DALTON

Synthesis, structure and reactions of a dinitrogen complex of iron(0), $[Fe(N_2)(depe)_2]$ (depe = $Et_2PCH_2CH_2PEt_2$)

Masafumi Hirano, Masatoshi Akita, Takashi Morikita, Hiroaki Kubo, Atsushi Fukuoka and Sanshiro Komiya*,†

Department of Applied Chemistry, Faculty of Technology, Tokyo University of Agriculture and Technology, 2-24-16 Nakacho, Koganei, Tokyo 184, Japan

Reduction of $[FeCl_2(depe)_2]$ (depe = $Et_2PCH_2CH_2PEt_2$) by sodium–naphthalene under nitrogen gave a dinitrogen complex of iron(0), $[Fe(N_2)(depe)_2]$ **1**, in 72% yield. The crystal structure of **1** shows that the dinitrogen ligand bonds in an end-on fashion in a trigonal-bipyramidal geometry. Protonolysis of **1** by HCl gave *trans*-$[FeH(Cl)(depe)_2]$ with quantitative evolution of molecular nitrogen and then $[FeCl_2(depe)_2]$ with molecular hydrogen. The dinitrogen ligand in **1** can be replaced by small molecules such as CO, CS_2 or H_2 to give $[Fe(CO)(depe)_2]$, $[Fe(CS_2)(depe)_2]$ and *cis*-$[FeH_2(depe)_2]$ respectively. The molecular structure of $[Fe(CO)(depe)_2]$ has been established by X-ray analysis.

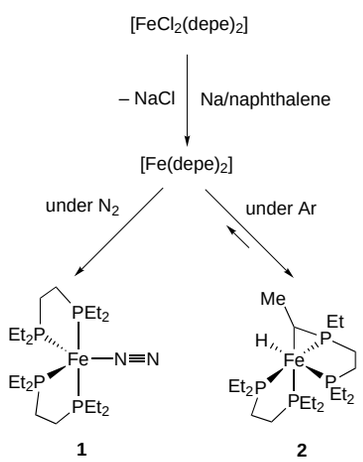
Synthesis and reactions of transition-metal dinitrogen complexes are extensively studied from the viewpoints of efficient utilization of resources as well as a model for the nitrogenase enzyme.[1,2] Recent structural[3] and theoretical inspection[4,5] of the nitrogenase enzyme has suggested the importance of the iron site rather than molybdenum for initial incorporation of nitrogen. Leigh and co-workers[2f,i,m] have proposed the generation of considerable amounts of ammonia and hydrazine by the protonation of *in situ* prepared $[Fe(N_2)(L{-}L)_2]$ [L–L = $Me_2PCH_2CH_2PMe_2$ (dmpe) or $Et_2PCH_2CH_2PEt_2$ (depe)] from $[FeH(N_2)(L{-}L)_2]BPh_4$. However, it is still unclear whether the zerovalent complex is responsible for the reduction of nitrogen, since the dinitrogen iron complex is not well characterized. On the other hand, dinitrogen is one of the labile ligands which give highly reactive co-ordinatively unsaturated species by simple liberation. Indeed, $[RuH_2(N_2)(PPh_3)_3]$[6] and $[CoH(N_2)(PPh_3)_3]$[7] show a variety of reactivities such as insertion of olefin, carbon dioxide and carbonyl compounds into Ru–H or Co–H bonds and C–H and C–O bond activation. They also act as catalysts for hydrogenation of olefins and ketones, polymerization, Tishchenko-type dimerization of aldehydes and reduction of nitrous oxide. These reactions include co-ordinatively unsaturated species as key intermediates, which are produced by simple liberation of the dinitrogen ligand. The compound *cis*-$[ReH(N_2)(PMe_2Ph)_4]$ also promotes catalytic aldol and Michael reactions accompanied by prior displacement of the dinitrogen and hydride ligands from the catalyst.[8]

We recently communicated the isolation and molecular structure of the dinitrogen complex of iron(0) having depe ligands $[Fe(N_2)(depe)_2]$ **1**,[2h] where the co-ordinated nitrogen can be displaced by carbon monoxide and carbon dioxide. Herein, we report the full account of the synthesis of complex **1**, and some reactions with carbon monoxide, carbon disulfide and hydrogen.

Results and Discussion

Preparation and molecular structure of $[Fe(N_2)(depe)_2]$ 1

Since Chatt and Davidson[9a] demonstrated the reduction of dichloro(diphosphine)iron(II) by sodium–naphthalene, a number of iron complexes have been prepared in this way, most reactions under nitrogen yielding the hydrido(naphthyl)iron(II) complex.[9a,10] When the dichloroiron(II) complex $[FeCl_2(depe)_2]$ was reduced by 2 equivalents of sodium–naphthalene under nitrogen in tetrahydrofuran (thf) at −40 °C a deep red dinitrogen complex $[Fe(N_2)(depe)_2]$ **1** was obtained. Recrystallization of the initially formed red oil from a mixture of thf–hexane gave highly air-sensitive deep red crystals of **1** in 72% yield (Scheme 1).



