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Reduction of Dinitrogen to Ammonia and Hydrazine in Iron(0) and Molybdenum(0) Complexes Containing the $N(CH_2CH_2PPh_2)_3$ Ligand. Crystal Structures of $[FeH(L)(N(CH_2CH_2PPh_2)_3)][BPh_4]$ (L = N_2, CO)

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The recent reports by Leigh, Jimenez-Tenorio, et al.[2] of the formation of ammonia from the reaction of HCl with $[Fe(N_2)(dmpe)_2]$ (dmpe = $Me_2PCH_2CH_2PMe_2$), $[Fe(N_2)(depe)_2]$ (depe = $Et_2PCH_2CH_2PEt_2$), and $[Fe(N_2)\{(Ph_2PCH_2CH_2PCH_2)_2\}]$ prompted us to investigate a similar iron(0) dinitrogen complex containing a chelating ligand. Although a number of iron(0) dinitrogen complexes were already known,[3] including $[Fe(N_2)(depe)_2]$, for which a crystal structure has been reported,[3d] we focused our attention on preparing the new complex $[Fe(N_2)(NP_3)]$ (NP_3 = $N(CH_2CH_2PPh_2)_3$) for two reasons. First, we were studying the reactions of the new complex *cis*-$[Mo(N_2)_2(NP_3)]$,[4] in which the tetradentate ligand imposes mutually cis stereochemistry on the two dinitrogen ligands. Second, we thought that the low yields of ammonia reported by Leigh et al. might have been due to the instability of the iron(0) complex; it was not isolated and was reported to lose dinitrogen in solution. The structure was reported to be trigonal bipyramidal according to the ^{31}P NMR spectrum with a phosphorus atom trans to the dinitrogen ligand. A phosphine ligand is well-known to labilize a trans dinitrogen ligand.[5] Therefore, the NP_3 ligand was chosen because it was likely that the nitrogen atom of NP_3 would be trans to dinitrogen in $[Fe(N_2)(NP_3)]$. The starting point for this work was the known complex $[FeH(N_2)(NP_3)][BPh_4]$.[6] In the course of this work we determined the crystal structure of $[FeH(N_2)(NP_3)][BPh_4]$ and its CO analogue. The syntheses of $[Fe(N_2)(NP_3)]$ and $[Mo(N_2)_2(NP_3)]$ and the results of reactions with CO and HBr are reported.

Experimental Section

Materials and Methods. All manipulations were carried out in an atmosphere of dried dinitrogen, argon, carbon monoxide, or dihydrogen by using standard Schlenk techniques or in a dinitrogen atmosphere glovebox or by using a high-vacuum line. All solvents were rigorously dried by heating at reflux over an appropriate drying agent, followed by distillation under dinitrogen as described previously.[7] The $^{31}P\{^1H\}$ and ^1H NMR spectra were obtained at room temperature with a Varian VXR 200 spectrometer operating at 80.984 MHz (^{31}P) and 200.00 MHz (^1H). Chemical shifts were referenced to PPh_3 (−5.8 ppm vs 85% H_3PO_4 = 0.0 ppm) and Me_4Si (^1H). Infrared spectra were recorded using an Analect RFX-65 FTIR spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Chemicals were purchased from commercial sources and used without further purification except for anhydrous HBr, which was purified by a series of trap-to-trap distillations on the vacuum line. NP_3 **[CAUTION: THE INTERMEDIATE $N(CH_2CH_2Cl)_3$ IS A MUSTARD AGENT. IT MUST BE HANDLED ONLY IN A WELL-VENTILATED HOOD. INHALATION AND CONTACT WITH ANY PARTS OF THE BODY MUST BE AVOIDED AND SUITABLE PROTECTIVE GLOVES MUST BE WORN AT ALL TIMES]**,[8] $[FeH(L)(NP_3)][BPh_4]$ (L = N_2, **1**; L = CO, **2**),[6] and $[MoBr_3(THF)_3]$[9] were prepared according to literature procedures.

