The first side-on bound metal complex of diazene, HN=NH†

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The side-on bound metal complex of diazene *cis*-[Fe(NH=NH)(dmpe)$_2$] 2 was synthesised by reaction of [Fe(dmpe)$_2$Cl$_2$] with hydrazine in the presence of potassium graphite and characterised by ^{15}N NMR spectroscopy and X-ray crystallography.

The prospect of catalytically converting dinitrogen to ammonia at room temperature and ambient pressure, such as in biological nitrogen fixation systems, has challenged scientists for over 50 years.[1] There are three distinct kinds of nitrogenase enzymes capable of such a transformation—those based on molybdenum and iron, vanadium and iron, and iron with no other metal present,[2] suggesting that iron is crucial in the active site of nitrogenase. Similarly in the industrial production of ammonia from N_2 (the Haber–Bosch process) the most effective catalysts are based on iron and ruthenium.

In the cascade of reactions where coordinated N_2 is reduced to ammonia, the intermediate stages may involve metal bound diazenes and hydrazines. As a pure compound, diazene, HN=NH, is unstable with a half life in the gas phase at room temperature of only several minutes.[3] Diazene is stabilised by metal complexation and in this paper we describe the synthesis of the first iron(0) complex of diazene by reduction of an Fe(II) complex in the presence of hydrazine.

Treatment of *trans*-[FeCl$_2$(dmpe)$_2$] (dmpe = 1,2-bis(dimethylphosphino)ethane) with an excess of hydrazine in tetrahydrofuran afforded the iron(II) complex with a side-on bound hydrazine *cis*-[Fe(N$_2$H$_4$)(dmpe)$_2$]$^{2+}$ **1** as the (Cl)$_2$ salt as well as some insoluble [FeCl$_2$(N$_2$H$_4$)$_2$] by-product.[4] Extraction with methanol allowed the removal of [FeCl$_2$(N$_2$H$_4$)$_2$] and **1** was isolated as the (BPh$_4$)$_2$ salt on treatment with NaBPh$_4$. The ^{31}P{^{1}H} NMR spectrum of **1** contains two apparent triplets at 68.9 and 58.3 ppm which are characteristic of a symmetrical octahedral complex with 2 dmpe ligands and two identical donors in *cis* coordination sites. The two ^{1}H hydrazine resonances at 5.39 and 4.69 ppm correlate to a single ^{15}N signal at −387.9 ppm in a 2D ^{1}H–^{15}N correlation experiment indicating that the two nitrogen donors are equivalent and thus hydrazine is bound side-on to the metal. The complex can also be isolated as the (PF$_6$)(Cl) salt on treatment of the ethanol extract of **1** with KPF$_6$, as confirmed by X-ray crystallography‡ (Fig. 1). Iron complexes generally bind hydrazine end-on,[5] bridging[6] or with the terminal nitrogen protonated (hydrazinium).[7] Side-on bound hydrazine complexes are rare[8] and only a few complexes have been crystallographically characterised.[9] The geometry about iron is severely distorted about the equatorial plane, the severest distortion caused by the side-on bound hydrazine ligand where the bite angle N1–Fe1–N2 is only 42.49(9)°. The N–N bond length of 1.444(3) Å is within the range of the N–N bond lengths in other Fe–hydrazine complexes (1.439–1.453 Å)[5] and is consistent with single bond values (1.45 Å).[10]

Reduction of *trans*-[FeCl$_2$(dmpe)$_2$] with KC$_8$ in tetrahydrofuran in the presence of excess hydrazine under argon afforded the Fe(0) complex with a side-on bound diazene *cis*-[Fe(N$_2$H$_2$)(dmpe)$_2$] **2** after extraction with pentane. A small amount of *cis*-[FeH$_2$(dmpe)$_2$] was also produced as a reaction by-product. Slow evaporation of a hexane solution afforded needles suitable for X-ray crystal analysis§ (Fig. 2). The geometry of the complex is distorted trigonal bipyramidal where the diazene can be regarded as a single π-bound ligand, analogous to olefin binding to transition metals. Previously reported diazene complexes have been bridging or end-on bound.[11] As far as we are aware, this is the first side-on bound diazene complex to be synthesised and structurally characterised. The N–N bond lengths (1.427(7) and 1.398(8) Å) of the two independent molecules in the unit cell are shorter than the

