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An Iron(II) Hydride Complex of a Ligand with two Adjacent β -Diketiminato Binding sites and its Reactivity

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Abstract

After lithiation of PYR-H₂ (PYR = [(HCCMeNC₆H₃(*i*Pr)₂(C₅H₅-N)]²⁻) – the precursor of an expanded β -diketiminato ligand system with two binding pockets – with KN(TMS)₂ the reaction of the resulting potassium salt with FeBr₂ led to a dinuclear iron(II) bromide complex [(PYR)Fe(μ -Br)₂Fe] (**1**). Through treatment with KHBet₃ the bromide ligands could be replaced by hydrides to yield [PYR)Fe₂(μ -H)₂] (**2**), a distorted analogue of known β -diketiminato iron hydride complexes, as evidenced by NMR, Mößbauer and X-ray absorption spectroscopy, as well as by its reactivity: For instance, **2** reacts with the proton source lutidinium triflate via protonation of the hydride ligands to form an iron(II) product [(PYR)Fe₂(OTf)₂] (**4**), while CO₂ inserts into the Fe-H bonds generating the formate complex [(PYR)Fe₂(μ -HCOO)₂] (**5**); in the presence of traces of water partial hydrolysis occurs so that [(PYR)Fe₂(μ -OH)(μ -HCOO)] (**6**) is isolated. Altogether, the iron(II) chemistry supported by the PYR²⁻ ligand is distinctly different from the one of nickel(II), where both, the arrangement of the two binding pockets and the additional pyridyl donor led to diverging features as compared with the corresponding system based on the parent β -diketiminato ligand.

Introduction

Enzymes like the [FeFe] hydrogenase or the nitrogenase are developing their functions via iron hydride units.^{1,2} Accordingly, hydride chemistry of diiron systems has received a lot of attention in recent years and major advances have been made.³ Synthetic hydride complexes often contain strong-field organic or phosphine ligands and thus diamagnetic metal centers.⁴ As on the other hand potential iron hydride intermediates within the catalytic cycle of the nitrogenase are expected to feature high-spin iron centers with coordination numbers less than five, Holland and coworkers have targeted the synthesis and investigation of low-

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Dedicated to Prof. Anthony J. Downs on occasion of his 80th birthday

coordinate, high-spin iron(II) hydride systems that became accessible utilizing the β -diketiminato ligand system (**I**, see Figure 1).⁵

Their reactivity was elucidated and a multitude of substrates were shown to insert into the Fe–H bonds.^{5a,5c,6} As the central intermediate within the catalytic cycle of the [NiFe] hydrogenase is assumed to contain a bridging hydride ligand between a Ni and an Fe center with all of the redox chemistry taking place at the nickel site,⁷ we got interested in fundamental investigations on the hydride chemistry of dinuclear nickel cores: In 2008 we reported the synthesis of compound **II** (Figure 1), which is formally an analogue of **I** but behaves very differently.⁸ Recently, we have extended this work by using the expanded β -diketiminato ligand system PYR^{2-} ($\text{PYR}^{2-} = [(\text{NC}(\text{Me})\text{C}(\text{H})\text{C}(\text{Me})\text{NC}_6\text{H}_3-(\text{Pr})_2)_2(\text{C}_5\text{H}_5\text{N})^{2-}]$; see Scheme 1), where two β -diketiminato units are prearranged by a pyridine linker for the complexation of two metal centers in a fashion that allows for their cooperation. PYR^{2-} was found to alter the electronic and steric situation in comparison to the unlinked β -diketiminato system significantly: Instead of a dinickel(II) dihydride compound, similar to **II**, reaction of the dinuclear nickel(II) bromide complex $[(\text{PYR})\text{Ni}(\mu\text{-Br})\text{NiBr}]$ with KHBET_3 led to $[(\text{PYR})\text{Ni}(\mu\text{-H})\text{Ni}]$, a mixed valence $\text{Ni}^{\text{I}}(\mu\text{-H})\text{Ni}^{\text{II}}$ complex.⁹ Naturally, this background motivated a corresponding investigation on iron hydride chemistry employing PYR^{2-} as the supporting ligand matrix.

Results and Discussion

In order to prepare a suitable iron(II) precursor compound for the synthesis of a diiron dihydride complex, the potassium salt of the ligand, PYR-K_2 , was treated with iron(II) bromide in tetrahydrofuran for 16 h at room temperature leading to the iron(II) complex $[(\text{PYR})\text{Fe}_2(\mu\text{-Br})_2]$ (**1**) as a deep orange solid in 82% yield (see Scheme 1). By layering a toluene solution of **1** with *n*-hexane, crystals suitable for X-ray diffraction analysis could be obtained. Compound **1** crystallizes in a tetragonal space group ($I4_1cd$) with half a molecule in the asymmetric unit cell. One half of each molecule is generated by a twofold rotation axis (C_2). The solid state structure of **1** is shown in Figure 2.

