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Between imide, imidyl and nitrene – an imido iron complex in two oxidation states†

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Imidyl and nitrene metal species play an important role in the *N*-functionalisation of unreactive C–H bonds as well as the aziridination of olefines. We report on the synthesis of the trigonal imido iron complexes $[\text{Fe}(\text{NMes})\text{L}_2]^{0,-}$ ($\text{L} = -\text{N}(\text{Dipp})\text{SiMe}_3$; Dipp = 2,6-diisopropyl-phenyl; Mes = (2,4,6-trimethylphenyl)) via reaction of mesityl azide (MesN_3) with the linear iron precursors $[\text{FeL}_2]^{0,-}$. UV-vis-, EPR-, ^{57}Fe Mössbauer spectroscopy, magnetometry, and computational methods suggest for the reduced form an electronic structure as a ferromagnetically coupled iron(II) imidyl radical, whereas oxidation leads to mixed iron(III) imidyl and electrophilic iron(III) nitrene character. Reactivity studies show that both complexes are capable of H atom abstraction from C–H bonds. Further, the reduced form $[\text{Fe}(\text{NMes})\text{L}_2]^-$ reacts nucleophilically with CS_2 by inserting into the imido iron bond, as well as electrophilically with CO under nitrene transfer. The neutral $[\text{Fe}(\text{NMes})\text{L}_2]$ complex shows enhanced electrophilic behavior as evidenced by nitrene transfer to a phosphine, yet in combination with an overall reduced reactivity.

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Introduction

Imido complexes of the late 3d-transition metals play a crucial role in nitrene transfer catalysis.^{1,2} As such there is an innate interest in understanding the structural and electronic features of the central imido metal unit to control and predict its reactivity.^{3–5} The imido ligand is classically regarded as a dianionic imide $[\text{NR}]^{2-}$ that forms either a double or triple bond, as it is the case for early transition metals.^{2,6} For the 3d-metals, the metal–imido bond becomes more covalent and $p \rightarrow d$ donation is reduced due to (partially) filled d-orbitals. This may result in intriguing bonding situations, namely metal stabilized imidyl radical $[\text{NR}]^{\cdot-}$ or even electrophilic nitrene $[\text{NR}]^0$ ligands, that are highly reactive.^{4,5} The former was observed in a few instances for iron,^{7,8} cobalt^{9,10} and nickel.^{11,12} 3d-Metal nitrenes

are mostly known for copper,^{13–15} with only two isolated examples.^{13,15} Given the overall reactive nature of late 3d-metal imido species, the impact of oxidation state changes onto the imido unit is only partially understood. For low-spin complexes, mostly found for isolable and rather unreactive late 3d-metal imidos, few reports of one-electron oxidation showed contraction of the imido metal bond.^{12,16–20} This can be explained by a metal centred oxidation, accompanied with ion radius contraction as well as increased $p \rightarrow d$ donation and depopulation of *anti*-bonding molecular orbitals.^{5,21} Contrastingly, in the only two reports of oxidation of high-valent high-spin 3d-metal imidos M–N bond elongation took place (Fig. 1).^{9,22}

This was attributed to a ligand-centred oxidation and spin density increase at the imido ligand, that resulted in an imidyl radical character. For a pseudo-trigonal bipyramidal imido

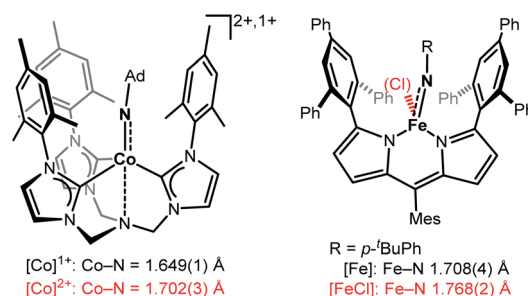


Fig. 1 Examples of imido metal complex oxidation leading to M–N bond lengthening and imidyl character (Ad = adamantyl, Mes = 2,4,6-trimethylphenyl).^{7–9}