Synthesis of $[FeH(N_2)(NP_3)][BPh_4]$ (1). This complex was prepared in 69% yield according to a published procedure,[6] but using methanol in place of ethanol. ^{31}P NMR (THF): δ 65.9 (d, 2, J_{PP} = 14.35 Hz), 53.0 (t, 1). ^1H NMR (THF): δ −7.5 (dt, J_{PH} = 65.7 Hz (cis), J_{PH} = 41.7 Hz (trans), hydride). IR (KBr): $\nu(NN)$ 2090 and $\nu(FeH)$ 1913 cm^{-1}. Single crystals were grown by diffusion of pentane into a THF solution of $[FeH(N_2)(NP_3)][BPh_4]$.

Synthesis of $[FeH(CO)(NP_3)][BPh_4]$ (2).[6] Carbon monoxide was bubbled (12 h) through a THF solution of $[FeH(N_2)(NP_3)][BPh_4]$. The product was obtained by removal of solvent *in vacuo.* ^{31}P NMR (CD_2Cl_2): δ 71.5 (d, 2, J_{PP} = 16.13 Hz), 63.2 (t, 1). ^1H NMR (CD_2Cl_2): δ −9.3 (dt, J_{PH} = 64.5 Hz (cis), J_{PH} = 34.9 Hz (trans), hydride). IR (KBr): $\nu(CO)$ and $\nu(FeH)$ 1913 cm^{-1}. Single crystals were grown by diffusion of pentane into a CH_2Cl_2 solution of $[FeH(CO)(NP_3)][BPh_4]$.

Synthesis of $[Fe(N_2)(NP_3)]$ (3). Two milliliters of 1.6 M *n*-BuLi (3.2 mmol) in hexanes (Aldrich) was added dropwise to a stirred mixture of $[FeH(N_2)(NP_3)][BPh_4]$ (0.293 g, 0.277 mmol) and THF (25 mL) cooled to 10 °C. After 0.25 h, dropwise addition of pentane (100 mL) caused precipation of a purple solid (0.26 g), which was filtered off and dried *in vacuo.* The purple solid was a mixture of **3** and $LiBPh_4$. ^{31}P NMR (THF): δ 62.08 (s). IR (KBr): $\nu(NN)$ 1967 cm^{-1}. Addition of methanol to the purple solid as a method of removing $LiBPh_4$ resulted in the regeneration of $[FeH(N_2)(NP_3)]^+$ according to the IR spectrum.

It was possible to remove $LiBPh_4$ by addition of 18-crown-6 in the pentane which was used to precipitate the purple product, but that caused contamination with crown ether.

Synthesis of $[MoBr_3(NP_3)]$. NP_3 (3.4 g, 5.0 mmol) dissolved in a mixture of CH_2Cl_2 (10 mL) and THF (10 mL) was added to a stirred solution of $[MoBr_3(THF)_3]$ (3.16 g, 5.8 mmol) in a mixture of CH_2Cl_2 (20 mL) and THF (20 mL). After the mixture was stirred for 14 h, unreacted $[MoBr_3(THF)_3]$ was removed by filtration. The yellow product was precipitated from the red filtrate by addition of diethyl ether (50 mL), filtered off, washed with diethyl ether (20 mL), and dried *in vacuo.* The yield was 4.85 g (98% yield based upon NP_3). Anal. Calcd (found) for $C_{42}H_{42}Br_3MoNP_3$: C, 50.9 (48.9); H, 4.2 (4.2). μ_{eff} = 3.90 μ_B (Evans' method; $CDCl_3$).