Each of the two iron centers is coordinated by two nitrogen atoms and two bridging bromide ligands in a pseudotetrahedral fashion, unlike the nickel centers in the analogous $[(\text{PYR})\text{Ni}_2\text{Br}_2]$, which are coordinated asymmetrically by one bridging and one terminal bromide ligand.⁹ The Fe–N distances (2.029(3) Å and 2.024(4) Å) are comparable to the corresponding values of earlier reported β -diketiminato iron(II) complexes.^{5,6}

The Fe_2Br_2 core in **1** exhibits two short Fe–Br distances (2.4756(7) Å) and two significantly longer ones (2.5998(7) Å), which are in the range of Fe–Br bond lengths observed previously for $\text{Fe}(\mu\text{-Br})_2\text{Fe}$ units.¹⁰ The dihedral Br–Fe–Br' angle is about 93.5° and the Fe···Fe distance amounts to 3.0332(7) Å, which is much shorter than the metal metal separation in the nickel complex $[(\text{PYR})\text{Ni}(\mu\text{-Br})\text{NiBr}]$ (Ni···Ni 3.4290(7) Å).⁹

The ^1H NMR spectrum of **1** shows ten resonances for the protons of the PYR^{2-} ligand with chemical shifts that range from 20 ppm to –30 ppm. The observed magnetic moment of **1** in the solid state ($\mu_{\text{eff}} = 6.6 \mu_{\text{B}}$) and in a benzene- d_6 solution ($\mu_{\text{eff}} = 5.9 \mu_{\text{B}}$) suggests a system

with four unpaired electrons at each iron(II) ion ($S = 2$) that are nearly uncoupled at room temperature ($\mu_{s.o.} = 6.9 \mu_B$). The Mössbauer spectrum for a solid sample of **1** exhibits one quadrupole doublet with an isomeric shift of $\delta = 0.94 \text{ mm s}^{-1}$ and a quadrupole splitting of $E_Q = 2.51 \text{ mm s}^{-1}$ (Figure S4, supporting information). These results are in accordance with the presence of two identical high-spin iron(II) centers in **1**.¹¹

After the successful preparation of the iron precursor $[\text{PYR}]\text{Fe}_2(\mu\text{-Br})_2$ (**1**) attempts were made to replace the bridging bromide ligands by hydrides, employing potassium triethylborohydride (KBHET_3). Adding a toluene solution of two equivalents KBHET_3 to **1** dissolved in toluene led to an immediate color change from orange to dark red, and a new paramagnetic set of signals for a C_{2v} symmetric complex occurred in the ^1H NMR spectrum (Figure S1, supporting information). This observation indicated the replacement of the bridging bromide ligands by hydrides without drastic geometrical changes in the molecular structure and thus the formation of $[(\text{PYR})\text{Fe}_2(\mu\text{-H})_2]$ (**2**); indeed also the results of elemental analysis were consistent with this formulation (see experimental section). With the aid of 2D experiments all resonances could be assigned to the ligand system PYR^{2-} . The signals for the proposed hydride ligands could not be detected, probably due to their rather large paramagnetic shift and the very short relaxation time. For **2** the solution magnetic moment at room temperature was determined to be $3.9 \mu_B$, suggesting weak antiferromagnetic coupling of the two high-spin iron(II) ions. This fits well to the magnetic moment of $4.0 \mu_B$ Holland and co-workers determined for **1** (with $R = \text{Me}$, $R' = \text{H}$).^{5b}

Hence, elemental analysis, NMR spectroscopy, and magnetism hint to the successful formation of **2** with a structure as depicted in Scheme 1. It has to be borne in mind though that the symmetry derived from the r.t. solution studies is only a result of a dynamic behavior that is fast on the NMR time scale. Accordingly, a Mössbauer spectrum was recorded at 80 K, and the results were surprising, yet in a different respect: Unlike in case of **1**, where – as expected – just one doublet was observed, the spectrum of **2** showed two superimposed doublets. The major signal (~60%) has an isomeric shift and a quadrupole splitting of $\delta = 0.68 \text{ mm s}^{-1}$ and $E_Q = 1.13 \text{ mm s}^{-1}$, whereas the minor component (~40%) appears at $\delta = 0.83 \text{ mm s}^{-1}$ with quadrupole splitting $E_Q = 2.11 \text{ mm s}^{-1}$ (see supporting information). The isomeric shifts of both signals lie in the range of shifts for high-spin iron(II) β -diketiminato complexes ($\delta = 0.62 - 0.86 \text{ mm/s}$), so that both could belong to a $\text{Fe}^{\text{II}}(\mu\text{-H})_2\text{Fe}^{\text{II}}$ core. Measurements were repeated with several different (independently prepared) samples but these never led to a spectrum, where one of the signals was significantly decreased or even to a single doublet; the highest ratio observed was 70:30 (see supplementary material). The fact that the intensity ratio of the signals differs from a 50:50 ratio argues against an asymmetric $\text{H-Fe}^{\text{II}}(\mu\text{-H})\text{Fe}^{\text{II}}$ structure as the origin, and thus for the presence of two different species/isomers, each of which has two equivalent iron centers. We cannot explain this finding at present. Interestingly, Holland and co-workers also observed two doublets for **1** (with $R = \text{Me}$, $R' = \text{H}$)⁶ and assigned the minor component (28%) to contamination from an unidentified Fe^{I} impurity based on the comparatively low isomeric shift ($\delta = 0.49(2) \text{ mm/s}$). As in our case the shifts are much higher, iron(I) does not seem to play a role in case of **2**, though.