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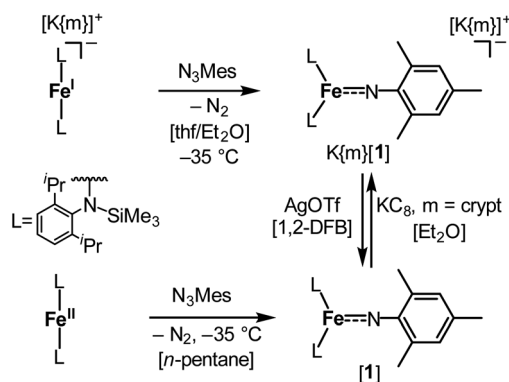
† Electronic supplementary information (ESI) available: General, experimental, analytical (NMR, IR, UV/vis, ^{57}Fe Mössbauer and EPR spectroscopy, SQUID magnetometry, cyclovoltammetry), computational and crystallographic details. CCDC 2130485–2130488. For ESI and crystallographic data in CIF or other electronic format see <https://doi.org/10.1039/d2sc01088g>

Results and discussion

a) ORTEP diagram of the [1][−] anion. The structure shows a central Fe atom coordinated by two N atoms (N1, N2) and a C atom (C1). The Fe atom is also coordinated by a Si atom (Si1). The N1 atom is coordinated by a C atom (C1). The Si1 atom is coordinated by a C atom (C1). The Fe atom is coordinated by a C atom (C1). The N1 atom is coordinated by a C atom (C1). The Si1 atom is coordinated by a C atom (C1).

b) Bond lengths and angles for the [1][−] anion. Bond lengths (Å): C1-Fe1 1.394(3), C1-N1 1.397(3), C1-Si1 1.398(4), C1-C1 1.385(2), C1-C1 1.378(4), C1-N1 1.387(2), C1-Si1 1.429(2), C1-Fe1 1.431(2), C1-N1 1.436(4), C1-Si1 1.339(2), C1-Fe1 1.337(3), C1-N1 1.774(15), C1-Si1 1.741(2), C1-Fe1 1.9541(14), C1-N1 1.9557(14), C1-Si1 1.894(2), C1-Fe1 1.905(2). Bond angles (°): [1][−] ∠Fe-N_{mid}-C = 173.6(13), [1] ∠Fe-N_{mid}-C = 177.5(2)°.

Next, we wanted to elaborate if we could electrochemically attenuate the electronic situation of $[\mathbf{1}]^-$. Cyclic voltammetry



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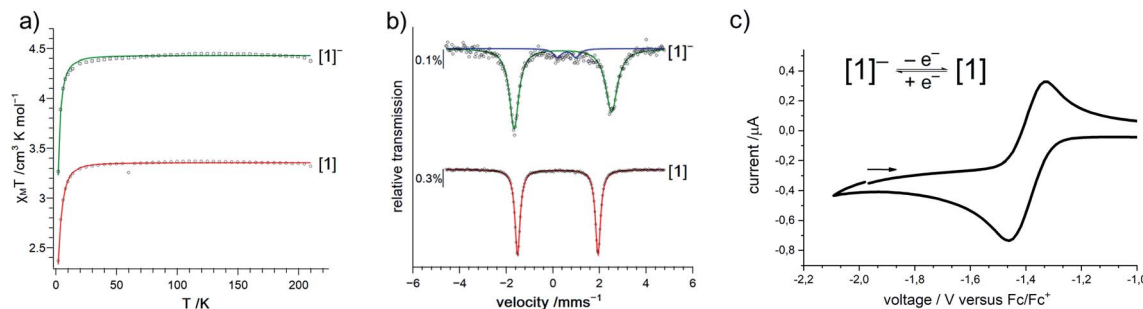


Fig. 3 (a) Variable-temperature magnetic susceptibility of solid $K(m)[1]$ (green) and $[1]$ (red) in the range of 2–210 K. (b) Zero-field ^{57}Fe Mössbauer spectra of solid $K(m)[1]$ (green) and $[1]$ (red) at 80 K. Parameters for $K(m)[1]$: $\delta = 0.43 \text{ mm s}^{-1}$, $|\Delta E_Q| = 4.18 \text{ mm s}^{-1}$ (92%); $[1]$: $\delta = 0.21 \text{ mm s}^{-1}$, $|\Delta E_Q| = 3.45 \text{ mm s}^{-1}$. (c) Cyclic voltammogram of $K(m)[1]$ (500 mV s^{-1} , thf, $0.1 \text{ m } n\text{Bu}_4[\text{PF}_6]$) vs. Fc/Fc^+ .