Synthesis of *cis*-$[Mo(N_2)_2(NP_3)]$ (4). To a stirred mixture of $[MoBr_3(NP_3)]$ (1.0 g, 1.0 mmol) in THF (100 mL) in a Fisher-Porter bottle was added sodium amalgam (0.50 g, 22 mmol of Na in 60 g of Hg). The bottle was pressurized to 75 psi with dinitrogen and the mixture allowed to stir for 12 h. The reaction solution was decanted from the amalgam. A sample of the filtrate showed only two resonances (a doublet and triplet) in the ^{31}P NMR spectrum and two peaks in the IR (KBr) spectrum at 1990 (vs) and 1900 (vs) cm^{-1} due to $\nu(NN)$. Solvent was removed from the filtrate by bubbling with dinitrogen. The resulting solid was dissolved in benzene (20 mL) and the suspension filtered. A rust-brown solid was obtained by the addition of 100 mL

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of pentane or diethyl ether, collected by filtration, and dried *in vacuo*. ^{31}P NMR (THF): δ 47.8 (d, 2, J_{PP} = 16.81 Hz), 44.0 (t, 1). Anal. Calcd (found) for $C_{42}H_{42}MoN_5P_3$: C, 62.56 (62.37); H, 5.21 (5.43); N 5.21 (1.83). The cyclic voltammogram of *cis*-[$Mo(N_2)_2(NP_3)$] in THF at −78 °C showed a quasi-reversible wave centered at −1.06 V vs the ferrocenium/ferrocene couple assigned to Mo^I/Mo^0. Complex **4** could also be prepared in similar yields by a one-step method[10] using $MoCl_5$ and NP_3.[4]

More frequently, a brown product was isolated from the reaction. Typically, once the solution was removed from the amalgam, *cis*-[$Mo(N_2)_2(NP_3)$] began to decompose, as evidenced by the appearance of a singlet in the ^{31}P NMR spectrum at ca. −20 ppm due to free NP_3 or an arm of NP_3 and broadening of resonances of *cis*-[$Mo(N_2)_2(NP_3)$]. A second N_2-containing complex was a frequent minor coproduct in this reaction which is believed to be [$Mo(N_2)(NP_3)$]. ^{31}P NMR (THF): δ 63.8 (s). IR (KBr): ν(NN) 1934 cm^{-1}.

Synthesis of [$Mo(CO)(N_2)(NP_3)$] (5). Carbon monoxide was bubbled (0.34 h) through the filtrate obtained after decanting the solution from a preparation of *cis*-[$Mo(N_2)(NP_3)$] from the amalgam (as described above). Solvent was removed *in vacuo*. The solid was dissolved in benzene (15 mL), the solution filtered, and yellow [$Mo(CO)(N_2)(NP_3)$] precipitated by addition of pentane (100 mL). ^{31}P NMR (THF): δ 48.40 (d, 2, J_{PP} = 16.98 Hz), 28.01 (t, 1). IR (KBr): ν(CO) and ν(NN) 1946, 1882, and 1788 cm^{-1}. The cyclic voltammogram of [$Mo(CO)(N_2)(NP_3)$] in THF at room temperature showed a quasi-reversible wave centered at −0.81 V vs the ferrocenium/ferrocene couple assigned to Mo^I/Mo^0.

Synthesis of *cis*-[$Mo(CO)_2(NP_3)$] (6).[11] Carbon monoxide was bubbled (30 h) through the filtrate obtained after decanting the solution from a preparation of *cis*-[$Mo(N_2)(NP_3)$] from the amalgam (as described above). The reaction was monitored by ^{31}P NMR spectroscopy until no more change occurred. Solvent was removed *in vacuo*. The solid was dissolved in benzene (15 mL), the solution filtered, and product precipitated by the addition of diethyl ether (100 mL). Product was recrystallized by dissolving in benzene (10 mL) and adding hexane (100 mL). Yellow [$Mo(CO)_2(NP_3)$] was collected in low yield by filtration and dried *in vacuo*. ^{31}P NMR (THF): δ 53.10 (d, 2, J_{PP} = 19.00 Hz), 36.88 (t, 1). IR (KBr): ν(CO) 1835 (vs) and 1750 (vs) cm^{-1}. The cyclic voltammogram of [$Mo(CO)_2(NP_3)$] in THF at room temperature showed a quasi-reversible wave centered at −0.74 V vs the ferrocenium/ferrocene couple assigned to Mo^I/Mo^0.

