Molecular N_2 complexes of iron stabilised by *N*-heterocyclic 'pincer' dicarbene ligands†

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The first N_2 complex stabilised by *N*-heterocyclic carbene ligands, Fe(C–N–C)$(N_2)_2$, has been obtained by the reduction of Fe(C–N–C)Br_2 where C–N–C = 2,6-bis(aryl-imidazol-2-ylidene)pyridine, aryl = 2,6-$Pr^i_2C_6H_3$, with Na(Hg); it serves as a convenient precursor for other iron NHC 'pincer' complexes of the type Fe(C–N–C)(N_2)L where L = C_2H_4, PMe_3 and Fe(C–N–C)$(CO)_2$.

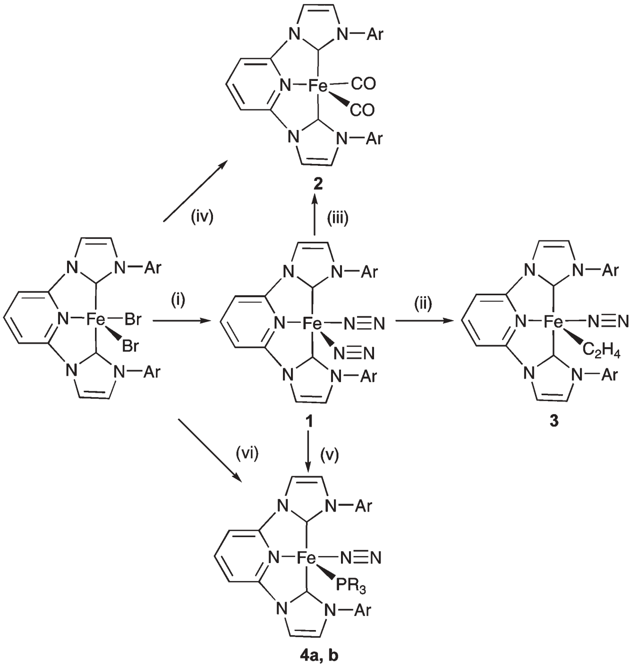
Since their discovery, N_2 complexes of the transition metals have been considered as important intermediates in plausible artificial systems for the fixation and activation of molecular nitrogen under mild conditions.[1] It is generally accepted that fixation of N_2 is accompanied by some 'activation', which can be probed by structural and spectroscopic means and may lead to increased reactivity. The degree of 'activation' is dependent on the type of the metal and the electronic properties of co-ligands present in the complex. Most of the coordinated N_2 cleavage reactions have been observed with low oxidation state phosphine complexes of group 5 and 6 metals.[1a] However, recent work with versatile higher oxidation state Mo amido complexes gave remarkable systems capable of N_2 cleavage and reduction.[1b,2]

In general, most synthetic Fe–N_2 complexes are considered as 'unactivated', even though iron plays an important role in biological and industrial nitrogen derivatisation.[3,4]

Recent work by Holland and Peters has given iron complexes with 'activated' bridging dinitrogen.[5] However, the search for new ligand topologies and donor environments which could give rise to iron complexes capable of dinitrogen fixation and activation is still an active area of research. We envisaged that dinitrogen complexes of iron with preorganised co-ligands incorporating strongly σ-donating NHCs could provide strongly π-basic metal centres capable of N_2 activation. In addition, they may serve as useful precursors to other reactive iron NHC complexes.

In this communication, we wish to report the first iron(0) dinitrogen complexes stabilised by NHC ligands. We also describe preliminary results on their use as convenient precursors for other iron NHC complexes.

Reduction of Fe(C–N–C)Br_2[6] with an excess of Na(Hg) in thf under N_2† gave red-brown solutions from which, after filtration and crystallisation from pentane, green-brown crystals of **1** can be isolated (see Scheme 1).



Scheme 1 The Fe complexes described in this paper; reagents and conditions: (i) Na(Hg), thf, N_2; (ii) C_2H_4, thf; (iii) CO, thf; (iv) Na(Hg)–CO; (v) PR_3, thf; (vi) Na(Hg), PR_3, R = Me, **4a**; cyclohexyl, **4b**.

The structure of **1** in the solid state determined by X-ray diffraction is shown in Fig. 1. The geometry is best described as distorted square pyramidal with one apical and one basal end-on dinitrogen ligand. The N≡N bond lengths are very similar and slightly elongated from the free N≡N value (1.0968 Å); they, as well as the Fe–N bond lengths, are comparable to those reported for other mono-N_2 complexes of iron.[4] The iron atom is positioned 0.3556(12) Å above the basal plane.