examination showed a reversible redox event at $E_{1/2} = -1.4 \text{ V}$ at 500 mV s^{-1} (THF, vs. Fc/Fc^+ , Fig. 3c), that becomes irreversible upon lowering the scan rate to 50 mV (Fig. S24†). The potential is in line with those for the oxidation of imido iron(III) and imido iron(II) species (≈ -1.3 to -0.7 V).^{16,17,33} Gratifyingly, chemical oxidation of $[1]^-$ in 1,2-difluorobenzene with AgOTf ($\text{OTf}^- = \text{F}_3\text{CSO}_3^-$) led to the formation of a new paramagnetic species which we attributed to neutral $[1]$. $[1]$ could not be isolated *via* this pathway due to partial degradation, but was independently synthesized by reacting $[\text{FeL}_2]$ with MesN_3 in *n*-pentane (yield 64%, Scheme 1). It can be reduced back to $[1]^-$ by KC_8 in the presence of crypt.222, evidencing the possibility of their chemical interconversion. X-ray diffraction analysis of $[1]$ showed in comparison with $[1]^-$ that all metal–nitrogen bonds contract upon oxidation with otherwise little changes in the $\text{Fe}-\text{N}-\text{C}$ unit ($\text{Fe}-\text{N}_{\text{imide}} 1.741(2) \text{ \AA}$, $\text{Fe}-\text{N}_{\text{imide}}-\text{C}_{\text{Aryl}} 177.5(2)^\circ$, $\text{N}_{\text{imide}}-\text{C}_{\text{Aryl}} 1.337(3) \text{ \AA}$; Fig. 2, right), where the contraction of the $\text{Fe}-\text{N}$ amide bonds was slightly more pronounced. Thus, it was suggestive of at least partial metal based oxidation. This was corroborated by ^{57}Fe Mössbauer spectroscopy showing an IS of $\delta = 0.21 \text{ mm s}^{-1}$ for $[1]$ (vs. $[1]^-$: 0.43 mm s^{-1}). It is in line with shorter Fe–ligand bonds and by that with the decrease of the radial extension of the $4s$ wave function in case of the oxidized species $[1]$. Further, a negative correlation of the IS with the Fe oxidation state is usually valid for high spin complexes.³⁴ The QS for $[1]$ is with $|\Delta E_Q| = 3.56 \text{ mm s}^{-1}$ (vs. $[1]^-$: 4.18 mm s^{-1}) only slightly reduced, and indicates a similar electron density distribution (electric field gradient) in both complexes. The IS value of $[1]$ is distinct from those of iron(IV) imides, which are found between -0.09 and -0.52 mm s^{-1} .^{26,35} This precludes for $[1]$ a formulation as an iron(IV) imide. Accordingly, its IS value is closer to those of high-spin iron(III) imides ($\delta = 0.37\text{--}0.47 \text{ mm s}^{-1}$, $|\Delta E_Q| \approx 0 \text{ mm s}^{-1}$ at 200 K),^{8,27,28} a trigonal intermediate-spin iron(III) imide ($\delta = 0.25 \text{ mm s}^{-1}$, $|\Delta E_Q| = 1.32 \text{ mm s}^{-1}$, at 200 K)²⁰ or four-coordinate high-spin iron(III) imidyls (e.g. $[(\text{dpm})\text{Fe}(\text{N}\{p\text{-}^t\text{Bu}-\text{C}_6\text{H}_4\})\text{Cl}]$ $\delta = 0.28 \text{ mm s}^{-1}$, $|\Delta E_Q| = 2.22 \text{ mm s}^{-1}$, at 90 K).^{7,8,22} Solid state SQUID measurements on $[1]$ (Fig. 3a) gave a $\chi_M T$ value of $3.3 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ ($\mu_{\text{eff}} = 5.14 \mu_B$) at 210 K with $D = -3.5 \text{ cm}^{-1}$ and $g = 2.12$. These values correspond to an overall $S = 2$ spin ground state that fits with the absence of pronounced X-band EPR features. $[1]$ and $[1]^-$ are

thus the first isostructural imido metal complexes in two oxidation states in which both exhibit a high-spin state.

