Aust. J. Chem. **2014**, *67*, 1011–1016 http://dx.doi.org/10.1071/CH14157

Full Paper

Low-valent Iron Complexes Stabilised by a Bulky Guanidinate Ligand: Synthesis and Reactivity Studies*

Lea Fohlmeister^A and Cameron Jones^{A,B}

^ASchool of Chemistry, PO Box 23, Monash University, Melbourne, Vic. 3800, Australia. ^BCorresponding author. Email: cameron.jones@monash.edu

A toluene-capped guanidinato iron(1) complex [(Pipiso)Fe(η^6 -toluene)] (Pipiso = [(DipN)_2C(*cis*-NC₅H₈Me₂-2,6)]⁻) was prepared by magnesium metal reduction of {[(Pipiso)Fe^{II}(μ -Br)]₂} in toluene. The reactivity of the closely related Fe^I-Fe^I multiply bonded species, {[Fe(μ -Pipiso)]₂} towards a range of unsaturated small molecule substrates was investigated, and found to be broadly similar to that of low-valent β -diketiminato iron complexes. That is, its reaction with CO yielded the iron(1) carbonyl complex [(Pipiso)Fe(CO)₃], whereas reaction with CO₂ formed the same product via an apparent reductive disproportionation of the substrate. In contrast, reaction between {[Fe(μ -Pipiso)]₂} and CS₂ led to reductive C=S bond cleavage and the isolation of {[(Pipiso)Fe]₂(μ -S)(μ -CS)}. Different reactivity was seen with AdN₃ (Ad = 1-adamantyl), which was reductively coupled by the iron(1) dimer to give iron(1) hexaazenyl complex {[(Pipiso)Fe]₂(μ -AdN₆Ad)}.

Manuscript received: 17 March 2014. Manuscript accepted: 9 April 2014. Published online: 29 May 2014.

Introduction

The kinetic stabilisation of low-oxidation state/low-coordination number first row transition metal complexes that are free of carbonyl ligands is a topic of considerable interest.^[1] From a fundamental standpoint, the appeal of such compounds is derived from the challenges they pose to existing concepts of bonding and inherent stability. At the same time, they have been applied in several areas owing to their high reactivity. As an example, low-coordinate iron(1) compounds, which have been stabilised by a variety of bulky mono- and higher-dentate ligands,^[2,3] have recently found roles in catalysis,^[4] the chemistry of magnetic materials,^[5] and bioinorganic chemistry.^[6]

A class of ligand that has proved particularly successful for the stabilisation of iron(I) and quasi-iron(I) complexes are the β-diketiminates (or Nacnacs). Examples of compounds these ligands have allowed access to include dinitrogen activated species 1^[7] and arene-coordinated compound 2 (Fig. 1).^[7] Owing to the reducing nature of these systems, these compounds have been applied in a range of catalytic and stoichiometric organic transformations,^[8] and inorganic synthetic methodologies.^[9] Moreover, compounds such as 1 can be further reduced by treatment with alkali metals to give, for example, $K_2[1]$, in which the bridging N₂ ligand is strongly activated.^[7] Compounds related to 1, but incorporating smaller Nacnac ligands are thought to be intermediates in related reductions of β-diketiminato iron(II) halides that lead to complete cleavage of the N2 molecule and formation of iron nitride species such as 3.^[10] Treatment of 3 with acids under ambient conditions was shown to generate NH₃, showing potential in the development of low energy, solution-based alternatives to the Harber-Bosch process.

In recent years, we have developed a range of extremely bulky amidinate and guanidinate ligands, featuring similar stabilising properties to those of the related β -diketiminate



Fig. 1. β -diketiminate- and guanidinate-stabilised low-valent iron complexes.

^{*}This invited submission is associated with the award of the Royal Australian Chemical Institute's HG Smith Memorial Medal to CJ.