Electrochemistry. Cyclic voltammetry experiments were carried out in a two-compartment, three-electrode cell fitted with a Luggin probe (connected to a silver pseudoreference electrode) using a Hi-Tek potentiostat type DT2101 and Chemical Electronics (Birtley) Ltd. waveform generator, type 01, and a Philips PM8041 X-Y recorder. The cell was fitted with a platinum-wire or -disk working electrode, a tungsten secondary electrode, and a silver-wire pseudoreference electrode. The electrolyte was 0.2 M [NBu^n_4][BF_4] in THF solution. Potentials quoted are referenced to the ferrocenium/ferrocene (Fc^+/Fc) couple = 0.00 V (0.535 V vs the SCE in this electrolyte).

General Procedure for Ammonia- and Hydrazine-Forming Reactions. HBr (20 mol) and solvent were condensed onto the sample at −196 °C and allowed to warm to room temperature. Details of the experimental and analytical procedures are given in ref 7. Ammonia was determined by the indophenol method,[12] and hydrazine, by the *p*-(dimethylamino)benzaldehyde method.[13]

X-ray Diffraction Studies of 1 and 2. Crystallographic details are provided in the tables and in the supplementary material.

Results and Discussion

[$Fe(N_2)(NP_3)$] (3) was prepared by the deprotonation of [$FeH(N_2)(NP_3)$][BPh_4] (1) with *n*-BuLi (eq 1) by following a

$$[FeH(N_2)(NP_3)][BPh_4] + LiBu^n \rightarrow [Fe(N_2)(NP_3)] + Li[BPh_4] + BuH \quad (1)$$

procedure analogous to that reported by Leigh and Jimenez-Tenorio[2] for the deprotonation ($KOBu^t$) of [$FeH(N_2)(dmpe)_2$][BPh_4]. The isolated product from the reaction was a mixture of purple **3** and Li[BPh_4], and although **3** appeared to be more stable than [$Fe(N_2)(dmpe)_2$], it did slowly decompose over a period of days under dinitrogen at room temperature. Subsequent reactions of **3** reported below were carried out using this mixture.

In THF solution, **3** exhibits a single resonance at 62.1 ppm in the $^{31}P\{^1H\}$ NMR spectrum, indicating a trigonal bipyramidal geometry with N_2 occupying one axial position and the nitrogen atom of the NP_3 ligand occupying the other. This assignment contrasts with the trigonal bipyramidal structure of [$Fe(N_2)(depe)_2$] determined by X-ray structure analysis[3d] with the dinitrogen ligand in the equatorial plane. Complex **3** slowly decomposed in solution ($t_{1/2} \approx$ 4 h in THF at 23 °C). The initial step in the decomposition of **3** was the dissociation of an arm of the NP_3 ligand. As the singlet at 62 ppm decreased in intensity, a pair of resonances in the ratio 2:1 grew in at 40 and −21 ppm, respectively. The latter resonance is very similar to that of free NP_3 at −21 ppm. Eventually, a brown solid formed. In the IR spectrum (KBr) of **3**, ν(NN) appears at 1967 cm^{-1}, compared with 2090 cm^{-1} for **1**,[6] 1955 cm^{-1} for [$Fe(N_2)(depe)_2$],[3d] and 1975 cm^{-1} for [$Fe(N_2)(dmpe)_2$], which was obtained in solution under N_2.[2]