1 2

Scheme 1

On the other hand, when $[FeCl_2(depe)_2]$ was reduced by sodium–naphthalene under an argon atmosphere [$\overline{FeH(MeCH\text{-}PEtC_2H_4PEt_2)}(depe)$] **2** was obtained as orange cubes. Complex **2** may be obtained by the reversible metallation of an ethyl group in co-ordinatively unsaturated $Fe(depe)_2$, since the same compound has been reported *in situ via* reductive elimination of methane from $[FeH(Me)(depe)_2]$ followed by metallation.[11] A NMR study showed that exposure of **2** to a nitrogen atmosphere yielded the dinitrogen complex **1**. Thus, **1** is considered to be formed by the addition of dinitrogen to $Fe(depe)_2$ which may exist as an equilibrium mixture with **2** given by the reduction of $[FeCl_2(depe)_2]$ with sodium–naphthalene.

The molecular structure of compound **1** was unambiguously determined by X-ray crystallography, and is the first structurally defined example of a zerovalent (dinitrogen)iron complex. The ORTEP[12] drawing of **1** is shown in Fig. 1 and details of

† E-Mail: komiya@cc.tuat.ac.jp

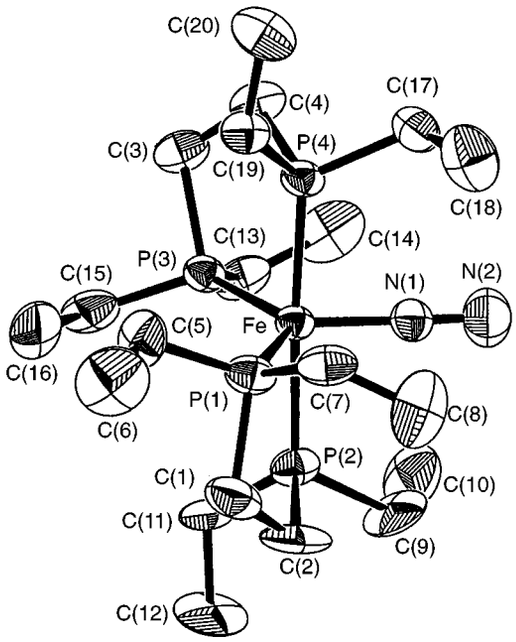


Fig. 1 An ORTEP drawing of $[Fe(N_2)(depe)_2]$ **1**. Hydrogen atoms are omitted for clarity[2h]

crystal data have been published as a communication.[2h,] ‡ The overall structure is best regarded as trigonal bipyramidal, where the dinitrogen ligand co-ordinates in the equatorial plane. This is consistent with the general trend of π-acceptor ligands to locate at the equatorial site in d^8 trigonal bipyramidal geometry.[13,14]

The IR spectrum of compound **1** showed a ν(N≡N) band at 1955 cm^{-1} in KBr. The ν(N≡N) bands of end-on dinitrogen in zerovalent iron complexes are reported to be in the range 1950–2141 cm^{-1} {$[Fe(N_2)(dmpp)_2]$ (dmpp = $Me_2PCH_2CH_2CH_2PMe_2$) (1950 cm^{-1}),[2c] $[Fe(N_2)(dmpe)_2]$ (1975 cm^{-1}),[2i] $[Fe(N_2)(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) (2068 cm^{-1}),[2a] $[Fe(N_2)(CO)_2(PEt_3)_2]$ (2098 cm^{-1})[2i] and $[Fe(N_2)(CO)_2\{P(OPr^i)_3\}_2]$ (2141 cm^{-1})[2l]} while those in divalent iron complexes are in the range 2060–2130 cm^{-1} {$[FeH_2(N_2)(PEtPh_2)_3]$ (2060 cm^{-1}),[2d] $[FeH(N_2)(dmpe)_2]Br$ (2094 cm^{-1}),[2e] $[Fe(\eta\text{-}C_5H_5)(N_2)(dippe)]BPh_4$ (dippe = $Pr^i_2PCH_2CH_2PPr^i_2$) (2112 cm^{-1}),[2k] $[FeH(N_2)(hptpd)]Br$ (2130 cm^{-1})[2b] and $[FeH(N_2)(hptpd)]I$ [hptpd = 3,6-diphenyl-4,8-bis(diphenylphosphino)-3,6-diphosphaoctane] (2130 cm^{-1})[2b]}. Thus, ν(N≡N) of **1** is one of the lowest values for end-on co-ordinated dinitrogen on iron, suggesting strong back donation from the electron-rich iron(0) centre.