Although Mössbauer spectra reveal the presence of a mixture of species in solid samples of **2**, as outlined above, NMR spectroscopy provides evidence in favor of the presence of a single species in solution. X-ray absorption spectral (XAS) measurements at the Fe K-edge were therefore performed on a frozen toluene solution to gain additional evidence for the solution structure and oxidation state of iron in its dihydride complex **2**. The X-ray absorption near edge spectral (XANES) feature of complex **2** was found to be typical of an iron (II) center (pre-edge = 7112.3 eV and edge = 7120.2 eV; see Figure S9, supporting information).

Extended X-ray absorption fine structure (EXAFS) analysis revealed further structural details. The first coordination sphere could be satisfactorily fitted by considering three N/O scatterers at a distance of 2.03 Å (see Table 1). In addition, Fe EXAFS of **2** showed a peak at 2.55 Å corresponding to the Fe scatterer, thereby strongly supporting the presence of a dinuclear Fe...Fe center in **2**. Notably, the estimated Fe...Fe distance of 2.55 Å in **2** is significantly shorter than that observed in **1** (3.0336(9) Å). This is likely a result of the smaller size of the bridging hydride ligands of **2** relative to the bromides in **1**. The additional outer-shell features could be satisfactorily accounted for by considering single scattering paths involving 4 carbons at 3.07 Å, 9 carbons at 3.92 Å, 2 nitrogens at 4.58 Å and 9 carbon donors at 5.19 Å distance from iron (see Table S1, in supporting information).

A geometry optimization of **2** at the B3LYP/def2-SVP/def2-TZVPD[†] level including simulation of the solvent effect was carried out setting out from the structure of **1** with the bromide ligands substituted by hydrido ligands. Notably, in contrast to the X-ray structure of **1** no C₂ axis is present in the optimized structure of **2**, so that all four Fe–H bonds are slightly different (1.77 – 1.82 Å). An open-shell singlet state, where four unpaired electrons per iron center couple antiferromagnetically, was found to represent the ground state of **2** (see Figure 4). The calculated metrical parameters for **2** are also in reasonable agreement with the EXAFS experiment; although the Fe–N distances are slightly overestimated, the experimentally determined Fe...Fe distance is well reproduced in the calculation (Table 1).

All attempts to crystallize **2** for a single crystal X-ray diffraction study failed due to its high sensitivity, but crystals of a secondary product were obtained: Slow evaporation of a benzene-*d*₆ solution afforded dark brown crystals suitable for X-ray structure analysis, which indicated the composition of [(PYR)₂Fe₄(μ-O)(μ-H)₂] (**3**, see supporting information). The complex contains a core of four iron(II) centers bridged by one oxo and two hydride ligands. Presumably, traces of water have led to its formation with the simultaneous release of molecular dihydrogen.

The reactivity of an iron(II) hydride complex towards water forming a diiron(II) oxo compound, which could be isolated and fully characterized, was reported earlier.¹³ However, structurally characterized complexes featuring a Fe^{II}(μ-O)Fe^{II} entity are rather rare.

[†]Geometry optimisations were performed with the program Gaussian 09, Rev. C.01, employing the B3LYP functional together with a def2-TZVPD basis set for Fe, N, and the two hydrido atoms and a def2-SVP basis for C atoms and the residual H atoms. The solvent effect was simulated by the PCM method. See Supporting Information.

To better understand the chemical properties of the iron hydride complex **2** its reactivity toward the weak acid lutidinium triflate has been investigated (see Scheme 2). Upon addition of 2,6-lutidinium triflate dissolved in tetrahydrofuran to a toluene solution of [(PYR)Fe₂(μ-H)₂] (**2**) immediately the color of the reaction mixture changed from dark red to orange, and quantitative conversion to the iron(II) compound [(PYR)Fe₂(OTf)₂] (**4**) occurred, concomitant with the evolution of molecular dihydrogen, which was verified by analyzing the gas phase of the reaction mixture using gas chromatography. Based on this analysis the existence of hydride ligands in complex **2** was further corroborated. In the ¹H NMR spectrum of **4** dissolved in benzene-*d*₆ a signal set for the protons of the PYR²⁻ ligand over the wide range from +25 ppm to -40 ppm was observed that was characteristic for a C_{2v} symmetrical paramagnetic iron(II) complex. ¹⁹F NMR spectroscopy revealed one signal at -33.3 ppm that was significantly shifted to low field compared to the free lutidinium triflate at -78.0 ppm. This indicates that the triflate anions are coordinated to the iron centers and that the resulting structure is symmetric, so that both triflates give rise to just one signal. In comparison to the IR spectrum of **2** the one of **4** shows three additional strong bands at 1227, 1027 and 636 cm⁻¹, which can be assigned to the triflate vibrations.¹⁴ Unfortunately, all attempts to crystallize **4** failed, yet.