***cis*-[$Mo(N_2)_2(NP_3)$] (4), [$Mo(CO)(N_2)(NP_3)$] (5), and *cis*-[$Mo(CO)_2(NP_3)$] (6).** Complex **4** is less stable than other bis(dinitrogen) complexes of molybdenum(0) that we have worked with, particularly toward oxidation and alcohols. Indeed, cyclic voltammetry showed that **4** was oxidized ca. 200 mV more easily than *cis*-[$Mo(N_2)_2(PMe_2Ph)_4$][5] and ca. 100 mV more easily than *trans*-[$Mo(N_2)_2(depe)_2$].[14] While in THF solution under dinitrogen and over sodium amalgam, **4** appeared to be stable. In fact, many reactions of **4** were carried out using the decantate from the preparation of **4** (see Experimental Section) rather than "purified" **4**. Once isolated, **4** began to decompose. One reason for the instability may be the trans-labilizing effect of a phosphine ligand on one of the N_2 ligands as previously noted (vide infra).[5] The $^{31}P\{^1H\}$ NMR spectrum of **4** indicated relatively rapid appearance of a resonance due to a free arm of the NP_3 ligand as the resonances due to **3** began to decrease in intensity. A further problem which undoubtedly contributed to the decomposition of **4** was the presence of paramagnetic impurities that could not be removed during purification. For example, the very stable complex *trans*-[$Mo(N_2)_2(dppe)_2$] was prepared using [$MoBr_3(THF)_3$]. The product of this reaction was brown, but upon washing with methanol, pure orange *trans*-[$Mo(N_2)_2(dppe)_2$] remained. Washing **4** with methanol and similar solvents caused decomposition and loss of dinitrogen.

The ^{31}P NMR and IR spectral data support a structure for **4** in which NP_3 is behaving as a tetradentate ligand (as observed in the crystal structures of [$FeH(L)(NP_3)$][BPh_4] where L = CO, N_2; vide infra) with the two N_2 ligands mutually cis. Complex **4** is unique in having two N_2 ligands that are trans to different types of donor atoms: P and N (of NP_3). The difference in chemical behavior between these two N_2 ligands was noted in the reaction of **4** with CO. The initial product [$Mo(CO)(N_2)(NP_3)$] (**5**) was formed rapidly. The ^{31}P NMR spectrum of **5** leads us to conclude that the N_2 ligand trans to the phosphorus atom was replaced by CO, since the chemical shift of this phosphorus atom changed by 16 ppm upfield compared to a change of only 0.6 ppm for the other two equivalent phosphorus

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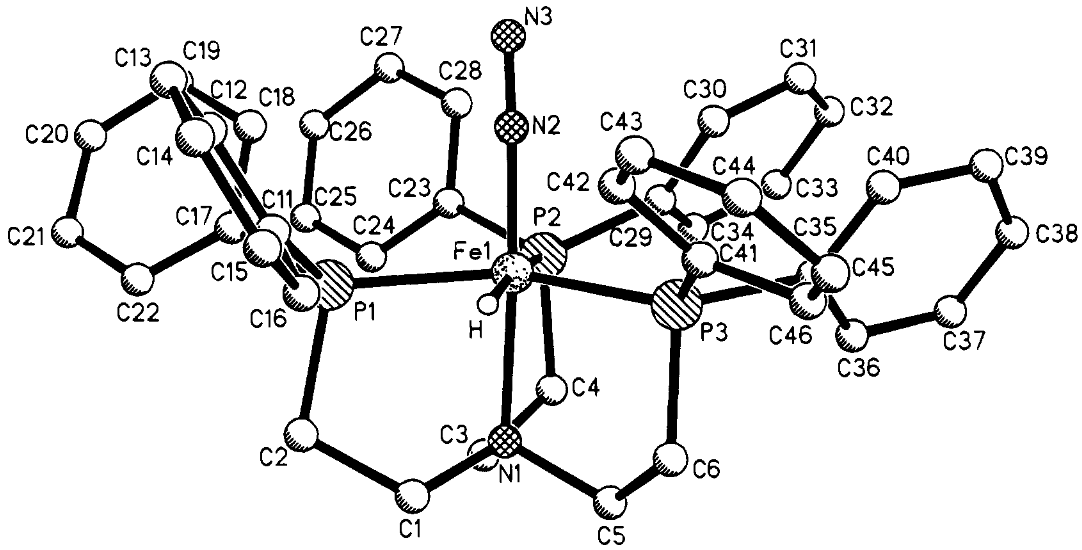

