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Ferrate(II) complexes with redox-active formazanate ligands

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The synthesis of mono(formazanate) iron complexes is described. In the presence of tetrabutylammonium halides, salt metathesis reactions afford the ferrate(II) complexes $[\text{Bu}_4\text{N}][\text{LFeX}_2]$ ($\text{L} = \text{PhNNC}(p\text{-tol})\text{NNPh}$; $\text{X} = \text{Cl}, \text{Br}$) in good yield, and the products are characterized in detail. The high-spin ferrate(II) complexes show cyclic voltammograms that are consistent with reversible, ligand-based one-electron reduction. The halides in these ferrate(II) compounds are labile, and are displaced by 4-methoxyphenyl isocyanide (4 equiv) as evidenced by formation of the low-spin, cationic octahedral complex $[\text{LFe}(\text{CNC}_6\text{H}_4(p\text{-OMe}))_4][\text{Br}]$. Thus, a straightforward route to mono(formazanate) iron(II) complexes is established.

Introduction

There is considerable recent interest in iron catalysts for organic synthesis, mainly due to the high abundance and low toxicity of Fe.¹ However, replacement of noble metal catalysts by iron-based systems (or other first-row transition metals) is challenging due to the prevalence of one-electron (radical) redox-chemistry for complexes based on these elements. Much focus is therefore on development of strategies to either capitalize on the new types of reactivity that metal-bound organic radicals offer,² or to implement redox-active ligand designs that potentially allow for multi-electron transformations with earth-abundant metals.³ The latter strategy holds considerable promise, as it facilitates access to complexes in unusually low (or high) overall oxidation states by involving reductions (or oxidations) that are principally ligand-based, and thereby prevent having to go through unfavourable metal-based redox-events. Although nature uses redox-active ligands in a variety of metalloenzyme active sites,⁴ it is often not straightforward to translate these ligands to simple, small-molecule synthetic analogues, as the protein environment is important in preventing degradation reactions. In order to develop this chemistry further, new organic ligand frameworks are desirable that feature high chemical stability across two (or more) oxidation states and tuneable redox-potentials. Given the widespread use of β -diketiminato ligands in organometallic chemistry and catalysis, we are interested in redox-active analogues of this versatile class of ligands. Replacement of two carbon atoms by nitrogen in the backbone

of β -diketiminato ligands, i.e., leading to the formazanate anion, has been shown to significantly decrease the LUMO energy level, and render reduction reactions in formazanate complexes more accessible and, moreover, tuneable in a predictable manner using ligand substituent effects.^{5,6,7} In recent iron chemistry using the formazanate $[\text{PhNNC}(p\text{-tol})\text{NNPh}]^-$ (L), we found that the low-lying LUMO of this class of ligands can engage in substantial π -backbonding interactions with the d^6 Fe(II) centre, which is maximized by flattening of the tetrahedral structure. As a result, the four-coordinate bis(formazanate) iron(II) complex (**1**, see Figure 1) shows spin-crossover between an unusual low-spin ($S = 0$) state and the regular high-spin ($S = 2$) state.⁸ A consequence of the metal-ligand π -backbonding interaction in **1** is that the empty orbitals that have predominant ligand character (i.e., the N-based π^* -orbitals) are pushed up in energy, and the LUMO in **1** has significant Fe d-character (Figure 1). In agreement with this notion, the one-electron reduced species $[\text{L}_2\text{Fe}]^-$ **2** shows EPR spectra consistent with a low-spin Fe(I) centre, instead of a ligand-based radical.⁸ Given this precedent, it was of interest to see how general π -backdonation is in formazanate chemistry, and whether ligand-based radicals are accessible.

In this paper we extend our studies to the heteroleptic formazanate iron halide derivatives, which are obtained in excellent yield as the ferrate(II) complexes $[\text{LFeX}_2]^-$ ($\text{X} = \text{Br}$ (**3**); Cl (**4**)).