ligand class.^[11] These bidentate ligands have been used in the preparation of low-oxidation state complexes involving metals from all blocks (s-,^[12] p-,^[13] d-,^[14] and f-^[15]) of the periodic table. For iron(1), these include the toluene-capped and dinitrogen-bridged amidinato complexes [(Piso)Fe(η^6 toluene)] and $\{[(Piso)Fe]_2(\mu-N_2)\}$, respectively where Piso = $[(\text{DipN})_2\text{CBu}^t]^-$ and $\text{Dip} = C_6\text{H}_3\text{Pr}_2^i2, 6.^{[16]}$ Both complexes have counterparts in the Nacnac chemistry e.g. 1 and 2. More recently, we have reported the unusual dinuclear, high-spin guanidinato-iron(I) compound 4, which exhibits the shortest Fe-Fe bond (2.1270(7) Å) reported to date in the literature.^[17] This compound was prepared by reduction of the precursor complex {[(κ^2 -N,N'-Pipiso)Fe(μ -Br)]₂} (Pipiso = [(DipN)₂) $C(cis-NC_5H_8Me_2-2,6)]^{-}$ with the magnesium(1) reagent { $[(^{Mes}Nacnac)Mg]_2$ } ($^{Mes}Nacnac = [(MesNCMe)_2CH]^{-}$). Given the rich coordination and redox chemistry of β-diketiminato iron(I) complexes, e.g. 1 and 2, and the lack of reactivity studies addressing low-valent, carbonyl-free Fe-Fe bonded systems, it seemed appealing to investigate further the reactivity of 4 and related species, and to compare the reactivity with that of β -diketiminato iron(1) complexes. The results of these studies are reported herein.

Results and Discussion

In the early stages of this study, attempts were made to prepare iron(I) compounds, other than 4, incorporating the Pipiso ligand. The previously reported reduction reaction that gave 4 was carried out in cyclohexane under an argon atmosphere.^[17] In an attempt to form an analogue of 1 and {[(Piso)Fe]₂(μ -N₂)}, the reduction process was repeated herein under an N2 atmosphere. Surprisingly, this did not give the N₂ complex, but afforded 4 in a yield (\sim 50%) similar to that obtained when the reaction was carried out under argon. Although 4 is unreactive towards N₂, it was proposed that treatment with toluene would lead to cleavage of the dimer and formation of a toluene-capped complex comparable to **2** and [(Piso)Fe(η^6 -toluene)]. However, under these conditions, 4 remained unreactive, even at temperatures of up to 80°C. As an alternative route the toluene-capped iron(I) complex, the reduction of precursor compound{[(κ^2 -N,N'-Pipiso)Fe $(\mu$ -Br)]₂ was carried out in toluene using activated magnesium metal as the reducing agent. This yielded the expected complex 5, in a low isolated yield as dark red crystals (Scheme 1). Although it was not possible to obtain a crystal structure of publishable quality for this compound, a structure of marginal quality was obtained, confirming the monomeric nature of the compound containing N,N'-chelating Pipiso and η^6 -coordinated toluene ligands. Its solution state magnetic moment (Evans method) was determined as $\mu_{\rm eff} = 2.59 \,\mu_{\rm B}$. Although this is higher than that expected for a low-spin d⁷ electron configuration $(S = 1/2, \mu_{so} = 1.73 \mu_B)$, it is very similar to the value ($\mu_{eff} = 2.5 \,\mu_B$) obtained for the analogous β -diketiminatocoordinated Fe^I complex 2.^[7]

The chemistry of 4 was further explored with respect to its reactivity towards small unsaturated molecules. Initially, treatment of a toluene solution of the compound with an excess of CO was carried out and this led to cleavage of the dimer and generation of the dark green guanidinato iron-tricarbonyl compound 6 in a low isolated yield (Scheme 2). Little useful information could be obtained from the ¹H NMR spectrum of the compound, of which the resonances were very broad because of the paramagnetic nature of 6. Its solution state magnetic moment (Evans method) was determined as $\mu_{eff} = 1.56 \,\mu_B$, which is lower than that for 5, but consistent with a low-spin



Scheme 1. Synthesis of compound 5.



Scheme 2. Synthesis of compounds 6–8 (Ad = 1-adamantyl).

 d^{7} electron configuration for the Fe^I centre. It is noteworthy that in a previous study, treatment of **1** with an excess of CO afforded an iron(1) tricarbonyl complex, $[(^{Dip}Nacnac)Fe(CO)_{3}]$ $(\mu_{eff} = 2.0 \,\mu_{B}, {}^{Dip}Nacnac = [(DipNCMe)_{2}CH]^{-}), {}^{[7]}$ very similar to **6**. Furthermore, the infrared spectrum of compound **6** exhibited strong CO stretching bands at similar wavenumbers to that of equivalent bands in the infrared spectra of related compounds $[(^{Dip}Nacnac)Fe(CO)_{3}]^{[7]}$ and $[(Piso)Fe(CO)_{3}].^{[16]}$