Figure 1. ORTEP view of the structure of $[FeH(N_2)(N(CH_2CH_2PPh_2)_3)]^+$ showing the atom-labeling scheme. In the carbonyl analogue, the carbonyl carbon atom is labeled C(47).

atoms. Replacement of the second N_2 ligand occurred much more slowly. The stepwise replacement of N_2 by CO had the expected effect of increasing the oxidation potential at which the molybdenum(0) complex was oxidized: **4**, −1.06 V; **5**, −0.81 V; **6**, −0.74 V.

Reactions $[Fe(N_2)(NP_3)]$ and $[Mo(N_2)_2(NP_3)]$ with HBr. Hydrazine and a very small amount of ammonia were produced when **3** was reacted with anhydrous HBr in CH_2Cl_2. The highest yield of hydrazine that we have recorded so far was 0.11 mol/mol of **3**. The reduction of N_2 to hydrazine requires four electrons, which are unlikely to come from a single iron center. A likely stoichiometry[2] for the reaction is shown in eq 2. The maximum yield of hydrazine would be 0.5 mol/mol of

$$2\{Fe^0(N_2)\} + 4H^+ \rightarrow N_2H_4 + 2\{Fe^{II}\} + N_2 \qquad (2)$$

3. Thus the highest yield of hydrazine that we obtained was 22% on the basis of this stoichiometry. This reaction could be accomplished by the initial formation of a diazene complex of iron(II) followed by disproportionation to yield hydrazine and dinitrogen. In the majority of examples in which hydrazine is the product of the protonation of coordinated dinitrogen, the N_2 ligand occupies a bridging position in the initial complex.[15] The maximum yield of ammonia obtained was 0.03 mol/mol of **3**. These results contrast with those obtained in the reaction of $[Fe(N_2)(dmpe)_2]$ with HCl in THF where ammonia (0.12 mol/mol of Fe) was formed but no hydrazine; hydrazine (0.004 mol/mol of Fe) and ammonia (0.066 mol/mol of Fe) were produced when $MgCl_2$ was added.[2] Furthermore, no ammonia was reported when $[Fe(N_2)(depe)_2]$ was treated with acid.[3d] There have been other reports of low yields of either hydrazine or ammonia and hydrazine formed but from poorly defined iron complexes.[16] The reaction of **3** with anhydrous HBr either with no solvent or in THF resulted in the loss of all nitrogen as dinitrogen.

The chemistry reported here supports the earlier observations[2] that protonation of N_2 attached to iron may occur if the iron center is sufficiently electron-rich. Low yields may reflect the inefficiency of electron transfer. In order to achieve higher yields of ammonia and hydrazine, $SnBr_2$, which has been shown to enhance the yields of ammonia produced from some bis(dinitrogen) complexes of molybdenum,[17] was added as a potential reducing agent to the initial reaction mixture. No change in the yields of ammonia and hydrazine was observed.

cis-$[Mo(N_2)_2(NP_3)]$ was synthesized for the specific purpose of studying the acid reactions of a bis(dinitrogen) complex in which available coordination sites on the metal would be restricted to two mutually cis positions. This is to be contrasted with acid (HX) reactions with *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo, W), which yield *trans*-$[MX(NNH_2)(PMe_2Ph)_4]X$ where the hydrazido(2−) ligand is trans to X.[18] However, in the reactions of **4** with acid, at least one of the arms of NP_3 readily dissociated from the molybdenum atom. Reaction of **4** with HBr in CH_2Cl_2 afforded both ammonia and hydrazine in yields similar to those found for example with *trans*-$[Mo(N_2)_2(dppe)(PPh_2Me)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$): 0.4 mol of ammonia and 0.2 mol of hydrazine/mol of complex.[19] The reaction of HBr with **4** in the absence of solvent produced a complex that showed all the characteristics of being the hydrazido(2−) complex, $[MoBr(NNH_2)(NP_3)]Br$.[20] Although the complex underwent a transformation in the solid state, as manifest in its decreasing solubility with time, it produced the same amounts of ammonia and hydrazine with HBr as **4**.