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Figure 1. Simplified MO schemes for low-spin L_2Fe (**1**) showing the 'flattened' tetrahedral structure and π -backdonation interaction (A), and a high-spin iron formazanate complex without π -backbonding (B).

While this manuscript was in preparation, Broere and Holland reported related three-coordinate formazanate iron complexes with a bulky bis(trimethylsilyl)amido co-ligand, and studied the influence of alkali metal coordination on the chemistry of the one-electron reduced species $[LFe(NSiMe_3)_2]^-$.⁹ In contrast to the bis(formazanate) complex **1**, the tetrahedral mono(formazanate) iron complexes described here are shown to have high-spin ground states, and voltammetric analyses suggests ligand-based reductions in these compounds. The halide co-ligands are labile, and may be displaced with 4-methoxyphenyl isocyanide to give a cationic low-spin iron(II) complex with an octahedral coordination geometry (**5**).

Results and discussion

Our initial synthesis of the compounds discussed in this paper was accidental and followed from a study of the reactivity of the bis(formazanate) complexes **1** and **2**. Attempts to effect oxidative addition of $BnBr$ to the anionic Fe(I) complex $[L_2Fe]^-$ (**2**)⁸ in THF solution was shown by NMR spectroscopy to lead to a multitude of (paramagnetic) complexes, from which we were unable to isolate a desired Fe(III) product. Instead, layering the THF solution with hexane gave a small amount of crystals that were shown by X-ray crystallography to be the ionic product $[Bu_4N][LFeBr_2]$ (**3**) (Figure 2), in which the iron centre is oxidized to Fe(II). Although the yield of this reaction is low, and the fate of the other formazanate ligand is unknown at present, the formation of **3** was of interest. Previous attempts to obtain mono(formazanate) iron halide complexes, for example by transmetalation between the formazanate potassium salt **LK** and $FeCl_2$ in a 1:1 ratio (L:Fe), invariably led to the homoleptic complex (L_2Fe , **1**) and unreacted $FeCl_2$. We attribute this to the small steric profile of the formazanate ligand L, which results in facile ligand exchange reactions from the putative three-coordinate product $LFeCl$ due to Schlenk-type equilibria, leading to the homoleptic compounds as thermodynamic products. The successful isolation and structural characterization of **3**, albeit as an unwanted side

product in the reaction of **2** with $BnBr$, prompted us to explore a rational synthesis of this mono(formazanate) ferrate(II) complex. Initially, the synthesis of **3** was attempted on an NMR scale by addition of $THF-d_8$ to an equimolar mixture of $FeBr_2(THF)_2$, **LK** and Bu_4NBr (Scheme 1A). Monitoring the reaction progress by NMR spectroscopy showed that, initially, the major product is **1**. After one hour at room temperature, integration of the 1H NMR spectrum showed **3** and **1** in a 1:1.1 ratio, after which gradual conversion to **3** was observed (after 1 day, the **3**:**1** ratio reached 1:0.5). Subsequently, the NMR tube was heated to $60^\circ C$ for four days, after which > 98% conversion to **3** was obtained. Similarly, treatment of **1** with 2 equiv. of Bu_4NBr in $toluene-d_8$ also affords compound **3** cleanly according to 1H NMR spectroscopy, concomitant with formation of a stoichiometric amount of the formazanate ammonium salt $[Bu_4N][L]$ (Scheme 1B).¹⁰ On a preparative scale, **3** was prepared from $FeBr_2(THF)_2$, **LK** and Bu_4NBr and isolated in 90 % yield as dark purple crystalline material. Similarly, the chloride analogue $[Bu_4N][LFeCl_2]$ (**4**) is obtained in 84 % yield when $FeCl_2$ and Bu_4NCl are used.

Scheme 1. Synthesis of compounds **3** and **4**.