The $^{31}P\text{-}\{^1H\}$ NMR spectrum of compound **1** showed a singlet at δ 89.30 at 25 °C. This peak is very sharp and neither significant shift nor broadening is observed at accessible low temperatures (δ 89.74, at −55 °C), indicating that the four phosphorus nuclei are equivalent within the NMR time-scale, in spite of the trigonal-bipyramidal geometry of **1** in the solid state. This fact can be interpreted by the following four possibilities: (*i*) rapid reversible dissociation of the dinitrogen ligand with facile ligand rearrangement; (*ii*) rapid dissociative exchange of depe ligands with free depe; (*iii*) square-pyramidal geometry of **1** in solution; (*iv*) facile interchange between the apical and the equatorial phosphorus ligands in a trigonal-bipyramidal structure. However, the proposal (*i*) is less likely because of the following reasons. The $^{15}N\text{-}\{^1H\}$ NMR spectrum showed two sharp singlets at δ −40.5 and −45.2 due to the dinitrogen ligand § in the range of those for zerovalent dinitrogen complexes reported: $[Fe(^{15}N_2)(CO)_2\{P(OPr^i)_3\}_2]$ [δ −40.6 (N_β), −69.4 (N_α)],[2l] $[Fe(^{15}N_2)(CO)_2(PEt_3)_2]$ [δ −39.7 (N_β), −62.1 (N_α)],[2l] *cis*-$[Mo(^{15}N_2)_2(PMe_3)_4]$ [δ −34.3 (N_β), −41.5 (N_α)],[15] $[Mo(^{15}N_2)(PMe_3)_5]$ [δ −35.1 (N_α), −41.2 (N_β)][15] and *cis*-$[W(^{15}N)_2(PMe_3)_4]$ [δ −36.8 (N_β), −61.9 (N_α)].[15] The observation of two resonances due to the N_α and N_β nuclei of the dinitrogen ligand in **1** excludes the reversible liberation of the dinitrogen ligand resulting in Fe–N bond rupture. This is also supported by the fact that **1** is stable even under high vacuum. Rapid dissociative exchange with free depe [proposal (*ii*)] is also less likely because both the chemical shift and the line shape of **1** remained unchanged in the $^{31}P\text{-}\{^1H\}$ NMR spectrum in the presence of free depe at room temperature. Proposal (*iii*) may be a favourable mechanism, despite the general preference for the trigonal-bipyramidal geometry with a π-acceptor ligand in the equatorial site rather than square-pyramidal geometry.[13] It is widely accepted that the benefit in energy due to the geometries and the preference for the five-co-ordinated d^8 complex would be small. Indeed, Jones and Libertini[14] isolated both trigonal-bipyramidal and square-pyramidal complexes with a $RuL(dmpe)_2$ framework. In addition, Ogasawara *et al.*[16] recently reported two independent molecules of $[Ru(CO)_2(PPr^i_2Me)_3]$, where the π-acceptor ligands are located either in the equatorial or axial sites in a distorted trigonal-bipyramidal geometry. The singlet peak in the $^{31}P\text{-}\{^1H\}$ NMR spectrum may also have arisen from interchange between the apical and the equatorial phosphorus ligands in trigonal-bipyramidal structure [proposal (*iv*)]. Berry's pseudo-rotation makes all the phosphorus nuclei equivalent.

$$\mathbf{1} \xrightarrow[-N_2]{+HCl} \textit{trans}\text{-}[FeH(Cl)(depe)_2] \xrightarrow[-N_2]{+HCl} \textit{trans}\text{-}[FeCl_2(depe)_2]$$

Scheme 2

Protonolysis of compound 1

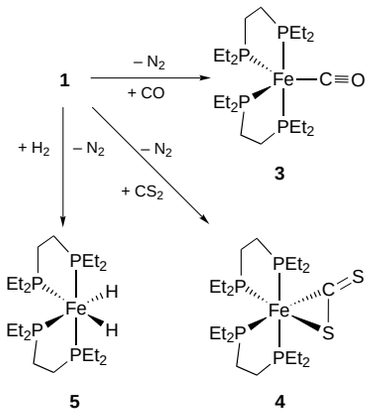
Although protonolysis of dinitrogen complexes of iron is interesting in view of nitrogen reduction, it has received less attention compared to that of Group 6 dinitrogen complexes.[1,17–19] Treatment of **1** with 10 equivalents of H_2SO_4 in thf at room temperature under vacuum resulted in the generation of only gaseous hydrogen (77%) and nitrogen (90%). Indophenol and *p*-(dimethylamino)benzaldehyde (pdmab) tests of the solution revealed the absence of ammonia and hydrazine (neither was detected in blank tests). Treatment of **1** with HCl gas in thf at room temperature under vacuum also resulted in the quantitative generation of hydrogen (96%) and nitrogen (100%). Only a negligible amount of hydrazine (0.1% by H_2SO_4, 0.3% by HCl) was detected in protonations of **1** under a nitrogen atmosphere.