Description of Structures. The structure of the cation $[FeH(N_2)(NP_3)]^+$ ($\mathbf{1}^+$) is illustrated in Figure 1. Crystal data for **1** and **2** are given in Table 1, atom coordinates in Tables 2 and 3, and relevant bond lengths and angles in Tables 4 and 5. The presence of the hydride in both structures was apparent from

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(20) $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 23 °C): δ 49.4 (t, 1, J_{PP} = 13.3 Hz), 41.3 (d, 2). IR (KBr): ν(N−H) 3220, 1616 cm^{-1}. No resonance in the ^1H NMR spectrum could be unambiguously assigned to the NH_2 protons.

Table 1. Crystallographic Data for Complexes **1** and **2**

	1	**2**
empirical formula	$C_{66}H_{63}BFeN_3P_3$	$C_{67}H_{63}BFeNOP_3$
fw	1057.8	1057.8
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a, Å	19.221(4)	19.284(4)
b, Å	18.047(4)	18.029(4)
c, Å	16.925(3)	16.936(3)
β, deg	113.41(3)	113.73(3)
V, Å^3	5388(3)	5390(3)
Z	4	4
density (calcd), Mg/m^3	1.304	1.303
abs coefficient, mm^{-1}	0.415	0.415
$F(000)$	2224	2224
T, K	193	213
goodness-of-fit	1.36	1.37
R^a	0.064	0.058
$R_w{}^b$	0.081	0.069

[a] $R = \sum[|F_o| - |F_c|/\sum|F_o|]$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o) + g(F_o)]$, $g = 0.002$.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for Non-Phenyl Atoms in $[FeH(N_2)(N(CH_2CH_2PPh_2)_3)]^+$

atom	x	y	x	U(eq)
Fe(1)	1875(1)	516(1)	1727(1)	21(1)
P(1)	2037(2)	82(2)	3013(2)	24(1)
P(2)	2522(2)	−232(2)	1191(2)	23(1)
P(3)	1516(2)	1509(2)	898(2)	22(1)
N(1)	2924(5)	1060(4)	2390(5)	23(4)
N(2)	984(6)	31(5)	1217(6)	30(5)
N(3)	449(5)	−281(5)	918(6)	35(5)
C(1)	2996(6)	1266(5)	3273(7)	28(3)
C(2)	2851(6)	613(6)	3763(7)	41(3)
C(3)	3579(6)	562(6)	2456(7)	30(3)
C(4)	3475(6)	204(6)	1621(7)	26(3)
C(5)	3005(6)	1765(5)	1954(7)	26(3)
C(6)	2247(5)	2168(5)	1536(7)	25(3)

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for Non-Phenyl Atoms in $[FeH(CO)(N(CH_2CH_2PPh_2)_3)]^+$

atom	x	y	x	U(eq)
Fe(1)	1877(1)	512(1)	1727(1)	23(1)
P(1)	2037(1)	81(1)	3003(1)	29(1)
P(2)	2510(1)	−225(1)	1184(1)	27(1)
P(3)	1512(1)	1504(1)	913(1)	25(1)
O(1)	463(3)	−291(3)	924(4)	51(3)
C(47)	1027(5)	37(4)	1244(5)	27(4)
N(1)	2930(3)	1059(3)	2387(4)	29(3)
C(1)	3012(5)	1253(4)	3277(5)	36(2)
C(2)	2858(5)	595(5)	3749(5)	43(2)
C(3)	3583(4)	568(4)	2455(5)	34(2)
C(4)	3450(4)	202(4)	1599(5)	34(2)
C(5)	3006(4)	1765(4)	1945(5)	35(2)
C(6)	2250(4)	2169(4)	1530(5)	33(2)