It is known that carbon dioxide can insert into iron hydride bonds under formation of the corresponding formate complexes. For instance, **1** has been demonstrated to undergo CO₂ insertion, and recently, Murray and coworkers reported a triron(II) trihydride complex Fe₃H₃L [where L³⁻ is a tris(β-diketimate) cyclophane] which is also able to react with CO₂ via insertion; interestingly, after insertion of the first CO₂ molecule the remaining Fe-H-Fe units showed a marked lack of reactivity.^{6,15}

Exposure of a dark red toluene solution of **2** to carbon dioxide resulted in a pale red solution within several minutes. Quantitative conversion was achieved within several hours, as indicated by ¹H NMR spectroscopic monitoring. A new paramagnetic signal set, as expected for the symmetrical compound [(PYR)Fe₂(μ-HCOO)₂] (**5**) in the range between +30 and -50 ppm was detected (Figure S2, supporting information). To validate that these signals belong to the bisformate diiron(II) complex **5** the easily accessible analogous diiron(II) bis(acetate) complex was prepared by adding two equivalents of potassium acetate to a tetrahydrofuran solution of **1** (independent preparation of **5** by reacting **1** with sodium formate posed problems due to the low solubility of the formate). After 16 h stirring and work-up [(PYR)Fe₂(μ-CH₃COO)₂] (**5'**) could be isolated as a red solid in 36% yield (for more detailed information on the experimental data of **5'** see supporting information). Crystals suitable for X-ray diffraction were grown from a *n*-hexane solution at -30 °C. As expected the two iron(II) centers in **5'** are bridged by two acetate ligands and their coordination environment is pseudotetrahedral as in case of **1** and **3** (for more detailed information on the molecular structure of **5'** see supporting information). The ¹H NMR spectrum of **5'** is almost identical to the one of **5**, except for one additional signal at 71.68 ppm for the methyl groups of the acetate ligands. The IR spectrum of **5** shows one characteristic very strong band at 1620 cm⁻¹, which is assigned to the asymmetric stretching vibration of the formate ligand.^{6,15} In case of the acetate compound **5'** this band is shifted to

a smaller wavenumber (1599 cm^{-1}). Replacement of the formate hydrogen atom for a methyl group has been shown to give such a red-shift.¹⁶

Moreover, the occurrence of carbon dioxide insertion into the Fe–H bonds of **2** could be confirmed by crystallization of $[(\text{Pyr})\text{Fe}_2(\mu\text{-HCOO})(\mu\text{-OH})]$ (**6**, see Figure 5) as hexane solvate (0.5 equiv.); the complex contains two iron(II) centers bridged by one formate and one hydroxo ligand. Compound **6** was formed when the reaction of **2** with carbon dioxide was carried out in toluene that still contained traces of water (for the synthesis of **5** these had been removed by addition of KC_8 before use). $6 \times 1/2$ hexane could be isolated as reddish brown crystals grown from a *n*-hexane solution at $-30\text{ }^\circ\text{C}$. $[(\text{Pyr})\text{Fe}_2(\mu\text{-HCOO})(\mu\text{-OH})]$ (**6**) crystallizes together with 0.5 equiv. of hexane solvent molecules in the space group $P2_1/m$ with two independent mirror-symmetric molecules in the asymmetric unit and a total of four molecules in the unit cell. Furthermore two *n*-hexane molecules can be found per unit cell. In Figure 5 only one independent molecule of **6** is shown with one half of the molecule generated by a mirror plane (σ). The second independent molecule shows slightly more electron density for the hydroxo ligand as would be expected. This observation might be attributed to substitutional disorder of the OH- ligand with Br-, originating from the starting material **1**. The structure was refined therefore as a solid solution.

The two iron(II) centers in **6** are coordinated by its ligands in a pseudotetrahedral fashion as already observed for the iron ions in the molecular structures of **1**, **3** and **5'**. The bridging formate ligand exhibits a *syn, syn* coordination mode, which is reflected by the Fe–O bond lengths: The Fe1–O1 distance was determined to be $2.040(2)\text{ \AA}$ [$2.048(3)\text{ \AA}$], and it is thus comparable to Fe–O distances reported for bridging formate or acetate ligands in *syn* conformations.^{6,17} For carboxylate groups binding two Fe^{II} nuclei in an *anti* conformation, longer distances of about $2.15\text{ \AA}$ would have been expected.¹⁷ The C–O bond length ($1.252(3)\text{ \AA}$ [$1.256(3)\text{ \AA}$]) is in the range of the values usually observed for $\mu\text{-}\eta^1\text{:}\eta^1$ coordinated formate ligands.⁶ The other bridging ligand is characterized as a hydroxo anion by the Fe1–O2 bond length of $1.972(2)\text{ \AA}$ [$1.967(3)\text{ \AA}$] which is different to the corresponding value determined for the diiron oxo complex **3** (Fe–O $1.7756(12)\text{ \AA}$) but in the typical range for diiron hydroxo compounds.¹² The Fe $\cdots$ Fe distance in $6 \times 1/2$ hexane ($3.1805(7)\text{ \AA}$ [$3.1533(7)\text{ \AA}$]) is comparable to the Fe $\cdots$ Fe separation in **1** ($3.0332(7)\text{ \AA}$), but shorter than in case of **5'** with two bridging acetate ligands between the two iron ions ($3.4741(7)\text{ \AA}$). In 2011 Gosh and coworkers reported a related compound, containing one bridging hydroxo and one bridging formate ligand, but in contrast to **6** the iron centers have the oxidation state +III.¹⁸ All in all, complexes displaying a $\text{Fe}(\mu\text{-OH})(\mu\text{-HCOO})\text{Fe}$ motif are rather rare.