Compound **6** was crystallographically characterised and its molecular structure is displayed in Fig. 2. The structure is closely comparable with that of $[(Piso)Fe(CO)_3]^{[16]}$ i.e. it is monomeric with a distorted square-based pyramidal Fe coordination environment. The base of the pyramid encompasses N(1), N(2), C(33), and C(35) (Sum (Σ) of the N–Fe–N angles = 353.77°), with C(34) taking up the apical position. Examination of the bond lengths within the CN₃ fragment of the complex suggests a degree of electronic delocalisation over the four atoms. However, given the fact that the dihedral angle between the CN₃ least-squares plane and that of the NC₂ unit of the piperidyl substituent is 22.6°, the participation of the C(1)–N(3) bond in the delocalisation is expected to be lower than that of the C(1)–N(1) and C(1)–N(2) bonds.

The reaction of **4** with an excess of dry CO_2 was subsequently examined. At $-60^{\circ}C$, no reaction occurred, but upon warming the mixture to room temperature and stirring for 16 h, the solution turned deep green. Infrared and ¹H NMR spectroscopic analyses of the reaction solution revealed a complex mixture of products that included the iron carbonyl complex **6**. All attempts to separate the product mixture were unsuccessful. Although the formation mechanism of **6** cannot be ascertained, it is likely that



Fig. 2. *ORTEP* diagram of **6** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Fe(1)–N(1) 1.9672(17), Fe(1)–N(2) 1.9753(15), Fe(1)–C(35) 1.780(3), Fe(1)–C(33) 1.805(2), Fe (1)–C(34) 1.852(2), N(1)–C(1) 1.355(2), N(2)–C(1) 1.342(2), N(3)–C(1) 1.358(2), N(1)–Fe(1)–N(2) 66.75(6), N(2)–C(1)–N(1) 107.07(15).

it involves the reductive disproportionation of CO₂ by **4**, thus generating CO which reacts with the remaining iron(1) dimer in the mixture to give the iron carbonyl complex. Although the generation of iron oxide and/or carbonate by-products would be expected in such a process, none were identified in the reaction mixture. Regardless, reductive disproportionations of CO₂ to CO and CO₃²⁻ are well known for transition metal complexes,^[18] including Nacnac-coordinated iron(1) compounds.^[19]

To investigate whether similar chemistry occurs for CS₂, two equivalents of this substrate were reacted with 4 in toluene. A rapid reaction occurred at -40° C, yielding a dark brown solution that was then warmed to ambient temperature. Subsequent workup afforded a moderate isolated yield of the thermally stable iron(II) complex 7 (Scheme 2). It is apparent that the reaction proceeds via the reductive cleavage of a C=S bond of CS_2 to give 7, which is unreactive towards excess substrate. Although the reductive disproportionation of CS₂ to CS and CS_3^{2-} did not occur under these conditions, compound 7 could be considered as an intermediate of this hypothetical reaction pathway. It is worth noting that the cleavage of a C=S bond in CS_2 , facilitated by low-valent iron centres, has precedent in the literature. For example, Lewis et al. showed that the reaction between [Fe₃(CO)₁₂] and excess CS₂ at 80°C in a CO atmosphere affords the tetra-nuclear cluster compound $[Fe_4(CO)_{12}(CS)S]$ as one of the reaction products.^[20] Although related to 7, both the CS and S ligands in $[Fe_4(CO)_{12}(CS)S]$ μ_3 -cap a Fe₃ triangular unit in that cluster.

The crystal structure of 7 contains one full and one half molecule (sitting on a crystallographic inversion centre) in the asymmetric unit; the molecular structure of the full molecule is displayed in Fig. 3. Both iron centres of the compound display distorted square planar coordination environments, with an average dihedral angle of 18.1° between the CN₂Fe and Fe₂CS least-squares planes. The Fe atoms are chelated by delocalised Pipiso ligands, and are symmetrically bridged by sulfide and thiocarbonyl units. All of the Fe–N, Fe–S, Fe–C and C=S distances in the complex are all well within the known ranges for such interactions.^[21] Although the Fe…Fe separation in the compound (2.5800(6) Å) is also within the sum of the covalent radii of the two iron centres (2.64 Å),^[22] it is unlikely that there is any significant bonding interaction between the atoms.