The latter reaction is considered to proceed in a stepwise manner according to the following experiments. Reaction of **1** with 1 equivalent of HCl in thf at room temperature gave *trans*-$[FeH(Cl)(depe)_2]$[9d,10b] (46%) with liberation of nitrogen (80%) (Scheme 2). On the other hand, the reaction of **1** with twice the amount of HCl produced $[FeCl_2(depe)_2]$[9d,10b] in 45% yield with quantitative generation of nitrogen and hydrogen. These results are in sharp contrast to the protonation of Group 6 dinitrogen complexes $[M(N_2)_2(depe)_2]$ (M = Mo or W) with HCl giving an acid adduct $[M(N_2)_2(depe)_2]\cdot HCl$ followed by further protonation to give $[M(NNH_2)Cl(depe)_2]Cl$.[18]

Leigh and co-workers[2f,m] reported the formation of $[Fe(N_2)(L\text{–}L)_2]$ (L–L = diphosphine) by the deprotonation of $[FeH(N_2)(L\text{–}L)_2]BPh_4$, though they could not isolate the (dinitrogen)iron(0) complex in pure form. They proposed direct pro-

‡ The linear absorption coefficient of compound **1** in ref. 2(*h*) should be corrected to 7.95 cm^{-1}.

§ The spin coupling between the nitrogen and phosphorus nuclei could not be observed. It is reported that $^2J(^{15}N\text{–}^{31}P)$ of dinitrogen complexes is small or negligible.[2l,14]



Scheme 3

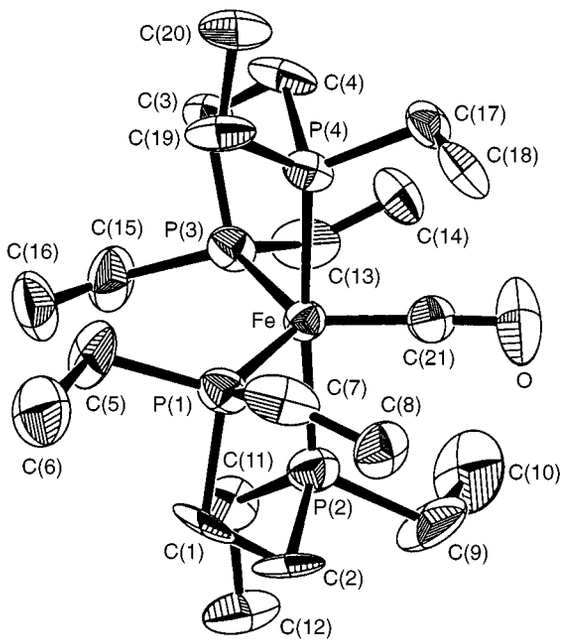


Fig. 2 An ORTEP drawing of [Fe(CO)(depe)$_2$] **3**. Hydrogen atoms are omitted for clarity

tonation of the co-ordinated dinitrogen in [Fe(N$_2$)(L–L)$_2$] would be responsible for the formation of ammonia. Recently, they found that deprotonation of [FeH(N$_2$)(depe)$_2$]BPH$_4$ followed by protonation by HCl in thf at room temperature produced ammonia at best in 20% yield, where the iron(0) species was expected to be formed *in situ*.[2m] However, our results clearly demonstrate that protonation of **1** under comparable reaction conditions yields neither ammonia nor hydrazine but liberates only nitrogen and hydrogen gases giving [FeCl$_2$(depe)$_2$].

Reaction of compound 1 with CO and the molecular structure of [Fe(CO)(depe)$_2$] 3

We recently reported that the dinitrogen ligand in compound **1** was displaced by carbon dioxide to give [Fe(CO$_2$)(depe)$_2$] with high reactivity toward Group 14 electrophiles.[20] Smooth displacement of the dinitrogen ligand by carbon monoxide also took place on treatment of **1** under carbon monoxide at room temperature in 2 h to give the zerovalent (carbonyl)iron complex [Fe(CO)(depe)$_2$] **3** (Scheme 3).[2h,j] The stretching vibration of CO in **3** appears at 1800 cm^{-1}, which is slightly lower than those observed for [Fe(CO)(dppe)$_2$] (1810 cm^{-1})[2a] and [Fe(CO)(dmpe)$_2$] (1830 cm^{-1}),[2i] reflecting stronger back bonding in **3** than that in the dppe or dmpe analogues.

A single crystal of compound **3** suitable for X-ray crystallography was obtained from pentane. The ORTEP drawing is depicted in Fig. 2, crystallographic data are summarized in Table 1 and selected bond distances and angles are given in Table 2. Complex **3** in the solid state is basically isostructural to **1** showing a typical trigonal-bipyramidal geometry, where P(1), P(2) and the carbonyl ligand constitute the equatorial plane. The observed structure is basically similar to that of [Ru(CO)(dmpe)$_2$].[13] Inconsistent with this solid-state structure, the ^{31}P-{^{1}H} NMR spectrum of **3** shows only one sharp singlet in [$^2H_8$]toluene even at low temperature (δ 96.77 at −55 °C). This may also be understood by a similar mechanism discussed for **1** including the geometry change to square pyramidal or rapid intramolecular exchange of phosphorus nuclei in solution.