The ^1H NMR spectrum of **6** dissolved in benzene- d_6 (see Figure S3, supporting information) shows an enlarged set of signals compared to the ^1H NMR spectrum of **5**. This observation can be explained due to the lower symmetry of **6** resulting from the exchange of one bridging formate ligand by one hydroxo ligand. For instance, instead of one signal for the four protons in the *meta* positions of the aryl rings ($-\text{iPr}_2\text{C}_6\text{H}_3$) occurring at a chemical shift of 20.15 ppm in case of **5**, two signals at 19.60 and 16.04 ppm are detected for **6**, each representing two protons. The asymmetry in **6** also leads to multiple signals for the *CH*- and CH_3 -protons of the *iPr*-groups.

Conclusions

A series of diiron(II) complexes based on an expanded β -diketiminate ligand system were prepared and – presumably due to the different preferences for coordination geometries, the slightly different ion radii, and the different redox properties – their structures and behavior are distinctly different from the corresponding nickel compounds. The iron bromide complex $[(\text{PYR})\text{Fe}_2(\mu\text{-Br})_2]$ (**1**) was synthesized and fully characterized. It features a symmetric $\text{Fe}_2(\mu\text{-Br})_2$ core, while the nickel analogue exhibits an asymmetric $\text{Ni}(\mu\text{-Br})\text{NiBr}$ moiety. The latter reacts with KHBET_3 to yield a mixed valence $\text{Ni}^{\text{I}}(\mu\text{-H})\text{Ni}^{\text{II}}$ complex, while the reaction of **1** with KHBET_3 provided the iron(II) hydride complex $[(\text{PYR})\text{Fe}_2(\mu\text{-H})_2]$ (**2**) as the product. The hydride ligands in **2** are rather reactive: The reaction of **2** with an acid leads to the formation of molecular dihydrogen and the iron(II) triflate complex $[(\text{PYR})\text{Fe}_2(\text{OTf})_2]$ (**4**). Furthermore, **2** activates CO_2 by insertion into the Fe–H bond generating the formate complexes $[(\text{PYR})\text{Fe}_2(\mu\text{-HCOO})_2]$ (**5**) or, in the presence of traces of water, $[(\text{PYR})\text{Fe}_2(\mu\text{-HCOO})(\mu\text{-OH})]$ (**6**). Hence, despite the distortion that is imposed onto the $\text{Fe}_2(\mu\text{-H})_2$ unit in **1** by linking the β -diketiminate ligand entities via a pyridyl unit and the addition of an N donor function provided by the latter, **2** could be isolated and behaves similar to **1**, while in case of nickel marked differences were observed.

Experimental Section

Materials and Methods

All manipulations were carried out under an argon or dinitrogen atmosphere by using a glove box or standard Schlenk techniques. Solvents were dried employing a MBraun Solvent Purification System SPS. ^1H and $^{19}\text{F}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker AV 400 NMR spectrometer at room temperature. ^1H and ^{19}F chemical shifts are reported in ppm and were calibrated internally to the solvent signals (^1H : 7.15 ppm for C_6D_6) or to an internal standard (^{19}F : –113.5 ppm for fluorobenzene). To determine the magnetic moments in solution at room temperature the Evans method was used. $^{19}\text{C}_6\text{D}_6$ containing 1% tetramethylsilane (TMS) was used as the solvent for the samples and as the internal standard in the central capillary tube. A magnetic balance of Alfa was used for the determination of the magnetic moment of a solid sample at room temperature. For the diamagnetic correction of the susceptibility Pascal's constants were used. 20 Infrared (IR) spectra were recorded using solid samples prepared as KBr pellets on a Shimadzu FTIR 8400S spectrometer. Microanalyses were performed with a HEKAtech Euro EA 3000 elemental analyzer. The detection of molecular hydrogen was carried out by gas chromatography using a Shimadzu-GC-17A spectrometer with a Resteks ShinCarbon packed column ST 80/100. The following temperature program was used: 40 °C for 5 min with an injection temperature of 200 °C. The carrier gas was helium with a flow rate of 50 mLmin $^{-1}$. For the thermal conductivity detector (TCD) a temperature of 320 °C was selected. The ligand precursor PYR- H_2 was prepared according to literature procedure. 21 PYR- K_2 was synthesized by the reaction of PYR- H_2 with potassium bis(trimethylsilyl)amide in toluene. 22

EXAFS—XAS measurements were performed on a NSLS X3B, which is equipped with a sagittally focusing Si(111) double-crystal monochromator and a post-monochromator Ni-

coated harmonic rejection mirror. Note that while the Ni mirror was in the beam path during data collection, metallic Ni contamination is not significant based on measurement of an experimental blank spectrum. The samples were prepared in Mössbauer/XAS cups made from Delrin® and the window side was sealed with Kapton® tape. All probes were made in toluene solution with a concentration of 8mM and immediately frozen and stored at 77K. The temperature was kept below the melting point during storage and transfer. A He Displex cryostat was used for temperature control during the measurement, with typical sample temperatures of ~20K. Data were collected as fluorescence spectra using a 31 element solid-state Ge detector (Canberra), over a k range $\sim 12 \text{ \AA}^{-1}$. Each scan required approximately 40 minutes. An Fe foil spectrum was collected simultaneously using a PMT for energy calibration; the first inflection point of the metal foil reference was set to 7112 eV. Data averaging was carried out using Athena[†] from the ifeffit package. Reference spectra for individual scans were carefully aligned to ensure that the energy scale was identical for all spectra. Sets of scans at each spot were examined for photo reduction effects. No evidence for photo reduction was observed based upon edge energies or spectral changes although slight burn marks were visible after the measurement. EXAFS analysis and fitting was performed with Artemis[†] from the ifeffit package and FEFF 6. The fitting process is summarized in Table S1 showing the major fitting parameters. The goodness of fit (GOF) is represented by the R -factor (value from ifeffit package) which is defined by