X-ray crystal structure determinations show that **3** and **4** have very similar tetrahedral geometries, with the iron centre surrounded by a bidentate formazanate ligand and two halides complementing the coordination sphere (Figure 2 for **3**, see ESI for **4**). The Fe-N bond lengths in **3** are significantly longer (1.979(2)/1.976(2) Å) than those in the bis(formazanate) iron(II) and iron(I) compounds (**1** and **2**) that we reported previously (Fe-N distances of 1.8207(16)/1.8278(15) and 1.8562(19)/1.8755(19) Å, respectively).⁸ Conversely, they are somewhat shorter than the Fe-N bonds in the structurally related $[(\text{amidinate})FeX_2]^-$ compounds reported by Hessen et al.,¹¹ and Lichtenberg, Grützmaier and co-workers (Fe-N bonds range between 2.083(2)-2.113(1) Å),¹² or the complex $(\beta\text{-diketiminato})FeCl_2 \cdot Li(DME)_2$ described by Ponikiewski et al. (Fe-N distances of 2.021(2) and 2.029(2) Å).

Figure 2. Molecular structure of compound **3** showing 50% probability ellipsoids. Hydrogen atoms, and one of the disorder components of the Bu₄N moiety are omitted for clarity.

A neutral Fe(III) analogue of the latter was published by Lippard,¹³ and its structure determination showed Fe–N bonds slightly shorter (1.9730(13)/1.9459(13) Å) than those in **3**, whereas an Fe(II) complex with a (neutral) β -diketimine ligand shows longer Fe–N distances of 2.073(8)/2.074(8) Å.¹⁴ In the previously reported bis(formazanate) iron(II) complex **1**, the short Fe–N distances were attributed to the unusual low-spin ($S = 0$) electronic configuration and relatively strong Fe $\rightarrow$ formazanate π -backbonding interactions. A second metrical parameter that is sensitive to these π -backbonding interactions is the formazanate N–N bond length; (partial) population of the ligand π^* -orbital leads to a measurable increase from the value that is typical for an electronically unperturbed, monoanionic formazanate ligand (~ 1.30 Å). For example, ligand-based one-electron reduction results in N–N bond elongation to 1.36–1.37 Å in Zn and B complexes with this class of ligands.^{7a, b, d, e, 15} The π -backdonation in **1/2** leads to a smaller increase to $\sim 1.33/1.35$ Å, respectively. For the anionic mono(formazanate) compound **3**, the N–N bonds are short at 1.313(2) and 1.317(2) Å, suggesting that π -backbonding interactions are weaker, despite the presence of an electron-rich ferrate(II) centre. It appears that in **3** the presence of only one potential π -acceptor formazanate ligand together with two π -donor bromides overall results in a relatively small ligand-field and thus a high-spin complex. Indeed, the geometry of the four ligands around the Fe centre in **3** is close to tetrahedral (the angle between the N–Fe–N and Br–Fe–Br planes, $\angle(\text{N–Fe–N})/(\text{Br–Fe–Br})$, is 86.72°, in marked contrast to that in the bis(formazanate) compound **1** ($\angle(\text{N–Fe–N})/(\text{N–Fe–N}) = 60.97^\circ$). The ‘flattening’ observed in the structure of **1**, which maximizes π -backdonation into the formazanate ligands and leads to its spin-crossover behaviour, is absent in the ferrate complexes **3**. The structure of the dichloride analogue **4** is very similar to **3**, with $\angle(\text{N–Fe–N})/(\text{Cl–Fe–Cl}) = 88.16^\circ$ and Fe–N bond lengths of 1.982(2) and 1.983(2) Å.

¹H NMR spectroscopy in THF-*d*₈ solution shows paramagnetically shifted resonances, the number of which is consistent with C_{2v} symmetry in solution. Again, there is little difference between the bromide **3** and the chloride **4**, and only