Fig. 3. *ORTEP* diagram of 7 (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Fe(1)-C(1) 1.942(3), Fe(1)-N(4) 1.988(2), Fe(1)-N(5) 1.996(2), Fe(1)-S(1) 2.1324(9), Fe(2)-C(1) 1.935(3), Fe(2)-N(1) 1.976(2), Fe(2)-N(2) 2.008(2), Fe(2)-S(1) 2.1336(9), N(3)-C(2) 1.361(3), N(1)-C(2) 1.342(4), N(2)-C(2) 1.347(3), N(6)-C(34) 1.364(3), N(5)-C(34) 1.349(4), N(4)-C(34) 1.337(3), N(4)-Fe(1)-N(5) 66.02(9), C(1)-Fe(1)-S(1) 100.97(9), N(1)-Fe(2)-N(2) 66.13(9), C(1)-Fe(2)-S(1) 101.17(9), N(1)-C(2)-N(2) 107.9(2), N(4)-C(34)-N(5) 107.8(2).

Square planar iron(II) complexes, though not rare, are atypical. Regardless, this geometry has been reported to be sterically enforced on iron when it is coordinated to amidinate ligands of a similar steric bulk to that of Pipiso, e.g. in [Fe(Phiso)₂] (Phiso = $[(DipN)_2CPh]^{-}$).^[23] Moreover, square planar iron(II) complexes often adopt intermediate spin (*S* = 1) electronic configurations.^[24] A combination of intermediate spin iron(II) centres in 7 and significant antiferromagnetic coupling between those centres would provide an explanation for the rather low solution state magnetic moment ($\mu_{eff} = 2.6 \mu_B$, Evans method) determined for the compound. However, confirmation of this hypothesis via a detailed variable temperature solid state magnetic moment analysis of 7 is beyond the scope of this preliminary reactivity study.

Holland and co-workers reported that the low-valent β -diketiminato iron complex 1 was able to reductively couple 1-adamantyl azide, AdN₃, producing the first reported metal hexaazenyl complex, $\{[(^{Dip}Nacnac)Fe]_2(\mu-AdN_6Ad)\}$.^[25] For comparison, reaction of 4 with two equivalents of AdN₃ was conducted. This led to the cleavage of the Fe-Fe bond in 4 and the low-yield formation of the analogous dark brown crystalline hexaazenyl complex 8 (Scheme 2). The major product of this reaction precipitated as a poorly soluble paramagnetic yellow solid. Crystals of this compound suitable for X-ray diffraction analysis could not be grown, and the spectroscopic data shed little light on its formulation. Similarly, the paramagnetic complex 8 is NMR inactive in solution. Given the very low yield of the complex, and the fact that it consistently cocrystallised with significant amounts (~ 10 %) of the free amine PipisoH, no meaningful magnetic data could be obtained. It is noteworthy, however, that magnetic and Mössbauer spectroscopic measurements of the closely related complex $\{[(^{Dip}Nacnac)$ $Fe]_2(\mu-AdN_6Ad)$ revealed that it possessed two high-spin Fe^{II} centres that are antiferromagnetically coupled.[25]

Despite the lack of spectroscopic data for **8**, an X-ray crystal analysis revealed the hexaazenyl-bridged diiron structure of the complex to be essentially isostructural to $\{[(^{Dip}Nacnac)Fe]_2 (\mu-AdN_6Ad)\}$ (see Fig. 4). Each N–C–N-delocalised Pipiso ligand chelates an iron(π) centre with similar Fe–N bond lengths.



Fig. 4. *ORTEP* diagram of **8** (25 % thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Fe(1)-N(6)' 2.013(4), Fe(1)-N(2) 2.019(5), Fe(1)-N(4) 2.027(4), Fe(1)-N(1) 2.053(5), N(1)-C(1) 1.342(6), N(2)-C(1), 1.322(7), N(3)-C(1) 1.392(6), N(4)-N(5) 1.300(6), N(5)-N(6) 1.308(6), N(6)-N(6)' 1.416(8), N(2)-Fe(1)-N(1) 65.14(18), N(6)'-Fe(1)-N(4) 75.63(16), N(2)-C(1)-N(1) 110.7(4), N(4)-N(5)-N(6) 117.5(4), N(5)-N(6)-N(6)' 113.5(5). Symmetry operation: '-x + 2, -y + 1, -z.