$$R = \sum [(\chi_{\text{dat}}(R_i) - \chi_{\text{th}}(R_i))^2 / (\chi_{\text{dat}}(R_i))^2]$$

Mössbauer Spectroscopy—⁵⁷Fe-Mössbauer spectra were measured with a Mössbauer spectrometer in uniform acceleration operating mode with a ⁵⁷Co/Rh γ -source. The minimum experimental line width is 0.28 mm/s. The temperature of the samples was held constant in a Janis CCS-850 closed cycle cryostat with sample in exchange gas (helium). Isomer shifts were determined relative to α -iron at 300K. The measurements were performed on samples with natural ⁵⁷Fe-abundance.

Synthetic procedures

[(PYR)Fe₂(μ -Br)₂] (1)—PYR-K₂ (320 mg, 0.48 mmol) was stirred together with iron(II) bromide (209 mg, 0.97 mmol) in tetrahydrofuran (25 mL) for 16 h at room temperature. After filtration of the resulting suspension the solvent was removed under vacuum. The residue was washed with *n*-hexane to yield **1** as a deep orange solid (340 mg, 0.40 mmol, 82%). ¹H NMR (400 MHz, C₆D₆): δ = 17.98 (1H, CH₄-Pyr), 17.34 (4H, CH_{Ar}), 9.16 (2H, CH_{3,5}-Pyr), 5.48 (12H, CH(CH₃)₂), 2.78 (12H, CH(CH₃)₂), -4.72 (4H, CH(CH₃)₂), -16.58 (2H, CH), -20.78 (2H, CH_{Ar}), -25.58 (6H, CH₃), -28.92 (6H, CH₃) ppm; μ_{eff} = 5.9 μ_{B} (solution, C₆D₆); μ_{eff} = 6.6 μ_{B} (solid); IR (KBr): $\tilde{\nu}$ = 3058 (w), 2961 (s), 2925 (m), 2867 (m), 1637 (m), 1570 (s), 1521 (vs), 1457 (s), 1437 (vs), 1403 (s), 1382 (vs), 1366 (vs), 1352 (vs), 1317 (vs), 1282 (s), 1227 (s), 1181 (s), 1164 (s), 1068 (m), 1055 (m), 987 (m), 935 (m), 872 (w), 790 (m), 760 (m), 730 (w), 707 (w), 625 (w), 599 (w), 549 (w), 526 (w) cm⁻¹; elemental analysis calcd (%) for C₃₉H₅₁Br₂N₅Fe₂ (861.37 g mol⁻¹): C 54.38, H 5.97, N 8.13; found (%): C 55.33, H 6.17, N 7.94.

[†]Footnotes relating to the title and/or authors should appear here.

[†]Demeter, Version 0.9.17, <http://bruceravel.github.io/demeter/>.

[(PYR)Fe₂(μ-H)₂] (2)—A solution of [(PYR)Fe₂(μ-Br)₂] (1) (80 mg, 93 μmol) in toluene (10 mL) was treated with a solution of KHBet₃ (26 mg, 185 μmol) in toluene (2.5 mL). After stirring for 5 min at room temperature the solvent of the resulting reddish brown suspension was removed under vacuum. The residue was extracted with toluene (15 mL), the solvent was removed under vacuum and the resulting solid was washed with *n*-hexane to yield **2** as a dark red solid (38 mg, 54 μmol, 58%). ¹H NMR (400 MHz, C₆D₆): δ = 35.42 (1H, CH₄-Pyr), 18.87 (2H, CH), 13.20 (4H, CH_{Ar}), 12.65 (6H, CH₃), 4.51 (6H, CH₃), 3.90 (12H, CH(CH₃)₂), 1.76 (12H, CH(CH₃)₂), -5.79 (2H, CH_{3,5}-Pyr), -6.96 (2H, CH_{Ar}), -15.78 (4H, CH(CH₃)₂) ppm; μ_{eff} = 3.9 μ_B (solution, C₆D₆); IR (KBr): $\tilde{\nu}$ = 3057 (w), 2959 (s), 2925 (m), 2867 (m), 1640 (w), 1565 (m), 1517 (s), 1457 (s), 1439 (s), 1406 (vs), 1392 (vs), 1353 (vs), 1319 (s), 1285 (m), 1253 (m), 1224 (s), 1184 (m), 1166 (m), 1106 (w), 1055 (w), 1022 (m), 985 (w), 936 (w), 793 (w), 776 (w), 760 (m), 730 (w), 709 (w), 673 (w), 623 (w), 599 (w), 522 (w), 438 (w) cm⁻¹; elemental analysis calcd (%) for C₃₉H₅₃N₅Fe₂ (703.58 g mol⁻¹): C 66.58, H 7.59, N 9.95; found (%): C 66.37, H 7.44, N 9.42.