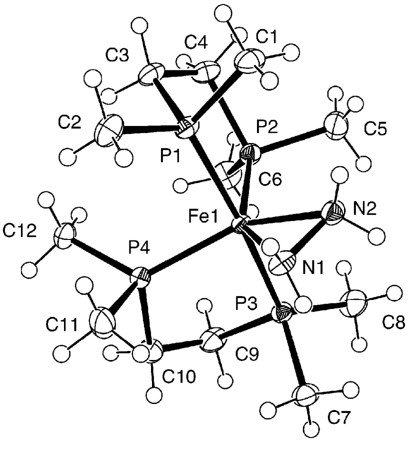

Fig. 1 ORTEP plot of **1** (50% displacement ellipsoids). Selected bond lengths (Å) and angles (°): Fe1–N1 1.981(2), Fe1–N2 2.003(2), Fe1–P4 2.1955(10), Fe1–P2 2.2117(9), Fe1–P1 2.2574(12), Fe1–P3 2.2598(11), N1–N2 1.444(3), N1–Fe1–N2 42.49(9), N1–Fe1–P4 104.93(7), N2–Fe1–P4 147.33(7), N1–Fe1–P2 149.17(7), N2–Fe1–P2 106.85(7), P4–Fe1–P2 105.81(3), N2–N1–Fe1 69.54(13), N1–N2–Fe1 67.97(13).

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† Electronic supplementary information (ESI) available: Experimental conditions and spectroscopic details for **1–3**. Crystallographic data. CCDC 676768–676770. See DOI: 10.1039/b802039f

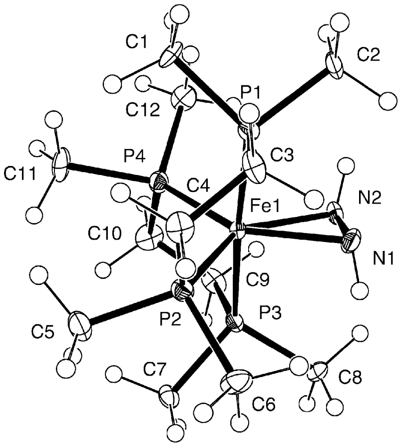

Fig. 2 ORTEP plot of **2** (50% displacement ellipsoids. Only one of the two independent molecules is shown). Selected bond lengths (Å) and angles (°): Fe1–N2 2.016(5), Fe1–N1 2.032(7), Fe1–P4 2.162(2), Fe1–P2 2.1667(19), Fe1–P1 2.196(2), Fe1–P3 2.2015(19), N1–N2 1.427(7), N2–Fe1–N1 41.3(2), N2–Fe1–P4 104.93(16), N1–Fe1–P4 145.34(18), N2–Fe1–P2 142.75(17), N1–Fe1–P2 102.45(17), P4–Fe1–P2 112.03(9), N2–N1–Fe1 68.8(3), N1–N2–Fe1 69.9(3).

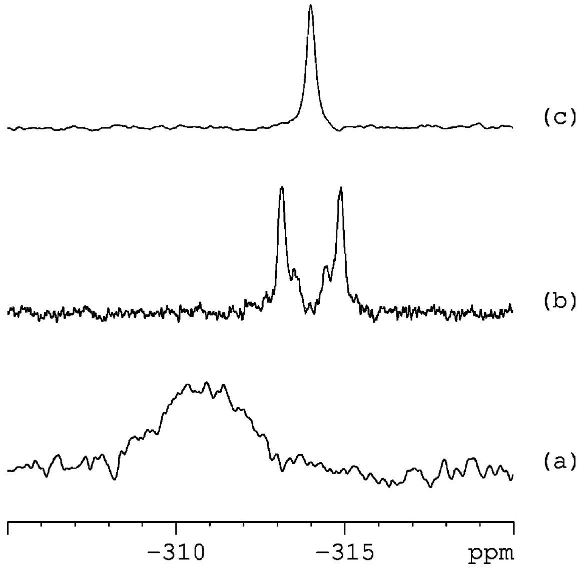

Fig. 3 ^{15}N NMR spectra (30 MHz) of **2** in thf-d_8 at (a) 298 K, (b) 220 K and (c) 220 K, ^{1}H decoupled.