To shed further light on the electronic structures of $[1]^-$ and $[1]$, DFT-(PBE, TPSSH, PBE0) and CASSCF/NEVPT2 calculations were performed.³⁶ All investigated computational methods afforded good to reasonable agreement with the XRD-, Mössbauer-, EPR- and SQUID data (bond lengths and angles, ΔE_Q , δ , g , A , D ; Tables S3–S6†). According to the CASSCF calculations, in $[1]^-$, six electrons populate the two pairs of π/π^* -interactions between the metal and imido ligand (Fig. 4, S43–S45†).

The two unpaired electrons in the antibonding combinations are thereby once metal centred (d_{xz}/π^* ; $\text{Fe} : \text{N} = 0.8 : 0.2$; Löwdin population analysis) and once rather located at the

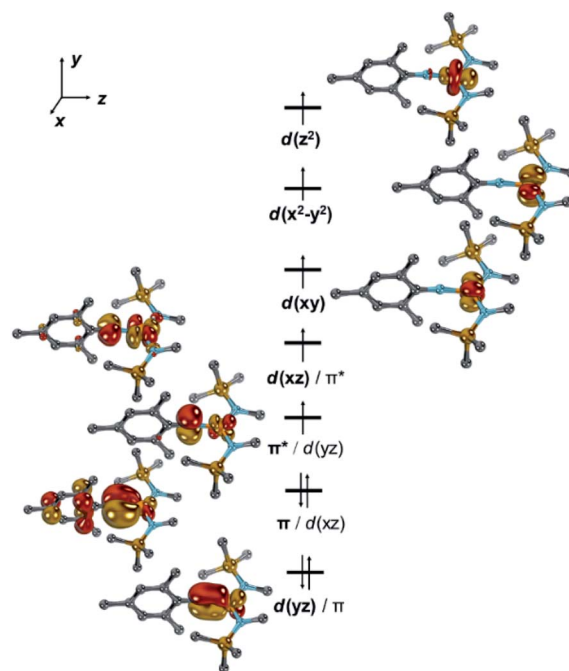


Fig. 4 Electronic structure of $[1]^-$ by CASSCF(11,9). Dipp groups were truncated by methyl groups, hydrogen atoms are omitted for clarity, one set of bonding and antibonding Dipp-centred π -orbitals is omitted for clarity.

ligand (π^*/d_{yz} ; N : Fe = 0.6 : 0.4). This tentatively gives rise to the electronic structure of an imidyl iron(II) complex for $[1]^-$. An oxidation state of iron(II) is also substantiated by the Löwdin spin density of +0.66 a.u. at the imido nitrogen atom.

Neutral $[1]$ features a quintet ground state ($\Delta E_{q/t} = +0.55$ eV; $\Delta E_{q/sept} = +1.16$ eV). The main configuration ($c = 0.63$) predicts thereby four unpaired electrons in d-orbitals (Fig. 5 and S40–S42†). Further two electrons are paired in the d_{xy} orbital, which combines with the imido ligand's p_x orbital (Fe : N = 7 : 3) and to a minor extent with the aromatic mesityl substituent. This gives overall rise to a formal d^6 (Fe^{II}) electron configuration of the metal and an electrophilic nitrene-type ligand. However, the second most important configuration ($c = 0.21$) relates to the π – π^* transition and thus suggests significant imidyl radical character.⁵ This is further corroborated by accumulation of spin density at the imido nitrogen atom (–0.21 a.u.), which is suggestive of considerable antiferromagnetic character. Accordingly, the doubly excited resonance structure is also of relevance ($c = 0.13$), which overall leads to a population of the LUMO by formally $0.49 e^-$ and a shift of electron density to the ligand. Thus, when going from $[1]$ to $[1]^-$ the additional electron populates the antibonding π^* orbital, and weakens the metal–imido bond by formally -0.5 . As such, the calculations highlight the electronic flexibility of the covalent iron–imido ligand interaction where the additional electron is not accepted by either the metal or the ligand, but by both. Since the electron is shared within the [FeNR] linkage, of course, rather similar Mössbauer spectroscopic features of $[1]$ and $[1]^-$ are expected, which aligns well with the experimental (*vide supra*) and

calculated (Table S4†) parameters. It is thus reasonable to consider the imido iron unit in both complexes in its entirety, as proposed for a linear imido cobalt(II) compound.³⁷ Using the Enemark–Feltham notation for nitrosyl complexes³⁸ this leads to notations {FeNR}⁸ for $[1]$ and {FeNR}⁹ for $[1]^-$, and by that avoids singling out or overemphasizing a particular resonance structure.