[(PYR)Fe₂(OTf)₂] (4)—A solution of 2,6-lutidinium triflate (15 mg, 56 μmol) in tetrahydrofuran (2 mL) was added to a dark red solution of [(PYR)Fe₂(μ-H)₂] (2) (20 mg, 28 μmol) in toluene (3 mL). The reaction mixture was stirred for 1 h at room temperature. Evaporation of the solvent yielded **4** as an orange solid (20 mg, 20 μmol, 70%). ¹H NMR (400 MHz, C₆D₆): δ = 20.37 (4H, CH_{Ar}), 17.45 (2H, CH₄-Pyr), 6–0 (br, 24H, CH(CH₃)₂), -9.12 (4H, CH(CH₃)₂), -17.57 (2H, CH_{3,5}-Pyr), -27.57 (2H, CH_{Ar}), -37.90 (6H, CH₃), -39.96 (6H, CH₃) ppm; ¹⁹F{¹H} NMR (471 MHz, C₆D₆): δ = -33.26 (6F, SO₃CF₃) ppm; IR (KBr): $\tilde{\nu}$ = 3058 (w), 2962 (m), 2927 (w), 2869 (w), 1631 (w), 1572 (m), 1532 (m), 1518 (m), 1460 (m), 1439 (s), 1404 (s), 1385 (vs), 1370 (s), 1353 (vs), 1318 (vs), 1280 (s), 1227 (vs), 1184 (s), 1101 (w), 1027 (s), 988 (w), 936 (w), 876 (w), 795 (w), 760 (w), 730 (w), 636 (m), 579 (w), 518 (w) cm⁻¹.

[(PYR)Fe₂(μ-HCOO)₂] (5)—[(PYR)Fe₂(μ-H)₂] (2) (25 mg, 36 μmol) was dissolved in toluene (6 mL, additionally dried by storage over KC₈). The argon atmosphere was replaced by a CO₂ atmosphere and the reaction mixture was stirred for 16 h at room temperature. All volatile materials of the resulting pale red solution were removed under vacuum, and the residue was washed with *n*-hexane. **5** was isolated as a red solid (11 mg, 14 μmol, 39%). ¹H NMR (400 MHz, C₆D₆): δ = 25.42 (1H, CH₄-Pyr), 20.15 (4H, CH_{Ar}), 5.09 (12H, CH(CH₃)₂), -3.58 (12H, CH(CH₃)₂), -6.14 (4H, CH(CH₃)₂), -27.63 (2H, CH_{Ar}), -47.38 (6H, CH₃), -47.77 (6H, CH₃) ppm; IR (KBr): $\tilde{\nu}$ = 3057 (w), 2961 (s), 2926 (m), 2866 (m), 1620 (vs), 1592 (s), 1574 (s), 1550 (s), 1515 (s), 1457 (s), 1437 (s), 1406 (vs), 1392 (vs), 1354 (vs), 1320 (vs), 1276 (s), 1253 (m), 1225 (s), 1184 (m), 1162 (m), 1104 (w), 1055 (w), 1021 (m), 982 (w), 935 (w), 796 (w), 777 (w), 760 (m), 730 (w), 709 (w), 695 (w), 624 (w), 598 (w) cm⁻¹; elemental analysis calcd (%) for C₄₁H₅₃N₅O₄Fe₂ (791.60 g mol⁻¹): C 62.21, H 6.75, N 8.85; found (%): C 62.45, H 6.95, N 8.34.

[(PYR)Fe₂(μ-HCOO)(μ-OH)] (6)—[(PYR)Fe₂(μ-H)₂] (2) (25 mg, 36 μmol) was stirred in toluene for 16 h in a CO₂ atmosphere analogously to the reaction procedure described for **5**. However, the used toluene had not been additionally dried by KC₈, but was directly used from the solvent purification system (containing about 1 ppm water). The solvent was

removed under reduced pressure and the residue was extracted with *n*-hexane. Cooling of the *n*-hexane solution to $-30\text{ }^{\circ}\text{C}$ afforded **6** as reddish brown crystals (14 mg, 18 μmol , 52%). ^1H NMR (400 MHz, C_6D_6): δ = 19.60 (2H, $\text{CH}_{m\text{-Ar}}$), 18.90 (1H, $\text{CH}_{4\text{-Pyr}}$), 16.04 (2H, $\text{CH}_{m\text{-Arr}}$), 13.18 (2H, $\text{CH}_{3,5\text{-Pyr}}$), 4.38 (6H, $\text{CH}(\text{CH}_3)_2$), 3.09 (12H, $\text{CH}(\text{CH}_3)_2$), -6.54 (2H, $\text{CH}(\text{CH}_3)_2$), -8.62 (2H, $\text{CH}(\text{CH}_3)_2$), -10.64 (6H, $\text{CH}(\text{CH}_3)_2$), -19.30 (2H, CH), -24.94 (2H, CH_{Ar}), -40.64 (6H, CH_3), -41.84 (6H, CH_3) ppm; IR (KBr): $\tilde{\nu}$ = 3649 (w), 3058 (w), 2961 (m), 2925 (w), 2867 (w), 1636 (w), 1591 (s), 1570 (m), 1512 (m), 1457 (m), 1437 (m), 1405 (vs), 1392 (vs), 1354 (vs), 1320 (s), 1280 (m), 1254 (w), 1225 (m), 1184 (m), 1164 (w), 1103 (w), 1056 (w), 1022 (m), 982 (w), 936 (w), 796 (w), 760 (m), 731 (w), 629 (w) cm^{-1} .

