

Isolation of a Zerovalent Iron Dinitrogen Complex with 1,2-Bis(diethylphosphino)ethane Ligands

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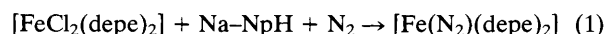
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A zerovalent iron dinitrogen complex $[\text{Fe}(\text{N}_2)(\text{depe})_2]$ having 1,2-bis(diethylphosphino)ethane ligands has been prepared by reduction of $[\text{FeCl}_2(\text{depe})_2]$ with sodium–naphthalene in tetrahydrofuran under nitrogen at room temperature.

Effective utilization of nitrogen using transition metal complexes has attracted intriguing and challenging interests in recent years in relation to biochemical catalytic processes.¹ Recent structural determination of nitrogenase suggested the importance of iron in the biological nitrogen fixation process.² Although coordination of dinitrogen to iron(0) is known, isolation of such complexes is still very limited and they have only been characterized spectroscopically.³ In the course of our recent investigation concerning the low valent group 8 transition-metal complexes having tertiary phosphine ligands,⁴ we isolated a stable dinitrogen complex of iron(0) by employing 1,2-bis(diethylphosphino)ethane (depe) ligands. Here we report the synthesis and the first structural determination of the iron(0) dinitrogen complex.

Two equivalents of sodium–naphthalene (Na–NpH) in tetrahydrofuran (THF) were added to a THF suspension of dichlorobis(depe)iron(II)⁵ at -40°C , the mixture was then stirred for a few hours at room temp. to give a deep-red solution. After evaporation of all the volatile matter *in vacuo*, the residual dark-red solid was recrystallized from pentane to afford deep-red prisms of (dinitrogen)bis(depe)iron(0), **1**, in 70% yield [eqn. (1)]. Complex **1** was characterized by NMR and IR spectroscopy and elemental analyses as well as by chemical reactions;† **1** is thermally stable, but decomposes rapidly in air. X-Ray structure analysis revealed the trigonal bipyramidal structure of **1**‡ (Fig. 1) in which a dinitrogen ligand occupies one of the equatorial coordination sites of iron by an end-on bonding fashion and each diphosphine occupies

both apical and equatorial positions. The $\text{N}=\text{N}$ bond length (1.14 Å) is slightly longer than those found for dinitrogen complexes of iron(II), suggesting strong π -back donation from iron(0) to the dinitrogen in **1**. Low-electric conductivity of **1** in THF suggests its non-ionic character and the molecular mass measurement reveals the mononuclearity of the complex in solution.



The IR spectrum of **1** shows a strong sharp $\nu_{\text{N}=\text{N}}$ band at 1955 cm^{-1} . The value is lower than those for previously known dinitrogen complexes of iron(0) such as $[\text{Fe}(\text{N}_2)(\text{dmpe})_2]$ ^{3a} and $[\text{Fe}(\text{N}_2)(\text{dpe})_2]$ ^{3b} which have only been characterized in solution. The ^{31}P NMR spectrum of **1** in $[\text{D}_8]\text{toluene}$ at -50°C shows only one singlet at δ 89.74 from ext. PPh_3 , suggesting the fluxionality of the complex in solution or the accidental coincidence of chemical shifts of axial and equatorial P nuclei. Thermolysis of **1** liberated an equimolar amount of nitrogen gas at 150°C for 3 h (94%/Fe). Acidolysis of **1** in THF with an excess of dry hydrogen chloride gave nitrogen and hydrogen gases in 100 and 96% yields, respect-

† Physical and spectroscopic data for **1**, **2** and **3**. **1**: Yield 70%; m.p. $88\text{--}90^\circ\text{C}$ (decomp.); M_r (cryoscopic method) 487 ± 30 (calc. for $\text{C}_{20}\text{H}_{48}\text{N}_2\text{P}_4\text{Fe}$ 496); Molar electric conductivity in THF $\Lambda = 0.009\text{ S cm}^2\text{ mol}^{-1}$; ^{31}P NMR (162 MHz, $\text{C}_6\text{D}_5\text{CD}_3$, PPh_3): δ 89.30 (s, 25°C), 89.74 (s, -55°C); ^1H NMR (200 MHz, C_6D_6 , SiMe_4): δ 0.5–1.5 (m); IR (KBr, ν/cm^{-1}): $\nu_{\text{N}=\text{N}}$ 1955. **2**: Yield 62%; m.p. $157\text{--}158^\circ\text{C}$ (decomp.); ^{31}P NMR (162 MHz, $\text{C}_6\text{D}_5\text{CD}_3$, PPh_3): δ 89.30 (s, 25°C), 89.74 (s, -55°C); IR (KBr, ν/cm^{-1}): $\nu_{\text{Fe-H}}$ 1852. **3**: Yield 42%; m.p. $198\text{--}201^\circ\text{C}$ (decomp.); ^{31}P NMR (162 MHz, $\text{C}_6\text{D}_5\text{CD}_3$, PPh_3): δ 91.59 (s, 25°C), 96.77 (s, -55°C); IR (KBr, ν/cm^{-1}): ν_{CO} 1800. Satisfactory elemental analyses were obtained for **1**, **2** and **3**. The signals in the ^{31}P NMR spectra of **1** and **3** did not show any fluxional behaviour even when the temperature was lowered to -55°C .