Table 1 Crystallographic data for [Fe(CO)(depe)$_2$] **3**

Formula	$C_{21}H_{48}FeOP_4$
M	496.35
Crystal system	Orthorhombic
Space group	$Pna2_1$
a/Å	14.333(3)
b/Å	10.486(2)
c/Å	17.954(3)
U/Å^3	2698(1)
Z	4
D_c/g cm^{-3}	1.222
μ/cm^{-1}	8.01
2θ/°	3.0–55.0
Scan type	2θ–ω
No. data collected	3501
No. of observed reflections	1774 ($\|F_o\| > 3\sigma\|F_o\|$)
R [a]	0.052
R' [b]	0.033

[a] $R = \Sigma(\|\|F_o\| - \|F_c\|\|)/\Sigma|F_o|$. [b] $R' = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

Table 2 Selected bond distances (Å) and angles (°) in [Fe(CO)(depe)$_2$] **3**

Fe–P(1)	2.171(3)	Fe–P(2)	2.209(3)
Fe–P(3)	2.225(3)	Fe–P(4)	2.199(3)
Fe–C(21)	1.716(8)	C(21)–O(1)	1.179(8)
P(1)–Fe–C(21)	122.0(4)	P(2)–Fe–C(21)	86.8(3)
P(3)–Fe–C(21)	116.1(4)	P(4)–Fe–C(21)	88.5(3)
P(1)–Fe–P(2)	85.8(1)	P(1)–Fe–P(3)	121.8(1)
P(1)–Fe–P(4)	97.5(1)	P(2)–Fe–P(3)	95.8(1)
P(2)–Fe–P(4)	175.2(1)	P(3)–Fe–P(4)	85.46(10)

Reaction of compound 1 with CS$_2$

Treatment of compound **1** with a stoichiometric amount of CS$_2$ in thf at room temperature gave a reddish brown solution. After removal of all volatile materials, the resulting brown solid was crystallized from a mixture of Et$_2$O–pentane to give air-stable brown crystals of [Fe(CS$_2$)(depe)$_2$] **4**. The IR spectrum shows intensive sharp peaks at 1056 and 1024 cm^{-1} assignable to ν(C=S) and ν(C–S) bands, respectively, suggesting η^2-*C*,*S* coordination but not the alternative η^1-*C* or η^2-*S*,*S*.[21,22] It is worthwhile noting that **4** has one of the lowest ν(CS$_2$) bands, suggesting also strong back donation from a highly reduced iron centre: ν(CS$_2$) bands for the carbon disulfide complexes of iron(0) have been reported in the range 1119–1168 cm^{-1} in KBr: [Fe(CS$_2$)(CO)$_2$(PEt$_3$)$_2$] (1119 cm^{-1}),[21b] [Fe(CS$_2$)(CO)$_2$(PMe$_3$)$_2$] (1128 cm^{-1}),[21c] [Fe(CS$_2$)(CO)$_2$(PMe$_2$Ph)$_2$] (1137 cm^{-1}),[21c] [Fe(CS$_2$)(CO)$_2$(PPh$_3$)$_2$] (1151,[21b] 1155[21d] cm^{-1}), [Fe(CS$_2$)(CO)$_2${P(OMe)$_3$}$_2$] (1157 cm^{-1})[21c] and [Fe(CS$_2$)(CO)$_2${P(C$_6$H$_4$Cl-*p*)$_3$}$_2$] (1168 cm^{-1}).[21b] The low molar electric conductivity of **4** in acetone (0.0700 S cm^2 mol^{-1}, 25 °C) indicated its neutral character.

Complex **4** would be basically isostructural to [Fe(CO$_2$)(depe)$_2$],[20] but contrary to it is quite stable. No significant change in the IR spectrum of **4** was observed after exposure to air for a week at room temperature.

Reaction of compound 1 with H_2

Upon bubbling hydrogen gas into a benzene solution of compound **1** the red solution turned to dark red. Proton and ^{31}P-$\{^1H\}$ NMR spectra of the solution showed the selective formation of a *cis*-dihydride complex, *cis*-$[FeH_2(depe)_2]$ **5**. No *trans* isomer was observed, in accordance with previous results.[2j] The reverse reaction of **5** with nitrogen did not occur under ambient conditions. Complex **5** is known to be obtained by the reaction of hydrogen with **2**, probably *via* the highly reactive 16e species $Fe(depe)_2$.[11a,23] However, laser photolysis of $[FeH_2(dmpe)_2]$ in a nitrogen-doped argon matrix is reported to give (dinitrogen)iron(0),[24] where the $Fe(dmpe)_2$ moiety kinetically favours (five-fold) dihydride rather than dinitrogen. This fact could explain the reason why **1** reacts with hydrogen to give **5** so easily, but the displacement of the dihydrido ligands in $[FeH_2(dmpe)_2]$ by dinitrogen needs UV irradiation.