N–N bond in **1** as expected, although significantly longer than those of previously reported end-on or bridging diazene complexes (1.13–1.35 Å).[11] This is consistent with lengthening of the double bond due to back-bonding from the electron-rich Fe(0) into the anti-bonding orbitals of the diazene ligand. The ^{31}P{^{1}H} NMR spectrum contains two apparent triplets at 67.5 and 60.0 ppm again characteristic of a symmetrically substituted octahedral complex with 2 dmpe ligands. The ^{15}N labelled complex was synthesised using $^{15}N_2H_4$ and this gave a broad resonance at −310.7 ppm in the ^{15}N NMR spectrum at 298 K. On cooling to 220 K, the ^{15}N spectrum appears superficially as a sharp doublet with fine structure typical of the AA′ part of an AA′XX′ splitting pattern. This collapsed to a singlet on ^{1}H decoupling (Fig. 3) and confirms the presence of the HN═NH moiety in the structure. The ^{1}H resonance at 2.04 ppm overlaps with other ligand resonances and was identified using a ^{1}H–^{15}N shift correlation experiment. The ^{1}H chemical shift of the coordinated diazene is approximately 10 ppm upfield of the shifts reported for other end-on and bridging diazene complexes which are typically in the range δ ^{1}H 11–17 ppm.[12,13] The ^{15}N resonance is some 400 ppm upfield from that reported for *trans*,*trans*-[W(NH═NH)(CO)$_2$(NO)(PPh$_3$)$_2$](SO$_3$CF$_3$) (δ ^{15}N 70–184 ppm).[12]¶ The unexpectedly high field ^{15}N shifts are not inconsistent with shielding observed in the ^{13}C and ^{1}H spectra of analogous Fe(olefin)(dmpe)$_2$ complexes.[14]

Because there is no precedent for the unexpected ^{15}N shifts in **2**, the known compound [Fe(PhN═NPh)(dmpe)$_2$] **3**[14] was re-examined. Complex **3** was prepared by the reaction of *trans*-[FeCl$_2$(dmpe)$_2$] with KC$_8$ in the presence of excess azobenzene. The resulting Fe(0) complex was crystallised by slow evaporation of a tetrahydrofuran solution to afford dark orange crystals. The structural analysis‖ (Fig. 4) showed that the azobenzene ligand was also π-bound with an N═N bond length of 1.412(4) Å similar to that for **2** and consistent with those for other side-on bound azobenzene complexes on iron (1.398–1.441 Å).[15] Labelling **3** with ^{15}N** revealed the ^{15}N chemical shift at −269.3 ppm which is also a highly shielded resonance, consistent with the chemical shift of **2**.

The mechanism for the formation of **2** from *trans*-[FeCl$_2$(dmpe)$_2$] is likely to involve initial reduction of Fe(II) to form the reactive coordinatively unsaturated Fe(0) species which oxidatively adds an N–H bond of hydrazine to form a hydrido hydrazide complex. Dehydrogenation of hydrazide to give hydrogen gas and coordinated diazene affords **2** (Scheme 1). The observed formation of [FeH$_2$(dmpe)$_2$] as a by-product would be the result of the reaction of [Fe(dmpe)$_2$] with H$_2$ in the reaction mixture.

Complex **2** (^{15}N labelled) decomposes in solution to form [Fe(dmpe)$_2$]$_2$(μ-dmpe)[14] and other unidentified products as well as $^{15}NH_3$ and $^{15}N_2$ as determined from ^{15}N NMR spectroscopy. At this stage we have no evidence that the reaction to form ammonia takes place on the metal and it could be due to loss of diazene from the complex with disproportionation of the unstable species to form NH$_3$ and N$_2$.

The chemistry of **2** may shed additional light on the role of Fe(0) in the Haber–Bosch process.