Given these computed electronic structures of the “iron(II) imidyl” $[1]^-$ as well as the “iron(II) nitrene” $[1]$, we were curious if and how they would translate to differences in chemical reactivity. Both complexes showed only limited H-atom abstraction capabilities in case of 1,4-cyclohexadiene (after 24 h: $[1]$: 39%; $[1]^-$: 73%). H atom abstraction from 1-hydroxy-2,2,6,6-tetramethyl-piperidine (TEMPO-H) was observed for $[1]$ (24 h: 25% TEMPO by X-band EPR spectroscopy), whereas for $[1]^-$ an ill-defined transformation of the imido complex was detected, without significant formation of TEMPO. These observations can be explained by the steric congestion. Possibly also to the ambivalent electronic nature of both complexes may contribute to the observed differences in reactivity. Reaction products of the H atom abstraction, *e.g.* the corresponding amides, could neither be identified nor isolated. This is attributed to subsequent reaction pathways such as scrambling of the amide ligands, as observed in a related cobalt system.²³ Subjecting $[1]$ to an excess PEt_3 resulted in initial disappearance of the ³¹P NMR signal of PEt_3 . This phenomenon pointed to reversible coordination of the phosphine to the paramagnetic metal centre leading to spin polarisation and disappearance of the ³¹P signal.³⁹ Addition of a stronger donor (2,2'-bipyridine) to such a reaction mixture after 24 h led immediately to reoccurrence of the PEt_3 signal, and more importantly small amounts of the nitrene transfer product $MesN=PEt_3$ (Scheme 2). This points to a slightly electrophilic behaviour of $[1]$. In contrast, $[1]^-$ is completely inert towards PEt_3 , as was also observed for the related cobalt complex.²³ On the other hand $[1]^-$ reacts with CO to give $MesNCO$ under nitrene transfer, whereas $[1]$ does not.

Isonitriles (*t*-BuNC, MesNC) interact with both complexes, however no reaction product could be identified (*i.e.*, the

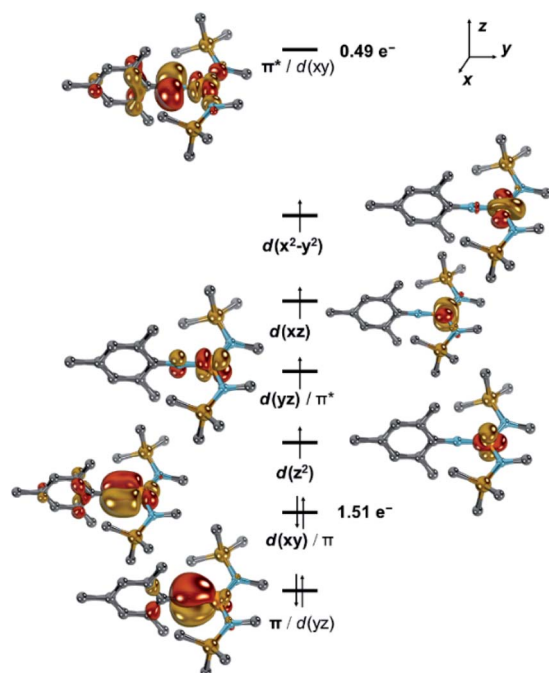
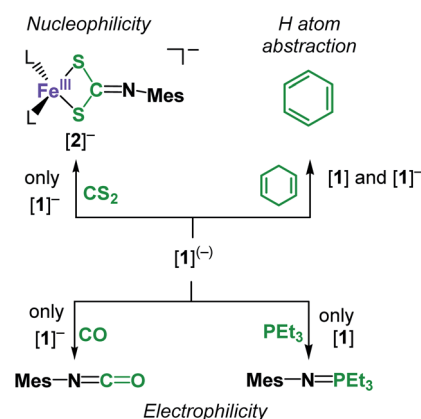


Fig. 5 Electronic structure of $[1]$ by CASSCF(10,9). Dipp groups were truncated by methyl groups, hydrogen atoms are omitted for clarity, one set of bonding and antibonding Dipp-centred π -orbitals is omitted for clarity.