Experimental

All manipulations were performed under dry nitrogen using standard Schlenk and vacuum-like techniques. All solvents were distilled from appropriate drying agents prior to use. The compound depe and its precursor 1,2-bis(dichlorophosphino)ethane were prepared by the literature method.[25] Dry HCl gas was prepared by the reaction of H_2SO_4 with flame-dried NaCl under vacuum. The compound $[FeCl_2(depe)_2]$ was synthesized according to the literature methods.[25] Proton and ^{13}C-$\{^1H\}$ NMR spectra were recorded on JEOL FX-200, EX-400, or LA-300 spectrometers and chemical shifts are reported in ppm from $SiMe_4$. The ^{31}P-$\{^1H\}$ NMR spectra were recorded on a JEOL LA-300 (121.6 MHz) or Bruker AM-400 (161.5 MHz) spectrometer with chemical shifts reported in ppm downfield from 85% H_3PO_4 in D_2O unless otherwise noted, the ^{15}N-$\{^1H\}$ NMR spectrum on a JEOL LA-300 (30.35 MHz) spectrometer with chemical shifts reported in ppm downfield from nitromethane. Infrared spectra were obtained on a JASCO FT/IR-5M spectrometer, UV spectra for indophenol and pdmab tests on a Shimadzu UV-120 UV/VIS photospectrometer. The volumes of gases generated were measured by a Toepler pump. The GLC analyses were performed with a Shimadzu GC-3 BT gas–liquid phase chromatograph using stainless-steel packed molecular sieves or active carbon with a thermal conductivity detector. Melting points were estimated under nitrogen with a Yazawa capillary melting apparatus and are uncorrected. Elemental analyses were performed with a Yanaco CHN autocorder. Molar electric conductivities were measured on a TOA model CM-7B instrument.

Preparation of the dinitrogen compound 1

To a thf solution (40 cm^3) of $[FeCl_2(depe)_2]$ (2.25 g, 4.35 mmol) was added dropwise a thf solution of sodium–naphthalene (20 cm^3, 16.3 mmol) at −40 °C under nitrogen. After reaction at room temperature for 14 h the insoluble materials were filtered off and all volatile materials were removed *in vacuo* and finally dried using an oil diffusion pump. Recrystallization of the resulting solid from cold pentane (20 cm^3) gave deep red crystals of $[Fe(N_2)(depe)_2]$ **1** in 72% yield (1.557 g, 3.14 mmol), m.p. 88–90 °C (decomp.) [Found: C, 47.95; H, 9.85; N, 4.91%; *M* (cryoscopic method) 487 ± 30. $C_{20}H_{38}FeN_2P_4$ requires C, 48.40; H, 9.75; N, 5.64%, *M* 496]; $\Lambda = 0.009\,25$ S cm^2 mol^{-1} (acetone, 25 °C); $\tilde{\nu}_{max}/cm^{-1}$ 1955vs (N≡N), 1456m (depe), 1418m (depe), 1372w (depe), 1167w, 1036m, 1023m, 867m, 786s, 757s, 693s, 611s, 475s and 420s [KBr, room temperature (r.t.)]; 1978vs (N≡N), 1463m (depe), 1419m (depe), 1396m, 1376m, 1265m, 1126m, 1038s, 1028s and 475s (cyclohexane, r.t.); δ_H(200 MHz, C_6D_6, r.t.) 1.05 (br), 1.38 (br) and 1.81 (br); δ_P(161.5 MHz, $C_6D_6CD_3$, standard PPh_3) 89.30 (s) (25 °C); 89.74 (s) (−55 °C); $\delta_{^{15}N}$(30.35 MHz, C_6D_6, r.t.) −40.5 (1 N, s) and −45.2 (1 N, s).

Reduction of $[FeCl_2(depe)_2]$ with sodium–naphthalene under argon

Similar treatment of a thf solution (3.5 cm^3) of $[FeCl_2(depe)_2]$ (94.4 mg, 0.175 mmol) with sodium–naphthalene (11 cm^3, 0.55 mmol) under argon followed by work-up gave on off-yellow tar (138.4 mg). Crystallization of the off-yellow tar from cold pentane resulted in the fractional crystallization of light yellow crystals of naphthalene and orange cubes of [FeH(MeCHPEt-$C_2H_4PEt_2$)(depe)] **2** (58.7 mg). However, it was difficult to separate **2** from naphthalene completely because naphthalene always crystallized as light yellow crystals at the same time. The ^{31}P-$\{^1H\}$ NMR spectrum of the orange cubes in thf solution at 23 °C showed δ 51.85 (m), 82.46 (m), 88.23 (m) and 92.10 (m) relative to external $P(OMe)_3$ at δ 141.18 [lit.,[11a] $\delta_P(C_4D_8O)$ 50.83, 81.44, 87.28 and 91.11]. These data were identical to those reported in ref. 11(*a*) within experimental error.