The distorted tetrahedral iron coordination spheres are completed by chelation with two N centres of the hexaazenyl unit. Examination of the N–N distances in that unit suggests that the central N(6)–N(6)' bond is single, whereas the other four N–N interactions are delocalised double bonds. In that respect, the N₆ fragment is best viewed as two triazaallyl moieties bridged by an N–N bond, similar to the AdN₆Ad fragment in {[(^{Dip}Nacnac) Fe]₂(μ -AdN₆Ad)}^[25] and other recently reported iron^[26] and magnesium^[27] hexaazenyl complexes.

Conclusion

A new monomeric, toluene-capped guanidinato iron(I) complex [(Pipiso)Fe(η^6 -toluene)] (5) was formed upon reduction of iron(II) precursor complex {[(κ^2 -N,N'-Pipiso)Fe(μ -Br)]₂} in toluene. In addition, the reactivity of the related Fe-Fe multiply bonded species { $[Fe(\mu-Pipiso)]_2$ } (4) towards a range of unsaturated small molecule substrates was investigated. The reaction with CO yielded the iron(1) carbonyl complex $[(Pipiso)Fe(CO)_3]$ (6), whereas that with CO_2 proceeded via an apparent reductive disproportionation of the gas, ultimately generating 6. In contrast, reaction between 4 and CS_2 led to reductive C=S bond cleavage and isolation of the iron(II) sulfide/thiocarbonylbridged system {[(Pipiso)Fe]₂(μ -S)(μ -CS)} (7). Differing reactivity was seen with AdN₃, which underwent reductive coupling upon treatment with 4 to give iron(II) hexaazenyl complex {[(Pipiso)Fe]₂(μ -AdN₆Ad)} (8). All reactions with 4 involved cleavage of the Fe-Fe bond of the compound, and its reactivity was shown to be broadly similar to that of low-valent β -diketiminato iron complexes, e.g. 1 and 2. We continue to explore the reactivity of 4 towards the activation of small molecules and will report on this work in due course.

Experimental

General Considerations

All manipulations were carried out using standard Schlenk and glove box techniques under a high-purity dinitrogen atmosphere. Toluene and hexane were distilled over molten potassium, whereas diethyl ether was distilled from Na/K alloy. Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected. Mass spectra were recorded at the EPSRC National Mass Spectrometric Service at Swansea University. The microanalysis was carried out at London Metropolitan University. Suitable microanalyses could not be obtained for compounds 6-8 because of their very high sensitivity to moisture and oxygen. In addition, recrystallisation of 8 consistently led to co-crystallisation with PipisoH, which could not be completely separated from the compound. Infrared (IR) spectra were recorded using a Perkin-Elmer RX1 FT-IR spectrometer as Nujol mulls between NaCl plates. ¹H NMR spectra were recorded on a Bruker Avance III 400 spectrometer and were referenced to the residual proton resonance of the solvent used. Solution state magnetic moments were determined by the Evans method. {[(Pipiso)Fe(μ -Br)]₂} and {[Fe(Pipiso)]₂} were prepared according to literature procedures.^[17] All other reagents were used as received.

Preparation of [(Pipiso)Fe(η^6 -toluene)] (5)

1,2-Dibromoethane (5 drops) and one crystal of I_2 were added to a suspension of Mg filings (50 mg, 2.0 mmol) in diethylether (15 mL). The mixture was stirred until the orange-brown iodine colour disappeared. The solvent was filtered off, the activated Mg filings were washed with toluene (15 mL), then dried under vacuum. A solution of $\{[(Pipiso)Fe(\mu-Br)]_2\}$ (222 mg, 0.18 mmol) in toluene (25 mL) was then added to the filings at ambient temperature. The reaction vessel was subsequently placed in an ultrasonic bath for 1 h, during which time the colour of the solution changed from yellow to brown. The solution was stirred for 3 days at room temperature before being filtered, and the filtrate was evaporated to dryness. The residue was extracted with hexane (20 mL); the extract was concentrated to \sim 5 mL, then stored at -30° C to yield compound 5 as dark red crystals (59 mg, 26 %), mp 180–187°C. μ_{eff} (C₆D₆) = 2.59 μ_{B} . ν_{max} (Nujol)/cm⁻¹ 1614 (vs), 1583 (s), 1079 (m), 1056 (w), 1024 (s), $986 (w), 973 (w), 924 (m), 789 (s), 769 (m). \delta_H (C_6 D_6, 400 \text{ MHz},$

298 K) -1.10, -0.14, 1.21, 2.47, 2.78, 4.63, 6.44, 11.30 (all broad). m/z (EI) 530.3 (1%, M⁺-toluene). Anal. Calc. for C₃₉H₅₆FeN₃: C 75.22, H 9.06, N 6.75. Found: C 75.39, H 9.15, N 6.86%.