Complex **1** is diamagnetic and is stable in C_6D_6 solutions for a limited time (*ca.* 1 day); the ^{1}H-NMR spectrum indicates that in solution it adopts a C_{2v} symmetric structure, supporting a trigonal bipyramidal geometry or fluxionality. The intense infrared absorptions‡ at 2109 and 2031 cm^{-1} can be assigned to either square pyramidal or trigonal bipyramidal geometry. However, the presence of a weaker band at 2044 cm^{-1} could be assigned as part of a partially obscured pair suggesting the presence of an equilibrium between trigonal bipyramidal and square pyramidal structures in solution. The position of the absorptions indicate reduced backbonding to the coordinated N_2 compared with other Fe(N_2)(P–P$)_2$ complexes (1950–2068 cm^{-1}).[4] Complex **1** is the first structurally characterised bis-dinitrogen complex of iron and the first dinitrogen complex stabilised by NHC ligands.§

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† Electronic supplementary information (ESI) available: experimental procedures and spectroscopic characterisation data. See http://www.rsc.org/suppdata/cc/b4/b415562a/

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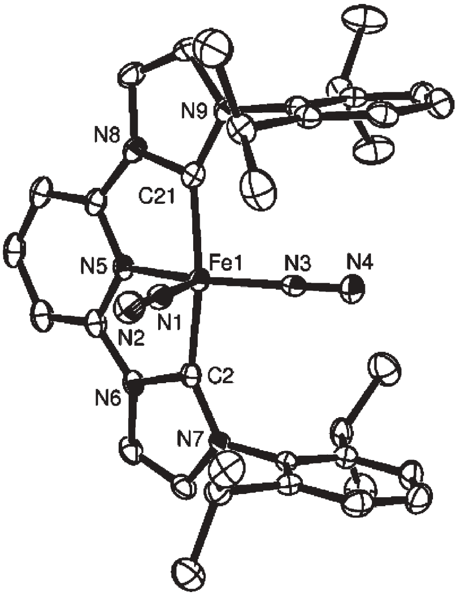

Fig. 1 ORTEP representation of the structure of **1** at 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Fe1–N1 = 1.847(2), Fe1–N3 = 1.820(2), Fe1–C21 = 1.912(3), Fe1–C2 = 1.915(3), N1–N2 = 1.115(3), N3–N4 = 1.113(3), Fe1–N3–N4 = 179.2(2), Fe1–N1–N2 = 175.0(2), N1–Fe1–N3 = 98.88(10).

Substitution of both N_2 ligands is observed after the reaction of **1** with CO.†¶ Complex **2** (see Scheme 1) was fully characterised by analytical, spectroscopic and diffraction methods. In an analogous way, **2** adopts a distorted square pyramidal geometry in the solid state. Details of this structural characterisation are included as supporting information.†

Reaction of **1** with ethene (thf, 80 psi, 1 day) results in substitution of one dinitrogen ligand and the formation of complex **3**. The crystal structure of **3** (Fig. 2) reveals a distorted square pyramidal geometry at iron with the ethylene occupying the axial site. The C–C axis is parallel to the Fe1–N1 vector. There is a slight elongation of the ethene bond length from the free ethylene value (1.35 Å); the $N\equiv N$ bond length is slightly longer than the one observed in **1**. Attempts to substitute the second N_2 ligand were not successful.

Substitution of one dinitrogen ligand is also occurring in the reaction of **1** with PR_3 (R = Me, Cy) giving **4a, b**. Complexes **4a**, **4b** are also obtained by the reduction of $Fe(C–N–C)Br_2$ with Na(Hg) in the presence of the phosphine under N_2.†¶ The green-brown complexes were obtained by crystallisation from ether (PMe_3) or petroleum (PCy_3). The molecular structure of **4a** is shown in Fig. 3. The distorted square pyramidal geometry is adopted in this case too, with the trimethylphosphine occupying the axial position. The strong σ-donating character of the phosphine is not reflected in the $N\equiv N$ bond distance, which is similar to the one observed in **1** and **3**.

In conclusion, we have prepared the first stable bis-dinitrogen iron complex stabilised by the 'pincer' NHC ligand. We have also shown that it undergoes facile substitution of one or two dinitrogen ligands serving as a versatile and clean precursor for further derivatisation.

Preliminary data show that **1** reacts with H_2, $PhSiH_3$ and alkynes. Work in progress is directed towards detailed understanding of the reactivity of **1** both in substitution and other catalytic reactions, by taking advantage of the high lability of the N_2 ligands and the increased nucleophilicity of the metal centre by virtue of the strongly σ-donating NHCs. This may lead to the expansion of the catalytic chemistry of the environmentally benign and inexpensive iron.

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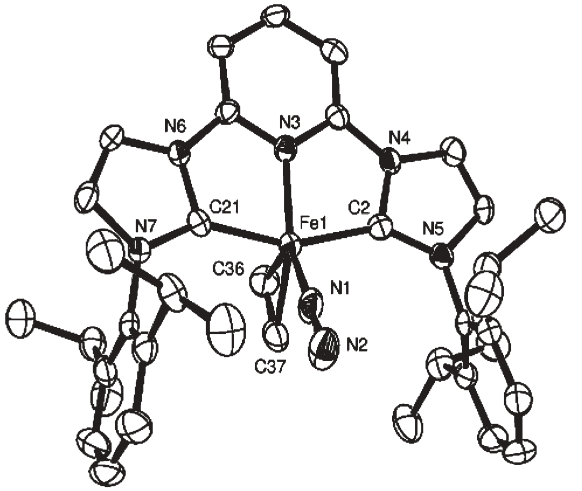

Fig. 2 ORTEP representation of the structure of **3** at 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Fe1–N1 = 1.820(5), Fe1–N3 = 1.905(4), Fe1–C21 = 1.927(6), Fe1–C2 = 1.933(6), N1–N2 = 1.121(5), C36–C37 = 1.379(6), Fe1–N1–N2 = 175.0(2), N3–Fe1–N1 = 139.96(17).