Reaction of compound 2 with nitrogen

This experiment was carried out in a NMR tube. Compound **2** (*ca.* 10 mg) was dissolved in C_6D_6 (600 μl) under nitrogen at room temperature. The ^{31}P-$\{^1H\}$ NMR spectrum of the solution showed formation of **1** with peaks due to *cis*- and *trans*-$[FeD(C_6D_5)(depe)_2]$, and residual **2**, where the molar ratio of **1**:*cis*-$[FeD(C_6D_5)(depe)_2]$:*trans*-$[FeD(C_6D_5)(depe)_2]$:**2** was 0.18:0.20:0.50:0.12. The peaks due to *cis*- and *trans*-$[FeD(C_6D_5)(depe)_2]$ were assigned by using data in ref. 11(*a*) [$\delta_P(C_6D_6)$ for *cis* 67.67, 76.23, 89.78 and 94.87; for *trans* 94.81]. δ_P(121.6 MHz, C_6D_6) for **1**, 84.7 (4 P, s); *cis*-$[FeD(C_6D_5)(depe)_2]$, 68.3 (1 P, m), 77.5 (1 P, m) and 90.3–92.6 (2 P, m, overlapped with the peak due to **2**); for *trans*-$[FeD(C_6D_5)(depe)_2]$, 96.0 (4 P, s); for **2**, 51.85 (1 P, m), 82.3 (1 P, m), 88.0 (1 P, m) and 90.3–92.6 {1 P, m, overlapped with the peak due to *cis*-$[FeD(C_6D_5)(depe)_2]$}.

Protonolysis of compound 1

With concentrated H_2SO_4 under vacuum. Complex **1** (60.2 mg, 0.121 mmol) was charged into a two-necked Schlenk tube equipped with a side arm containing sulfuric acid (65 μl, 1.22 mmol, 10-fold excess over **1**). The Schlenk tube was connected with a vacuum line, evacuated, and then thf (3 cm^3) was transferred into the side arm under vacuum. The stopcock was closed and the thf solution of sulfuric acid was poured onto **1** by rotating the side-arm elbow.[26] The reaction mixture immediately turned colourless with a small amount of white solid. The mixture was allowed to react at room temperature under vacuum for 12 h. Dihydrogen (0.094 mmol, 78% per **1**) and N_2 (0.11 mmol, 90% per **1**) were detected by Toepler pump. Then argon gas was introduced into the Schlenk tube and 40% KOH solution was dropped in to liberate basic products. The solution was distilled at 130 °C for 4 h under reduced pressure using an aspirator, during which the volatile materials were bubbled through a dilute H_2SO_4 solution (1 M, 10 cm^3). To the H_2SO_4 solution was added distilled water to adjust the total volume to 50.00 cm^3. To check the indophenol test, 1.00 cm^3 of the solution was removed by a hole pipette. No ammonia was detected by the indophenol test (625 nm). A 5.00 cm^3 aliquot of the solution was similarly removed for the pdmab test. No formation of hydrazine was detected by spectroscopic analysis using pdmab at 458 nm. Calibration of both tests confirmed that our methods can detect the amount (*ca.* 0.1 μmol) of ammonia and hydrazine under the experimental conditions.

With concentrated H_2SO_4 under nitrogen. Complex **1** (50.2 mg, 0.101 mmol) was protonated with H_2SO_4 (110 μl, 2.08 mmol, 21-fold excess over **1**) under nitrogen by the method described above. While no ammonia was detected by the indo-

phenol test, a small amount of hydrazine (0.33%) was observed by the pdmab test.

With an excess of HCl under vacuum. Into the two-necked Schlenk tube containing complex **1** (49.4 mg, 0.100 mmol) in thf (3 cm^3) was introduced water- and air-free HCl gas (2.1 mmol, 21-fold excess over **1**) from a manometer. The mixture was stirred for 10 h at room temperature under vacuum. Dihydrogen (0.095 mmol, 96% per **1**) and N_2 (0.10 mmol, 100% per **1**) were detected. Neither ammonia nor hydrazine was detected by the indophenol and pdmab test, respectively.

With an excess of HCl under nitrogen. Hydrogen chloride gas dissolved in Et_2O (3.4 cm^3, 2.0 mmol of HCl, 20-fold excess over **1**) was added to an Et_2O solution (3 cm^3) of compound **1** (50.7 mg, 0.102 mmol) and allowed to react at room temperature for 12 h under nitrogen. No ammonia formation was observed by the indophenol test. A small amount of hydrazine (0.07% per **1**) was detected by pdmab test.

With 1 equivalent of HCl. A Schlenk tube was charged with compound **1** (55.5 mg, 0.112 mmol), thf (3 cm^3) and dry HCl (2.6 cm^3, 0.12 mmol) under vacuum. The red solution turned yellow and finally orange within 20 min. The mixture was stirred for 18 h at room temperature under vacuum. Dihydrogen (0.072 cm^3, 0.032 mmol, 3% per **1**) and N_2 (2.01 cm^3, 0.0899 mmol, 80% per **1**) were detected by GLC. All volatile materials were removed *in vacuo* and the resulting solid was recrystallized from a mixture of MeOH–Et_2O to give orange crystals of *trans*-[FeH(Cl)(depe)$_2$] in 46% yield (26.2 mg, 0.0519 mmol), m.p. 157–158 °C (lit.,[25] 154.5–155.5 °C) (Found: C, 47.42; H, 9.37; Cl, 8.25. $C_{20}H_{39}ClFeP_4$ requires C, 47.59; H, 9.78; Cl, 7.02%): $\tilde{\nu}_{max}/cm^{-1}$ 1852 (FeH) (lit.,[25] 1849 cm^{-1}) (KBr); δ_H(200 MHz, C_6D_6, r.t.) −31.92 [1 H, qnt, *J*(HP) 48 Hz, FeH] and 0.85–2.72 (48 H, m, depe).

