^4.

Final positional and thermal parameters are listed in Tables 2 and 3. Tables of structure factors may be obtained from the authors on request.

Results and discussion

Solutions of the cationic complexes $[FeX(P_4)]^+$ (X = Br, I) [9] react with sodium tetrahydroborate and nitrogen gas, at room temperature and atmospheric pressure, to give crystalline complexes of formula $[FeH(N_2)(P_4)]X$. When the reaction between the chromophore $[FeX(P_4)]^+$ and tetrahydroborate is carried out under helium gas, hydrido complexes of formula $[FeH(P_4)]X$ are obtained. These hydrides react in solution with nitrogen to give the hydridodinitrogen complexes $[FeH(N_2)(P_4)]X$. The above results may be summarized as follows:

$$\begin{tikzcd}[\mathrm{FeX(P_4)}]^+ \arrow[r, "\mathrm{BH_4}^-", "\text{under He}"'] \arrow[rr, bend right, "\mathrm{BH_4}^-", "\text{under } \mathrm{N_2}"'] & [\mathrm{FeH(P_4)}]^+ + \mathrm{X}^- \arrow[r, "\text{under } \mathrm{N_2}"'] & [\mathrm{FeH(N_2)(P_4)}]^+ + \mathrm{X}^-\end{tikzcd}$$

When the same reactions are carried out with solutions of $[Fe(NCS)_2(P_4)]$ [9] only the hydride derivative $[FeH(NCS)(P_4)]$ is obtained.

$$[\mathrm{Fe(NCS)_2(P_4)}] \xrightarrow[\text{under } \mathrm{N_2}]{\mathrm{BH_4}^-} [\mathrm{FeH(NCS)(P_4)}]$$

All the complexes are diamagnetic and air sensitive; the dinitrogen derivatives are 1 : 1 electrolytes in acetone and slowly decompose in chlorinated solvents such as chloroform and methylene chloride even under nitrogen; the hydrides of formula $[FeH(P_4)]X$ are 1 : 1 electrolytes in methylene chloride [10], Table 1. The thiocyanate derivative is a non-electrolyte. Infrared spectra of the complexes in the 2000 cm^{-1} region are reported in Table 1. All the hydrido derivatives show a band of medium intensity at ca. 1900 cm^{-1} assigned to the