the former is discussed. A tentative assignment of the NMR resonances was based on integration ratios; the paramagnetic line-broadening is sufficiently small that a 2D COSY NMR spectrum shows several key correlations to aid in unambiguous assignment of the spectrum. Similar to **1**, half of the six resonances are shifted to low field (δ 25–36 ppm), and the other half are found upfield (between δ -7 and -20 ppm) of the diamagnetic range. For example, the *p*-tolyl CH₃ group in **3** is found as a relatively sharp signal ($\Delta\nu_{1/2} = 28$ Hz) at δ 35.1 ppm in the room temperature ¹H NMR spectrum, whereas the N-Ph *o*-H resonance is at δ -19.4 ppm but significantly broadened ($\Delta\nu_{1/2} = 1720$ Hz) due to its proximity to the paramagnetic iron centre. The paramagnetically shifted NMR spectra are consistent with the results from the solid state structures that, in contrast to the bis(formazanate) iron compounds **1** and **2**, the anionic mono(formazanate) complexes **3** and **4** do not have a low-spin ground state. Indeed, the room temperature magnetic moment of **3** in THF solution was determined to be 5.4 μ_B by the Evans method, indicative of a high-spin ($S = 2$) ground state, which does not change upon cooling to -60 °C. The magnetic moment is somewhat larger than the spin-only value for four unpaired electrons, and indicates that a small orbital contribution is present. Zero-field Mössbauer spectroscopy of **3**, measured

Figure 3. Zero-field Mössbauer spectrum of **3** measured as a frozen THF solution (80 K).

either as a solid (see ESI) or as frozen THF solution (Figure 3), showed a quadrupole doublet at $\delta = 0.73$ mm·s⁻¹ with $\Delta E_Q = 1.82$ mm·s⁻¹. The observed isomer shift is significantly different than that in **1** ($\delta = 0.03$ mm·s⁻¹), but typical for four-coordinate high-spin Fe(II) complexes.¹⁶

Compounds **3** and **4** are intensely coloured and show UV/Vis spectra that have broad absorption maxima in the visible range around 515–520 nm ($\epsilon \sim 10000$ – 12000 L·mol⁻¹·cm⁻¹). Absorption maxima in this range are typically observed for complexes containing formazanate ligands, and are attributed to $\pi \rightarrow \pi^*$ transitions in the ligand framework. In addition to the large molar extinction coefficient, the similar energies of this absorption for both **3** and **4** further corroborates their ligand-based nature.

To characterize the redox-behaviour of **3** and **4**, cyclic voltammograms were recorded in THF solution using 0.1 M

[Bu₄N][PF₆] as the supporting electrolyte (Figure 4). Scanning towards negative potential reveals a quasi-reversible reduction at $E^0 = -1.58$ and -1.60 V for the bromide (**3**) and chloride (**4**), respectively (all potentials are referenced to the Fc^{0/+} couple). A second, irreversible reduction is observed at peak potentials of -2.58 and -2.65 V. The first reduction occurs at more negative potential than in the bis(formazanate) iron complex **1** (-1.21 V).⁸ However, it is similar to ligand-based reduction in an anionic zinc complex with the same ligand: the redox-couple L₂Zn^{-2/-} is observed at -1.55 V.^{7a} Moreover, voltammetric characterization of this zinc complex shows that the corresponding trianion (L₂Zn³⁻) is accessible at -2.55 V, which is again at a very similar potential as observed for the (irreversible) reductions in **3/4**. Although attempts to isolate and characterize the reduction products of **3** (generated in THF solvent using Na/Hg or Cp⁺₂Co as reductant) were unsuccessful, the cyclic voltammetry data are in agreement with ligand-based one- and two-electron reductions taking place. An anodic sweep (0.1 V/s) for **3** shows an irreversible oxidation event at a peak potential of 0.05 V vs. Fc^{0/+}, which results in the appearance of additional features in the return wave at ca. -0.50 and -0.91 V (Figure S9). As expected for electron-transfer followed by a (slow) subsequent chemical reaction (EC mechanism in Testa-Reinmuth notation¹⁷), changing the scan rate from 0.05 V/s to 0.5 V/s shows an increase in the cathodic current at the [LFeBr₂]^{-1/0} couple (Figure S10). Similar data are observed for the chloride complex **4**, but the oxidation appears to be somewhat more reversible and is shifted by ca. 80 mV in a negative direction.