With 2 equivalents of HCl. A Schlenk tube was charged with compound **1** (48.0 mg, 0.0967 mmol), thf (3 cm^3) and dry HCl (4.3 cm^3, 0.16 mmol) under vacuum. The red solution turned reddish brown and finally green. Quantitative amounts of H_2 (0.0890 mmol, 93% per **1**) and N_2 (0.0837 mmol, 87% per **1**) were detected. After removal of all volatile materials, the resulting green solid was recrystallized from benzene to give green *trans*-[FeCl$_2$(depe)$_2$] in 45% yield (22.7 mg, 0.0439 mmol). These crystals were characterized by their IR spectrum:[9d] $\tilde{\nu}_{max}/cm^{-1}$ 1460m, 1416m and 1375w.

Reactions of compound 1

With CO. Carbon monoxide was bubbled through a hexane solution (5 cm^3) of compound **1** (200.5 mg, 0.404 mmol) at room temperature for 2 h. A small amount of insoluble material was filtered off, and the filtrate was concentrated for crystallization. Recrystallization of the resulting crude crystals from pentane gave yellow crystals of [Fe(CO)(depe)$_2$] **3** in 58% yield (116.8 mg, 0.235 mmol), m.p. 198–201 °C (decomp.) (Found: C, 51.39; H, 9.99. $C_{21}H_{48}FeOP_4$ requires C, 50.82; H, 9.75%); $\tilde{\nu}_{max}/cm^{-1}$ 1800vs (CO) (KBr); δ_H(200 MHz, C_6D_6) 0.88–1.93 (48 H, m, depe); δ_P(161.5 MHz, $C_6D_5CD_3$, standard external PPh_3) 91.59 (s) (25 °C) and 96.77 (s) (−55 °C).

With CS_2. Treatment of compound **1** (80.5 mg, 0.165 mmol) in thf (2 cm^3) with CS_2 (10.0 μl, 0.169 mmol) at room temperature for 14 h resulted in the quantitative generation of N_2 (0.161 mmol, 98% per **1**). The solution was filtered and evaporated to dryness. Recrystallization of the resulting reddish brown solid from Et_2O gave reddish brown crystals of [Fe(CS$_2$)(depe)$_2$] **4** (28.3 mg, 0.0516 mmol, 32%), m.p. 116–118 °C (decomp.) (Found: C, 46.32; H, 8.89. $C_{21}H_{48}FeP_4S_2$ requires C, 45.0; H, 8.84%); $\tilde{\nu}_{max}/cm^{-1}$ 1454m (depe), 1416m (depe), 1380w (depe), 1056vs (C=S) and 1024vs (C–S); $\Lambda = 0.0700$ S cm^2 mol^{-1}; δ_H(200 MHz, C_6D_6) 0.74–4.02 (48 H, br, depe).

With hydrogen. A certain amount of compound **1** (*ca.* 10 mg) was dissolved in benzene (5 cm^3) and hydrogen was bubbled for 75 min, during which the solution turned from orange to reddish brown. After removal of the solvent *in vacuo*, C_6D_6 was added and the ^1H and ^{31}P-{^1H} NMR spectra showed formation of *cis*-[FeH$_2$(depe)$_2$] **5**.[23] The *trans* isomer, *trans*-[FeH$_2$(depe)$_2$] was not detected. δ_H(300 MHz, C_6D_6) −14.66 (1 H, m, FeH); δ_P(121.6 MHz, C_6D_6, external standard H_3PO_4) 89.11 (2 P, br) and 102.35 (2 P, br).

Crystallography

Crystals were mounted in a glass capillary (GLAS, 0.7 mm diameter) under an argon atmosphere. The data were collected at 20 °C using TEXSAN automatic data collection series on a Rigaku AFC5R diffractometer using Mo-Kα radiation (λ = 0.710 69 Å). Data for **1** are available as supporting information to ref. 2(*h*) or by application to the Cambridge Crystallographic Data Centre.

Clear yellow crystals of compound **3** were grown from a saturated solution in pentane. A crystal of suitable size was selected and mounted in a glass capillary tube. Crystal and instrument stabilities were checked by measuring three standard reflections after every 150 observations. No crystal decay was noticed during the data collection. Using the criteria $|F_o| > 3.0\sigma|F_o|$, 1774 out of 3501 reflections were used. The structure was solved by the direct method. The hydrogens were located at the ideal positions and not refined. The final *R* (*R′*) value was 0.052 (0.033). We used a *p* factor (0.002) to down-weight the intense reflections and then a goodness of fit of 1.88 was obtained. Plots of $\Sigma w(|F_o| - |F_c|)^2$ *versus* $|F_o|$, reflection order in data collection, (sin θ)/λ and various classes of indices showed no unusual trends.

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