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Notes and references

‡ **Crystal data for 1**. C$_{12}$H$_{36}$ClF$_6$FeN$_2$P$_5$, M = 568.58, monoclinic, a = 10.030(5), b = 16.000(5), c = 15.012(5) Å, β = 93.687(5)°, V = 2404.1(16) Å^3, T = 150(2) K, space group $P2_1/n$(#14), Z = 4, N = 23 374, N_{ind} 5752 (R_{merge} = 0.0480), w$R(F_2)$ = 0.0914. Hydrogen atoms on the nitrogens were located and refined.

§ **Crystal data for 2**. C$_{12}$H$_{34}$FeN$_2$P$_4$, M = 386.16, orthorhombic, a = 18.053(2), b = 14.6836(17), c = 14.5977(17) Å, V = 3869.7(8) Å^3, T = 100(2) K, space group $Pca2_1$, Z = 8, N = 25 282, N_{ind} 5088 (R_{int} = 0.0903), w$R(F_2)$ = 0.087, Flack parameter 0.01(3), estimate of Friedel pairs measured = 2159, fraction of Friedel pairs measured = 0.737. Four restraints (corresponding to the 4 NH bonds) were applied in order to place and refine hydrogen atoms of the diazenes.

¶ Conversion factor to nitromethane scale used is −380 ppm.[16]

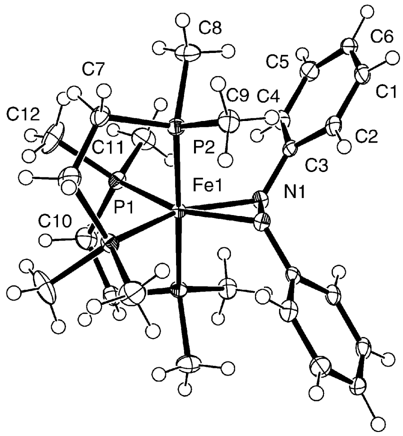
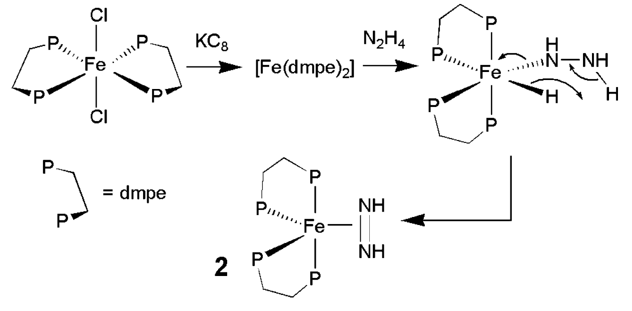


Fig. 4 ORTEP plot of **3** (50% displacement ellipsoids. Molecule has crystallographically imposed twofold symmetry). Selected bond lengths (Å) and angles (°): Fe1–N1 2.002(2), Fe1–P1 2.1880(8), Fe1–P2 2.2342(7), N1–N1a 1.412(4), N1a–Fe1–N1 41.30(11), N1a–Fe1–P1 152.94(6), N1–Fe1–P1 111.88(6), P1–Fe1–P1a 95.10(4), N1–Fe1–P2a 85.81(6), N1–Fe1–P2 95.46(6), C3–N1–N1a 114.2(2), C3–N1–Fe1 127.61(16), N1a–N1–Fe1 69.35(5).

‖ **Crystal data for 3**. $C_{24}H_{42}FeN_2P_4$, $M = 538.35$, monoclinic, $a = 8.9761(13)$, $b = 16.911(3)$, $c = 17.931(3)$ Å, $\beta = 99.899(7)°$, $V = 2681.4(8)$ Å^3, $T = 100(2)$ K, space group $C2/c$, $Z = 4$, $N = 8539$, N_{ind} 1999 ($R_{\text{int}} = 0.0345$), $wR(F_2) = 0.0653$.

** Azobenzene–$^{15}N_2$ was prepared by oxidation of aniline–^{15}N with MnO_2.[17]



Scheme 1 Proposed mechanism for formation of **2**.

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