Preparation of [(Pipiso)Fe(CO)₃] (6)

Compound **4** (118 mg, 111 µmol) was dissolved in toluene (15 mL) and the solution cooled to -78° C. The headspace of the reaction flask was then purged with CO for 2 min and the flask was sealed. The solution was warmed to room temperature during which time a slow colour change from dark red to green was observed. After stirring for a further 1.5 h, all volatiles were removed under vacuum and the residue was extracted with hexane (10 mL). The extract was concentrated to ~5 mL and stored at -30° C for several weeks, after which dark green crystals of **6** were isolated (22 mg, 16 %), mp 125–140°C. μ_{eff} (C₆D₆) = 1.56 µ_B. ν_{max} (Nujol)/cm⁻¹ 2043 (s, CO str.), 1967 (m, CO str.), 1957 (ν ., CO str.), 1180 (m), 1111 (m), 1010 (w), 935 (m), 797 (m). $\delta_{\rm H}$ (C₆D₆, 400 MHz, 303 K) –0.9, 0.97, 1.87, 3.87, 5.89, 9.25 (all broad). m/z (EI) 530.3 (13 %, M⁺–3CO).

Preparation of { $(Pipiso)Fe]_2(\mu-S)(\mu-CS)$ } (7)

Neat CS₂ (5 μ L, 0.08 mmol) was added using a micro-pipette to a solution of **4** (152 mg, 0.14 mmol) in toluene (30 mL) at -40°C, leading to an immediate colour change from dark red to brown–black. The resultant mixture was slowly warmed to room temperature and stirred for 20 h. After evaporation of all volatiles, the residue was extracted with hexane (20 mL). The extract was then filtered and the filtrate concentrated to 5 mL before being stored at -30°C to yield compound **7** as brown crystals (54 mg, 36%), mp 208–215°C. μ_{eff} (C₆D₆)=2.6 μ_{B} . ν_{max} (Nujol)/cm⁻¹ 1614 (m), 1583 (w), 1092 (s), 1080 (s), 1015 (s), 934 (w), 855 (m), 795 (m). δ_{H} (C₆D₆, 400 MHz, 303 K) -2.79, 0.41, 0.79, 0.93, 2.48, 3.63, 8.07, 8.8, 10.16 (all broad). *m/z* (EI) 476.4 (13%, PipisoH⁺), 432.3 (100%, PipisoH⁺–Prⁱ).

Preparation of {[(Pipiso)Fe]₂(μ -AdN₆Ad)} (**8**)

A solution of AdN₃ (26 mg, 150 µmol) in hexane (10 mL) was added to a solution of 4 (80 mg, 70 µmol) in hexane (15 mL) at -80° C. The resultant dark brown reaction mixture was warmed to room temperature and stirred for 2 h, after which a yellow precipitate was filtered off. The filtrate was concentrated to ~ 2 mL and stored at 5°C for three days to give an inseparable mixture of dark brown crystals of 8 and colourless crystals of PipisoH in an approximate ratio of 9:1 (\sim 15 mg, 16%), mp 116–125°C. v_{max} (Nujol)/cm⁻¹ 1612 (vs), 1582 (s), 1099 (w), 1079 (m), 1058 (m), 1022 (s), 973 (w), 934 (m), 855 (w), 801 (vs). *m/z* (EI) 722.4 (1%, PipisoFeN₃Ad⁺), 432.3 (100%, PipisoH⁺–Prⁱ).

Note, C_6D_6 solutions of 8 are NMR silent.

X-ray Crystallography

Crystals of **6–8** that were suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were performed on either a Bruker Apex X8 diffractometer using a graphite monochromator with $Mo_{K\alpha}$ radiation (λ 0.71073 Å) or the MX1 beamline at the Australian Synchrotron (λ 0.71080 Å), for compound **8**. Software package *Blu-Ice*^[28] was used for synchrotron data acquisition, whereas program $XDS^{[29]}$ was employed for synchrotron data reduction. All structures were solved by direct methods and refined on F^2 by full matrix least-squares (*SHELX97*)^[30] using all unique data.

All hydrogen atoms were included in calculated positions (riding model). Crystal data, details of data collection and refinement are given in Table S1 (Supplementary Material). Crystallographic data (CIF files) for all structures have been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 991289–991291).