Scheme 2 Diverging reactivity of $[1]$ and $K(m)[1]$ towards nucleophiles, electrophiles, and C–H bonds.



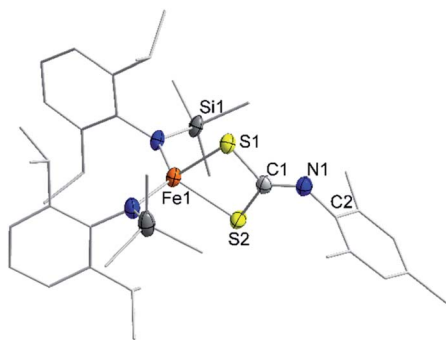


Fig. 6 Solid state structure of $K\{m\}[2]$. The $K\{m\}$ cation as well as H atoms are omitted for clarity.

presumed carbodiimide $RNC=NMe$ s). Probing the nucleophilicity using CS_2 as a substrate revealed that $[1]$ is unaffected for a prolonged period of time. $[1]^-$ on the other hand reacted readily *via* insertion into the imido metal bond resulting in the dithiocarbonimidate complex $[L_2Fe(\eta^2-S_2C=NMe)]^-$, $[2]^-$ (Fig. 6, Scheme 2). The assembly of a dithiocarbonimidate ligand *via* this reaction is remarkable, as in the coordination sphere of a metal it was only achieved by a $[2 + 2]$ addition of organo isothiocyanates with transient terminal metal sulfides⁴⁰ or oxidation of isonitriles with metal persulfides.⁴¹ The formation of $[2]^-$ resembles the insertion of a carbodiimide into the iron(II) imido bond of the nucleophilic $[(Ph_2B(^tBuIM)_2)Fe(NDipp)]^-$. In both cases it likely results from an initial $[2 + 2]$ cycloaddition of one of the $C=X$ bonds with the $M-N$ unit, in resemblance to the reaction of an imido nickel(II) complex with CO_2 or an imido iron(IV) complex with a carbodiimide ($PhNCNPh$).^{26,42} $[2]^-$ exhibits in solution a magnetic moment of $5.39 \mu_B$ that is close to the spin-value of an $S = 5/2$ ion ($\mu_{s.o.} = 5.92 \mu_B$). It shows that despite its mostly iron(II) imidyl character $K\{m\}[1]$ reacts with an electrophile as an iron(III) imide, thus underscoring the electronic flexibility of the imido iron unit.

Conclusion

Concluding, we describe with $[Fe(NMe)_2L_2]^{0,-}$ ($L = -N(Dipp)SiMe_3$) a pair of isostructural imido iron complexes in two oxidation states. The electronic structures of the two compounds were comprehensively assessed, amongst others by EPR and ^{57}Fe Mössbauer spectroscopy and magnetometry, and revealed for both complexes a high-spin state. In line with the computational analysis and structural features, the neutral compound shares iron(II) nitrene and iron(III) imidyl character, whereas the reduced form is described best as an iron(II) imidyl. The change of the complexes' oxidation state is thus ligand and metal based, revealing the electronic flexibility of the imido metal bond. The ambiguity of the $[FeNR]$ unit is reflected best by $[Fe(NMe)_2L_2]^-$ which shows a nucleophilic and electrophilic behaviour. Upon oxidation to $[Fe(NMe)_2L_2]^0$ the nucleophilicity is lost in accordance with a shift to a more nitrene-like electronic situation. We foresee these reactivity shifts to be relevant for directing NR group transfer reactivity of metal imidos towards different functionalities in organic substrates.

Data availability

All experimental procedures, spectral data, and computational data are included in the ESI.† Xyz coordinates may be obtained *via* the ESI,† output files can be obtained by D. M upon request. NMR/EPR/IR/Mössbauer raw data is so far only available upon request to C. G. W.

Author contributions

S. R. carried out the synthetic work and analytical characterization, including the crystallographic studies. S. D. recorded the SQUID and ^{57}Fe Mössbauer data, and both S. D. and F. M. analyzed the data. B. B., A. R., A. S. and C. L. recorded and analyzed the EPR data. C. S. performed the cyclic voltammetric analysis. D. M. performed the quantum chemical calculations. S. R. and C. G. W. wrote the manuscript with contributions from all authors.

Conflicts of interest

There are no conflicts to declare.

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