Crystallography

Crystallographic data for complexes **1** and **3** were collected on a STOE IPDS 2T diffractometer at 100 K using MoK_α radiation ($\lambda = 0.71073\text{ \AA}$) and on a Bruker D8 VENTURE area detector for complexes **5** and **6** $\times \frac{1}{2}$ hexane. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least squares with SHELXL-97 and SHELXL-2013.²³ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added geometrically and refined by using a riding model except for the bridging hydrides in complex **3** and the hydrogen atoms in the hydroxo groups in complex **6** $\times \frac{1}{2}$ hexane which were found in the difference Fourier map. Multi-scan absorption corrections implemented in SADABS²³ were applied to the data. CCDC 1425738 (**1**), CCDC 1425739 (**3**), CCDC 1425740 (**5'**) and CCDC 1425741 (**6** $\times \frac{1}{2}$ hexane) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Fig. 1. Bulky β -diketiminate supported diiron(II) dihydride complexes **I** (R = Me (R' = H) or *t*Bu (R' = H or *i*Pr)) and the nickel analogue **II**.

Fig. 2.

Molecular structure of $[(\text{PYR})\text{Fe}_2(\mu\text{-Br})_2]$ (**1**); ellipsoids are set at 50% probability.

Hydrogen atoms have been omitted for clarity. Selected bond lengths /Å and angles /°: Fe1–N1 2.029(3), Fe1–N2 2.024(4), Fe1–Br1 2.4756(7), Fe1–Br1' 2.5998(7), Fe1⋯Fe1' 3.0332(7), N1–Fe1–N2 90.25(14), Br1–Fe1–N1 114.29(9), Br1–Fe1–N2 135.91(10), N1–Fe1–Br1' 119.68(9), N2–Fe1–Br1' 105.71(10), Br1–Fe1–Br1' 93.47(2), Fe1–Br1–Fe1' 73.26(2).

Fig. 3. Fourier transform EXAFS spectra of **2** (dotted line) and the best fit (red line); the inset shows the EXAFS data on a wave vector scale weighted by k^3 with respective representation. See supporting information for further details.

Fig 4.

Calculated molecular structure for the ground state of $[\text{PYP})\text{Fe}_2(\mu\text{-H})_2]$ (**2**), B3LYP/Def2-SVP/Def2-TZVPD. Hydrogen atoms apart from H1, H2 have been omitted for clarity. Selected bond lengths /Å and angles /°: Fe1–N1 2.053, Fe1–N2 2.098, Fe1–H1 1.796, Fe1–H2 1.821, Fe1···Fe2 2.626, N1–Fe1–N2 89.9, H1–Fe1–N1 120.2, H1–Fe1–N2 133.8, N1–Fe1–H2 116.9, N2–Fe1–H2 116.9, H1–Fe1–H2 78.9, Fe1–H1–Fe2 94.0.

Fig. 5.

Molecular structure of one of the two independent molecules in the unit cell of $[(\text{PYR})\text{Fe}_2(\mu\text{-HCOO})(\mu\text{-OH})] \times 1/2\text{hexane}$ ($6 \times 1/2\text{hexane}$); ellipsoids are set at 50% probability. Hydrogen atoms and the solvent molecules have been omitted for clarity. Selected bond lengths /Å and angles /° [the values for the second molecule per unit cell are listed in square brackets]: Fe1–N1 2.032(3) [2.037(3)], Fe1–N2 2.026(3) [2.024 (3)], Fe1–O1 2.040(2) [2.048(3)], Fe1–O2 1.972(2) [1.967(3)], Fe1···Fe1' 3.1805(7) [3.1533(7)], O1–C1 1.252(3) [1.256(3)], Fe1–O2–Fe1' 107.48(16) [106.6(2)], N1–Fe1–N2 91.53(11) [90.83(11)], O2–Fe1–N1 118.45(12) [121.67(14)], O2–Fe1–N2 129.42(12) [127.23(14)], O2–Fe1–O1 95.27(12) [99.81(13)], N1–Fe1–O1 109.82(10) [105.55(10)], N2–Fe1–O1 112.57(11) [110.59(11)].

Scheme 1. Reaction pathway for the synthesis of $[(\text{PYR})\text{Fe}_2(\mu\text{-H})_2]$ (**2**).

Scheme 2.

Reactivity of the diiron(II) dihydride compound **2** toward H⁺ (LutHOTf = lutidinium triflate) and CO₂.

Table 1

A Comparison of the EXAFS determined metrical parameters of **2** with the DFT calculated values (for an isolated molecule in Å). (n) represents the number of atoms.

	Fe-N	Fe...Fe	Fe-C	Fe-C
EXAFS	2.03(3)	2.55(1)	3.07(4)	3.92(9)
DFT	2.19(3)	2.61(1)	2.95(4)	3.88(9)