Supplementary Material

Crystal data, and details of data collection and refinement for all structures are available on the Journal's website.

Acknowledgements

The authors gratefully acknowledge financial support from the Australian Research Council. LF thanks the Monash Institute of Graduate Research for financial support in the form of a Postgraduate Publications Award. The EPSRC Mass Spectrometry Service (Swansea University) is also thanked. Part of this research was undertaken on the MX1 beamline at the Australian Synchrotron, Victoria, Australia.

References

- [1] Selected reviews: (a) J. P. Krogman, C. M. Thomas, *Chem. Commun.* 2014, *50.* doi:10.1039/C3CC47537A
 (b) Y. C. Tsai, *Coord. Chem. Rev.* 2012, *256*, 722. doi:10.1016/J.CCR.
 - (b) Y. C. 1sai, *Coord. Chem. Rev.* **2012**, *256*, 722. doi:10.1016/J.CCR 2011.12.012
- [2] See for example: T. Nguyen, W. A. Merrill, C. Ni, H. Lei, J. C. Fettinger, B. D. Ellis, G. J. Long, M. Brynda, P. P. Power, *Angew. Chem. Int. Ed.* 2008, 47, 9115. doi:10.1002/ANIE.200802657
- [3] See for example: P. L. Holland, Accounts Chem. Res. 2008, 41, 905. doi:10.1021/AR700267B
- [4] (a) C. J. Adams, R. B. Bedford, E. Carter, N. J. Gower, M. F. Haddow, J. N. Harvey, M. Huwe, M. Á. Cartes, S. M. Mansell, C. Mendoza, D. M. Murphy, E. C. Neeve, J. Nunn, *J. Am. Chem. Soc.* 2012, *134*, 10333. doi:10.1021/JA303250T
 (b) K. Weber, E.-M. Schnöckelborg, R. Wolf, *ChemCatChem* 2011, *3*, 1572. doi:10.1002/CCTC.201100199
- [5] J. M. Zadrozny, D. J. Xiao, M. Atanasov, G. J. Long, F. Grandjean, F. Neese, J. R. Long, *Nat. Chem.* **2013**, *5*, 577. doi:10.1038/NCHEM. 1630
- [6] R. M. Davydov, M. P. McLaughlin, E. Bill, B. M. Hoffman, P. L. Holland, *Inorg. Chem.* 2013, 52, 7323. doi:10.1021/IC4011339
- [7] J. M. Smith, A. R. Sadique, T. R. Cundari, K. R. Rodgers, G. Lukat-Rodgers, R. J. Lachicotte, C. J. Flaschenriem, J. Vela, P. L. Holland, *J. Am. Chem. Soc.* 2006, *128*, 756. doi:10.1021/JA052707X
- [8] See for example: R. E. Cowley, M. R. Golder, N. A. Eckert, M. H. Al-Afyouni, P. L. Holland, *Organometallics* 2013, *32*, 5289. doi:10.1021/OM400379P
- [9] See for example: Y. Yu, J. M. Smith, C. J. Flaschenriem, P. L. Holland, *Inorg. Chem.* 2006, 45, 5742. doi:10.1021/IC052136+
- [10] M. M. Rodriguez, E. Bill, W. W. Brennessel, P. L. Holland, *Science* 2011, 334, 780. doi:10.1126/SCIENCE.1211906
- [11] C. Jones, Coord. Chem. Rev. 2010, 254, 1273. doi:10.1016/J.CCR. 2009.07.014
- [12] S. P. Green, C. Jones, A. Stasch, *Science* 2007, 318, 1754. doi:10.1126/ SCIENCE.1150856
- [13] (a) C. Jones, P. C. Junk, J. A. Platts, A. Stasch, *J. Am. Chem. Soc.* 2006, *128*, 2206. doi:10.1021/JA057967T
 (b) S. J. Bonyhady, D. Collis, G. Frenking, N. Holzmann, C. Jones, A. Stasch, *Nat. Chem.* 2010, *2*, 865. doi:10.1038/NCHEM.762
 (c) C. Jones, S. J. Bonyhady, N. Holzmann, G. Frenking, A. Stasch, *Inorg. Chem.* 2011, *50*, 12315. doi:10.1021/IC200682P
 (d) S. P. Green, C. Jones, G. Jin, A. Stasch, *Inorg. Chem.* 2007, *46*, 8. doi:10.1021/IC062163F
- [14] (a) C. Jones, C. Schulten, L. Fohlmeister, A. Stasch, K. S. Murray, B. Moubaraki, S. Kohl, M. Z. Ertem, L. Gagliardi, C. J. Cramer, *Chem. Eur. J.* 2011, *17*, 1294. doi:10.1002/CHEM.201002388
 (b) C. Jones, C. Schulten, R. P. Rose, A. Stasch, S. Aldridge, W. D. Woodul, K. S. Murray, B. Moubaraki, M. Brynda,