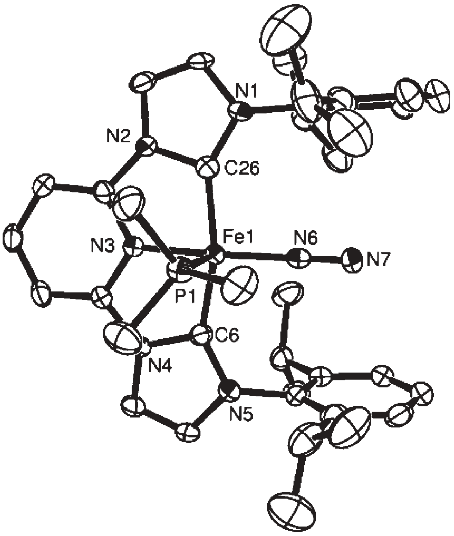

Fig. 3 ORTEP representation of the structure of **4a** at 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Fe1–N3 = 1.880(3), Fe1–N6 = 1.779(3), Fe1–C6 = 1.888(3), Fe1–C26 = 1.881(3), N6–N7 = 1.129(4), Fe1–N6–N7 = 178.4(3), P1–Fe1–N6 = 100.95(10), P1–Fe1–N3 = 93.58(9).

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Notes and references

‡ IR data (N_2 region, cm^{-1}): for **1**: 2109, 2031 and 2044 (sh); for **2**: 1928 and 1865; for **3**: 2056; for **4a**: 2032; for **4b**: 2012.

§ During the submission of this communication, Chirik *et al.*[7] described the synthesis, characterisation and alkyne and bis-silane derivatives of an analogous, square pyramidal but paramagnetic Fe[(2,6-(ArN=CMe)$_2$-C_5H_3N](N_2)$_2$. The higher π-acidity of the imine donor set is reflected on the position of the IR absorptions of the coordinated N_2 [2124, 2053 and 2062 (sh) cm^{-1}] and the N≡N bond lengths [1.090(2) and 1.104(3) Å for basal and apical N_2, respectively]. The IR and structural data for Fe[(2,6-(ArN=CMe)$_2$$C_5H_3N$](CO)$_2$, which was also prepared, support this trend.

¶ Crystal data: for **1**: $C_{40}H_{53}FeN_9$, $M = 715.76$, triclinic, $a = 8.7070(17)$, $b = 15.226(3)$, $c = 15.788(5)$ Å, $\alpha = 73.78(2)$, $\beta = 79.44(2)$, $\gamma = 76.978(16)^\circ$, $U = 1941.8(8)$ Å^3, $T = 120$ K, space group $P\bar{1}$, $Z = 2$, μ(Mo-Kα) = 0.428 mm^{-1}, $\lambda = 0.71073$ Å, 34076 reflections measured, 8972 unique ($R_{\text{int}} = 0.0698$) which were used in all calculations. The final $wR(F^2)$ was 0.1221 (all data) and $R = 0.0583$ [$I > 2\sigma(I)$]. For **3**: $C_{37}H_{45}FeN_7$, $M = 643.65$, monoclinic, $a = 31.84(5)$, $b = 8.911(12)$, $c = 23.56(5)$ Å, $\beta = 92.3^\circ$, $U = 6679(20)$ Å^3, $T = 120$ K, space group $C2/c$, $Z = 8$, μ(Mo-Kα) = 0.489 mm^{-1}, $\lambda = 0.71073$ Å, 32529 reflections measured, 7073 unique ($R_{\text{int}} = 0.1619$) were used in all calculations. The final $wR(F^2)$ was 0.1614 (all data) and $R = 0.0797$ [$I > 2\sigma(I)$]. For **4**: $C_{42}H_{60}FeN_7OP$, $M = 765.79$, orthorhombic, $a = 18.2286(17)$, $b = 17.4745(18)$, $c = 13.7220(15)$ Å, $U = 4370.9(8)$ Å^3, $T = 120$ K, space group $Pna2_1$, $Z = 4$, μ(Mo-Kα) = 0.420 mm^{-1}, $\lambda = 0.71073$ Å, 24392 reflections measured, 9009 unique ($R_{\text{int}} = 0.051$) which were used in all calculations. The final $wR(F^2)$ was 0.1249 (all data) and $R = 0.0517$ [$I > 2\sigma(I)$]. CCDC 252527–252530. See http://www.rsc.org/suppdata/cc/b4/b415562a/ for crystallographic data in .cif or other electronic format.

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