‡ Crystal data for **1**: $\text{C}_{20}\text{H}_{48}\text{N}_2\text{P}_4\text{Fe}$, $M = 496.35$, orthorhombic, space group $\text{Pna}2_1$; $a = 14.349(1)$, $b = 10.554(1)$, $c = 17.951(2)$ Å; $V = 2718.3(5)$ Å³; $Z = 4$; $D_c = 1.213\text{ g cm}^{-3}$; $\text{Mo-K}\alpha$ ($\lambda = 0.71069$ Å); $\mu = 4.71\text{ cm}^{-1}$, $3 < 2\theta < 50^\circ$. The intensity data were collected at room temp. on a Rigaku AFC-5R four circle diffractometer; the structure was solved and refined using the CRYSTAN program system (Rigaku), no absorption correction was applied. 2828 Unique reflections of which 1936 [$I > 3\sigma(I)$] are observed. The structure was solved by the heavy-atom method and refined by a full-matrix least-squares procedure. All the non-hydrogen atoms were refined anisotropically. Hydrogens were included in the calculation, but they were not refined. Final $R(R_w) = 0.092(0.103)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

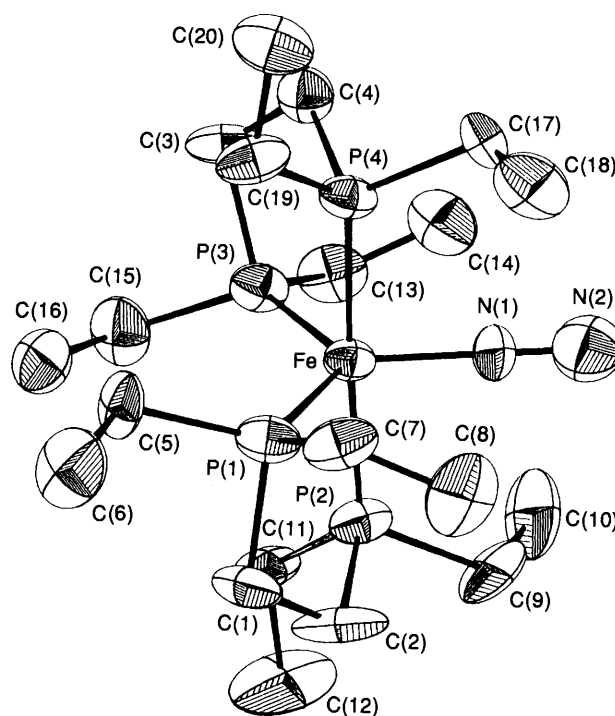


Fig. 1 Perspective view of the molecular structure of **1**. Selected bond lengths (Å): Fe–P(1) 2.205(3), Fe–P(2) 2.206, Fe–P(3) 2.176(3), Fe–P(4) 2.41(3), Fe–N(1) 1.748(8), N(1)–N(2) 1.139(13). Bond angles ($^\circ$) P(1)–Fe–N(1) 118.0(3), P(2)–Fe–N(1) 89.1(3), P(3)–Fe–N(1) 118.7(3), P(4)–Fe–N(1) 88.1(3), P(1)–Fe–P(2) 84.8(1), P(1)–Fe–P(3) 123.2(1), P(1)–Fe–P(4) 95.1(1), P(2)–Fe–P(3) 97.3(1), P(2)–Fe–P(4) 176.7(1), P(3)–Fe–P(4) 85.5(1).

ively. When hydrogen chloride (1–2 equiv.) was employed *trans*-[FeHCl(depe)₂], **2**, was isolated, suggesting that the first step of the reaction is the liberation of coordinated dinitrogen by the oxidative addition of HCl. Reaction of **1** with conc. sulfuric acid also liberated nitrogen (77%) and hydrogen (90%). Protonation of the coordinated nitrogen did not take place in both cases, although the formation of a small amount of ammonia was reported in the *in situ* protonolysis of the dmpe [1,2-bis(dimethylphosphino)ethane] analogue.^{3a}

Replacement of coordinated dinitrogen in **1** with carbon monoxide took place smoothly in THF at room temp. to give [Fe(CO)(depe)₂], **3**.

Further studies on the chemical reactivities of the novel iron(0) dinitrogen complex including reduction of the coordinated dinitrogen are now in progress. We thank Professor M. Hidai and Dr Y. Mizobe of the University of Tokyo for the analysis method of the reduction products and

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