G. La Macchia, L. Gagliardi, *Angew. Chem. Int. Ed.* **2009**, *48*, 7406. doi:10.1002/ANIE.200900780

- [15] D. Heitmann, C. Jones, P. C. Junk, K.-A. Lippert, A. Stasch, *Dalton Trans.* 2007, 187. doi:10.1039/B614028A
- [16] R. P. Rose, C. Jones, C. Schulten, S. Aldridge, A. Stasch, *Chem. Eur. J.* 2008, 14, 8477. doi:10.1002/CHEM.200801071
- [17] L. Fohlmeister, S. Liu, C. Schulten, B. Moubaraki, A. Stasch, J. D. Cashion, K. S. Murray, L. Gagliardi, C. Jones, *Angew. Chem. Int.* Ed. 2012, 51, 8294. doi:10.1002/ANIE.201203711
- [18] R. Alvarez, J. L. Atwood, E. Carmona, P. J. Perez, M. L. Poveda, R. D. Rogers, *Inorg. Chem.* **1991**, *30*, 1493. doi:10.1021/IC00007A014
- [19] A. R. Sadique, W. W. Brennessel, P. L. Holland, *Inorg. Chem.* 2008, 47, 784. doi:10.1021/IC701914M
- [20] P. V. Broadhurst, B. F. G. Johnson, J. Lewis, P. R. Raithby, J. Chem. Soc. Chem. Commun. 1980, 812. doi:10.1039/C39800000812
- [21] As determined from a survey of the Cambridge Crystallographic Database, March 2014, **2014**.
- [22] B. Cordero, V. Gomez, A. E. Platero-Prats, M. Reves, J. Echeverria, E. Cremades, F. Barragan, S. Alvarez, *Dalton Trans.* 2008, 2832. doi:10.1039/B801115J
- [23] (a) C. A. Nijhuis, E. Jellema, T. J. J. Sciarone, A. Meetsma, P. H. M. Budzelaar, B. Hessen, *Eur. J. Inorg. Chem.* 2005, 2089. doi:10.1002/EJIC.200500094

(b) For selected other examples of neutral, square planar iron complexes, see S. H. Strauss, M. E. Silver, K. M. Long, R. G. Thompson, R. A. Hudgens, K. Spartalian, J. A. Ibers, *J. Am. Chem. Soc.* **1985**, *107*, 4207. doi:10.1021/JA00300A021

(c) M. W. Bouwkamp, S. C. Bart, E. J. Hawrelak, R. J. Trovitch, E. Lobkovsky, P. J. Chirik, *Chem. Commun.* 2005, 3406. doi:10.1039/ B504063A

- [24] P. L. Holland, Nat. Chem. 2011, 3, 507. doi:10.1038/NCHEM.1078
- [25] R. E. Cowley, J. Elhaik, N. A. Eckert, W. W. Brennessel, E. Bill, P. L. Holland, J. Am. Chem. Soc. 2008, 130, 6074. doi:10.1021/ JA801375G
- [26] J. A. Bellow, P. D. Martin, R. L. Lord, S. Groysman, *Inorg. Chem.* 2013, 52, 12335. doi:10.1021/IC402517M
- [27] S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards, G. J. McIntyre, *Chem. Eur. J.* 2010, *16*, 938. doi:10.1002/CHEM. 200902425
- [28] T. M. McPhillips, S. E. McPhillips, H. J. Chiu, A. E. Cohen, A. M. Deacon, P. J. Ellis, E. Garman, A. Gonzalez, N. K. Sauter, R. P. Phizackerley, S. M. Soltis, P. Kuhn, *J. Synchrotron Radiat.* 2002, 9, 401. doi:10.1107/S0909049502015170
- [29] W. Kabsch, J. Appl. Crystallogr. 1993, 26, 795. doi:10.1107/ S0021889893005588
- [30] G. M. Sheldrick, SHELX-97, 1997 (University of Göttingen).