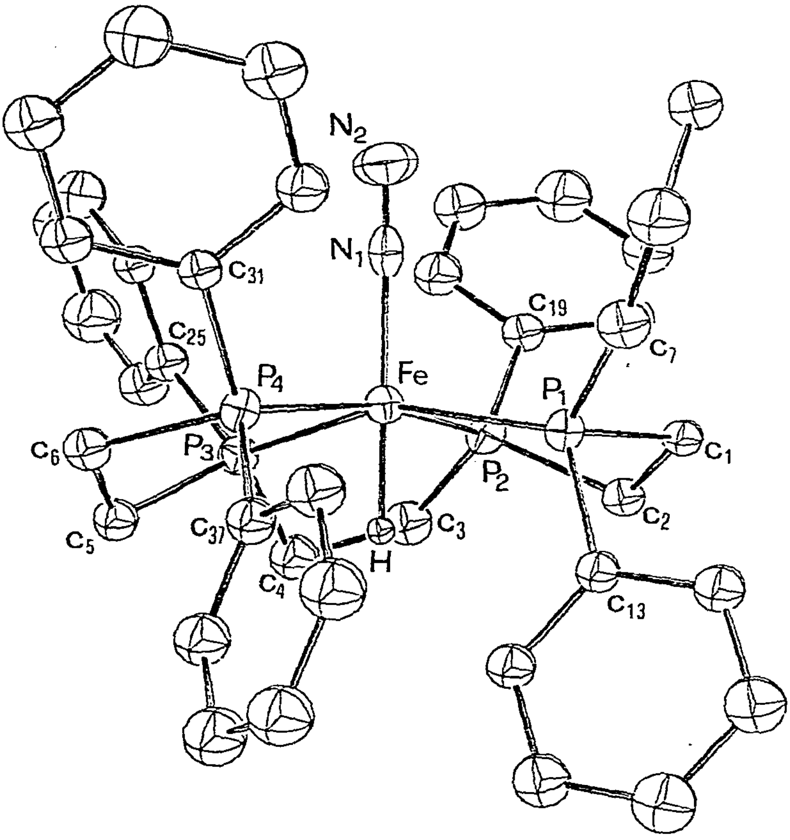

Fig. 1. Perspective view of the $[FeH(N_2)(P_4)]^+$ cation.

Fe—H stretching vibration; the ν(CN) stretching frequency at 2105 cm^{-1} in the thiocyanate derivative is characteristic of the ion bound to the metal through the nitrogen atom [11]. Hydrido-dinitrogen complexes show an intense band at 2130 cm^{-1} which can be attributed to the $\nu(N_2)$ stretching vibration; no bands attributable to the Fe—H stretching mode were observed in the spectra. Other hydrido-dinitrogen-iron(II) complexes also fail to exhibit Fe—H stretching frequencies [12].

The reaction of the hydrido-dinitrogen complexes with carbon monoxide [13] afforded $[FeH(CO)(P_4)]X$ compounds, whose composition was confirmed by infrared spectroscopy and conductivity measurements.

The molecular structure of $[FeH(N_2)(P_4)]Br$ consists of discrete $[FeH(N_2)(P_4)]^+$ cations, Br^- anions, and solvating C_2H_5OH molecules. Figure 1 shows a perspective view of the cation. Selected bond distances and angles are reported in Table 4. The metal atom is octahedrally coordinated, with the four phos-

TABLE 4

BOND LENGTHS (Å) AND ANGLES (deg)

About the metal atom			
Fe—P(1)	2.238(5)	Fe—N(1)	1.865(15)
Fe—P(2)	2.213(5)	Fe—H	1.53(9)
Fe—P(3)	2.200(5)	N(1)—N(2)	1.076(15)
Fe—P(4)	2.239(5)		
P(1)—Fe—P(2)	86.0(2)	N(1)—Fe—P(3)	104.9(4)
P(1)—Fe—P(3)	153.9(2)	N(1)—Fe—P(4)	95.7(4)
P(1)—Fe—P(4)	101.4(2)	N(1)—Fe—H	172.8(3.5)
P(2)—Fe—P(3)	82.5(2)	H—Fe—P(1)	77.4(3.5)
P(2)—Fe—P(4)	165.1(2)	H—Fe—P(2)	90.4(3.4)
P(3)—Fe—P(4)	85.4(2)	H—Fe—P(3)	79.3(3.5)
N(1)—Fe—P(1)	99.5(4)	H—Fe—P(4)	78.7(3.4)
N(1)—Fe—P(2)	95.9(4)	Fe—N(1)—N(2)	178.5(1.7)
In the rest of the cation			
P(1)—C(1)	1.84(1)	P(3)—C(25)	1.82(1)
P(1)—C(7)	1.83(1)	P(4)—C(6)	1.86(2)
P(1)—C(13)	1.85(1)	P(4)—C(31)	1.84(1)
P(2)—C(2)	1.82(1)	P(4)—C(37)	1.85(1)
P(2)—C(3)	1.86(2)	C(1)—C(2)	1.52(2)
P(2)—C(19)	1.83(1)	C(3)—C(4)	1.54(2)
P(3)—C(4)	1.83(1)	C(5)—C(6)	1.51(2)
P(3)—C(5)	1.83(1)		
Fe—P(1)—C(1)	108.5(2)	C(4)—P(3)—C(5)	106.2(7)
Fe—P(1)—C(7)	118.6(3)	C(4)—P(3)—C(25)	107.6(6)
Fe—P(1)—C(13)	120.2(3)	C(5)—P(3)—C(25)	103.4(6)
C(1)—P(1)—C(7)	103.0(3)	Fe—P(4)—C(6)	108.9(5)
C(1)—P(1)—C(13)	99.9(3)	Fe—P(4)—C(31)	118.2(3)
C(7)—P(1)—C(13)	103.9(4)	Fe—P(4)—C(37)	121.0(4)
Fe—P(2)—C(2)	107.1(5)	C(6)—P(4)—C(31)	103.1(5)
Fe—P(2)—C(3)	111.4(5)	C(6)—P(4)—C(37)	101.9(6)
Fe—P(2)—C(19)	121.1(4)	C(31)—P(4)—C(37)	101.3(5)
C(2)—P(2)—C(3)	108.9(7)	P(1)—C(1)—C(2)	105.9(1.0)
C(2)—P(2)—C(19)	105.4(6)	P(2)—C(2)—C(1)	108.9(1.0)
C(3)—P(2)—C(19)	102.5(6)	P(2)—C(3)—C(4)	111.0(1.1)
Fe—P(3)—C(4)	108.8(5)	P(3)—C(4)—C(3)	108.8(1.1)
Fe—P(3)—C(5)	109.6(5)	P(3)—C(5)—C(6)	107.7(1.0)
Fe—P(3)—C(25)	120.3(4)	P(4)—C(6)—C(5)	110.0(1.0)