Figure 4. Cyclic voltammogram of **3** measured in THF solution (1.5 mM), with 0.1 M [Bu₄N][PF₆] electrolyte recorded at a scan rate of 100 mV s⁻¹.

Treatment of a THF-*d*₈ solution of **3** with successive (stoichiometric) amounts of the isocyanide CNC₆H₄(*p*-OMe) shows uptake of up to 4 equivalents of isocyanide, and formation of an intense green solution (Scheme 2). Due to the similar solubility of **5** and Bu₄NBr (which is formed as a co-product), we were unable to obtain **5** in analytically pure form as it was always contaminated with Bu₄NBr. Nevertheless, a sample containing crystalline **5** could reproducibly be obtained from THF, and was characterized as the salt [LFe(CNC₆H₄(*p*-OMe))₄][Br] (**5**), in which the cationic iron complex is in an octahedral coordination environment that consists of a bidentate formazanate ligand complemented by four isocyanides (Figure 5). In contrast to compound **3** and **4**, where the Fe centre is located in the ligand plane, a significant

distortion is observed in **5**, with the Fe atom displaced by 0.737 Å out of the plane defined by the N atoms of the ligand backbone. Despite the fact that **5** is low-spin, the Fe-N bond lengths of 1.970(2) and 1.978(2) Å are similar to those in **3** and **4**, which is likely the result of the six-coordinate geometry in **5**. The N-N bonds in the ligand are short at 1.290(3)/1.282(3) Å, suggesting that the ligand is bound in its monoanionic form and π -backdonation is minimal.

Scheme 2. Synthesis of compound **5**.

The ¹H NMR spectrum of **5** (as a mixture with Bu₄NBr) in CD₂Cl₂ solution shows sharp resonances in the range for diamagnetic compounds, confirming an *S* = 0 ground state for **5**, as expected for an octahedral complex with strong-field ligands. The number of NMR resonances is indicative of a C_{2v} symmetric complex in solution. Two inequivalent OMe groups are observed in the ¹H NMR spectrum that correspond to the isocyanides in the equatorial and axial positions, and the C≡N moieties are found at δ 161.5 and 161.2 ppm in the ¹³C NMR. In THF-*d*₈ solution, the ¹H NMR spectrum of **5** is considerably more complex and shows the presence of free isocyanide, which can be attributed to an equilibrium involving isocyanide/Br⁻ exchange that likely forms a mixture containing the neutral complex LFe(CNC₆H₄(*p*-OMe))₃Br. Thus, solvent polarity seems to be important in determining the speciation of **5** in solution.

Figure 5. Molecular structure of compound **5** showing 50% probability ellipsoids. Hydrogen atoms, THF solvate molecules and the Br⁻ counterion are omitted; the N-Ph groups are shown as wireframe for clarity.

The zero-field Mössbauer spectrum of a solid sample of **5** (Figure S3) shows a major species (82%) at $\delta = 0.08 \text{ mm}\cdot\text{s}^{-1}$, which has a small quadrupole splitting ($\Delta E_Q = 0.25 \text{ mm}\cdot\text{s}^{-1}$). These values are consistent with a low-spin, octahedral Fe(II) centre.¹⁶ A minor component (18%) is observed with $\delta = 0.39 \text{ mm}\cdot\text{s}^{-1}$ and $\Delta E_Q = 1.07 \text{ mm}\cdot\text{s}^{-1}$ which is due to an unknown impurity.¹⁸