Table 4. Principal Bond Lengths (Å) in Complexes **1** and **2**

	1[a]	**2**[b]		**1**[a]	**2**[b]
Fe−P(1)	2.216(4)	2.198(2)	Fe−X	1.809(9)[a]	1.735(8)[b]
Fe−P(2)	2.257(4)	2.237(3)	X−Y	1.102(13)[a]	1.162(10)[b]
Fe−P(3)	2.210(3)	2.194(3)	Fe−H	1.40(12)	1.43(9)
Fe−N(1)	2.119(8)	2.126(6)			

[a] X = N(2); Y = N(3). [b] X = C(47); Y = O(1).

Table 5. Principal Bond Angles (deg) in Complexes **1** and **2**

	1[a]	**2**[b]
P(1)−Fe−P(2)	107.4(1)	108.1(1)
P(1)−Fe−P(3)	142.8(1)	142.1(1)
P(2)−Fe−P(3)	108.2(1)	108.4(1)
P(1)−Fe−N(1)	84.9(3)	85.5(2)
P(2)−Fe−N(1)	86.0(3)	85.9(2)
P(3)−Fe−N(1)	87.2(2)	87.1(2)
P(1)−Fe−X	92.0(3)	91.3(3)
P(2)−Fe−X	95.0(4)	94.6(3)
P(3)−Fe−X	95.3(3)	95.8(3)
N(1)−Fe−X	176.8(4)	176.7(3)
Fe−X−Y	178.2(9)	178.9(8)
P(1)−Fe−H	70(4)	79(4)
P(2)−Fe−H	170(3)	168(4)
P(3)−Fe−H	73(5)	63(4)
N(1)−Fe−H	84(4)	86(3)
X−Fe−H	95(4)	94(3)

[a] X = N(2); Y = N(3). [b] X = C(47); Y = O(1).

the difference Fourier maps calculated on the basis of anisotropic refinement of heavy atoms and isotropic refinement of all non-hydrogen atoms of the cation and anion. The hydride positions were again confirmed by high-angle refinement of non-hydrogen atoms, followed by difference Fourier synthesis of the inner shell data.

Complexes **1** and **2** are isoelectronic and isostructural with no differences in common bond lengths. The cations display a distorted octahedral coordination environment about Fe with three phosphorus atoms and a hydride ligand defining an equatorial plane about iron and a nitrogen atom (of NP_3) and the N_2 or CO ligand occupying the axial positions. The iron atom occupies a position below a plane described by the three phosphorus atoms and toward the N_2 or CO ligand. Although the Fe−P distance trans to the hydride is longer than the others, all Fe−P, Fe−N(2), and N−N distances are within the range found in other phosphine complexes of iron(II) containing N_2.[21] No increase is observed in the Fe−N(1) bond length upon replacing N_2 by CO.

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Supplementary Material Available: An ORTEP view of **2**, showing atom labeling, and tables of crystal data and experimental details, bond lengths, bond angles, atomic coordinates, anisotropic displacement coefficients, and H atom coordinates and isotropic displacement coefficients (20 pages). Ordering information is given on any current masthead page.

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(21) (a) $[FeH(N_2)(Ph_2PCH_2CH_2P(Ph)CH_2CH_2P(Ph)CH_2CH_2PPh_2)]Br\cdot C_2H_5OH$: Ghilardi, C. A.; Midollini, S.; Sacconi, L.; Stoppioni, P. *J. Organomet. Chem.* **1981**, *205*, 193−202. (b) $[Fe(H)_2(N_2)(PEtPh_2)_3]$: Van Der Sluys, L. S.; Eckert, J.; Eisenstein, O.; Hall, J. H.; Huffman, J. C.; Jackson, S. A.; Koetzle, T. F.; Kubas, G. J.; Vergamini, P. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 4831−4841. (c) $[FeH(N_2)(Me_2PCH_2CH_2PMe_2)_2][BPh_4]$: Hills, A.; Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J. *J. Organomet. Chem.* **1990**, *391*, C41−C44.