phorous atoms of the ligand in the equatorial plane and with the hydrogen atom and one atom of the nitrogen molecule in the axial positions.

The metal atom is 0.34 Å out of the equatorial plane towards the nitrogen molecule, this distortion is caused mainly by the requirements of the linear ligand whose ethylenic chains do not allow the P—Fe—P angles to reach 90°. In this way the ligand is bent towards the hydride to take advantage of the reduced steric requirement of the hydride.

The Fe—P bond distances are fully comparable with the values reported for the confacial bisoctahedral complex $[Fe_2(\mu\text{-}SH)_3(PPP)_2]ClO_4$, where PPP = bis[2-(diphenylphosphino)ethyl]phenylphosphine [14]. The nitrogen molecule is "end on" bonded to the metal atom with a Fe—N—N angle of 178.5(1.7)°. The value of the Fe—N distance of 1.865(15) Å seems to exclude multiple bonding and support for this is provided by the short N—N distance of 1.076(15) Å which is shorter than that of 1.098 Å reported for molecular nitrogen [15], and matches the value of 1.074(7) reported for the complex $[RhH(N_2)(P(C_6H_5)(C_4H_9)_2)_2]$ [16]. Although the N—N distance must be regarded with caution, being uncorrected for thermal motion, the $\nu(N_2)$ stretching frequency is also indicative of a weak metal—N_2 interaction.

The hydrido ligand is *trans* to the nitrogen molecule, with a N—Fe—H angle of 172.8(3.5)° and a Fe—H bond distance of 1.53(9) Å, which matches the average value recently reported for terminal Fe—H bonds [17].

A five-coordinate structure with a probable distorted square pyramidal geometry is assigned to the hydrido complexes on the basis of the physical and chemical measurements (Table 1). The five-coordinate geometry is rather unexpected for these compounds when compared with that of other hydridoiron(II) complexes [2c,12]. In particular, the $[FeHX(L_2)]$ compounds (X = halide, L = $(C_2H_5)_2PC_2H_4P(C_2H_5)_2$, $(CH_3)_2PC_2H_4P(CH_3)_2$) having the same potential donor set (HXP_4), are octahedral, with hydride hydrogen and halogen *trans* to each other. The non-coordination of the halogen atom in the present compounds may be attributed to the steric requirements of the P_4 ligand, and inspection of the structure of the closely related compound $[FeBr(P_4)]^+$ which contain the same P_4 ligand [18] shows that the ligand arrangement seems to prevent the coordination of a sixth ligand even as small as hydride. Furthermore, in the structure reported here there are some short contact distances between the phenyl rings and the hydrido and nitrogen ligands.

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