Two IR bands are observed at 2171 and 2152 cm^{-1} , in the range that is diagnostic for $\text{C}\equiv\text{N}$ stretching vibrations. An intense absorption band is observed at $\lambda_{\text{max}} = 621 \text{ nm}$ in the UV/Vis spectrum of **5**, which is bathochromically shifted from that in **3/4**. Although the nature of these electronic transitions is not known in detail, the substantial shift of the visible absorption maxima in the tetrahedral anions **3/4** and the octahedral cation **5** suggests that they are not solely due to $\pi \rightarrow \pi^*$ transitions within the ligand framework (as in boron and zinc compounds with these ligands). The cyclic voltammogram of compound **5** in DCE solution (0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ electrolyte) shows a cathodic wave at a potential ($E_{\text{p,c}} = -1.62 \text{ V}$ vs $\text{Fc}^{0/+}$) that is similar to the reductions in **3/4**, but the reduction is irreversible in **5** (Figure S14). An oxidation peak (albeit with lower current) is seen in the return sweep at $E_{\text{p,a}} = -0.45 \text{ V}$, which is absent when the potential is not swept past the reduction event (Figure S15). It thus seems that (ligand-based) reduction in **5** is accompanied by a chemical step (possibly loss of isocyanide), rendering the reduction electrochemically irreversible. At more positive potentials, several oxidations are observed between +0.1 and +0.7 V, which (at least in part) are due to bromide oxidation (Figure S16).¹⁹ However, the presence of an additional (reversible) oxidation in addition to that for Br^- suggest that the $[\text{LFe}(\text{CNC}_6\text{H}_4(p\text{-OMe}))_4]^{+/2+}$ couple also occurs in that range.

Conclusions

The formazanate ferrate(II) dihalides, $[\text{LFeX}_2]^-$ ($\text{X} = \text{Br}$, **3**; Cl , **4**), described here provide an entry into exploring the chemistry of mono(formazanate) iron complexes. These heteroleptic, tetrahedral complexes have a quite different electronic structure than the corresponding homoleptic bis(formazanate) iron(II) complexes (L_2Fe , **1**), as they are shown to have high-spin ground states. Characterization by cyclic voltammetry suggests that reduction occurs at the formazanate ligand, again highlighting the electronic structure differences between the two classes of compounds. On the basis of these results and a comparison of X-ray structural data, it is proposed that π -backdonation from the iron centre into the ligand π^* -orbitals is much less important in these mono(formazanate) complexes, leading to reduced Fe-N bond covalency. Thus, ligand-based redox reactions occur in these compounds at relatively accessible potentials, similar to formazanate complexes with redox-inactive metals. The halide ligands in **3** are shown to be labile, and displacement by the isocyanide $\text{CNC}_6\text{H}_4(p\text{-OMe})$ forms the octahedral cationic complex $[\text{LFe}(\text{CNC}_6\text{H}_4(p\text{-OMe}))_4]^+$. Given the success of β -diketiminates and other anionic bidentate N-ligands in (low-coordinate) iron chemistry,²⁰ we anticipate that related compounds that

incorporate redox-active ligands such as those presented here can be of relevance in finding new modes of reactivity. Research in this direction is currently underway in our laboratory.

Experimental Section

General Considerations.

All manipulations were carried out under nitrogen or argon using standard glovebox, Schlenk, and vacuum-line techniques. THF (Aldrich, anhydrous, 99.8%) was dried by percolation over columns of Al_2O_3 (Fluka); toluene, hexane and pentane (Aldrich, anhydrous, 99.8%) were passed over columns of Al_2O_3 (Fluka), BASF R3-11-supported Cu oxygen scavenger, and molecular sieves (Aldrich, 4 Å). THF- d_8 (Euriso-top) was vacuum transferred from Na/K alloy and stored under nitrogen. CD_2Cl_2 (Euriso-top) was used as received. The compounds $\text{K}[\text{PhNNC}(p\text{-tol})\text{NNPh}] \cdot 2\text{THF}$ (**LK**),¹⁰ $\text{FeBr}_2(\text{THF})_2$ ²¹ and **18** were synthesized according to literature procedures. Tetrabutylammonium bromide (Sigma-Aldrich, 99%), tetrabutylammonium chloride (Sigma-Aldrich, 99%), anhydrous FeCl_2 (Aldrich, 98%), FeBr_2 (Aldrich, 98%), 4-methoxyphenyl isocyanide (Sigma-Aldrich, 97%) were used as received.

NMR spectra were recorded on a Varian Mercury 400, Inova 500, or Bruker 600 spectrometer. The ^1H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances and reported in ppm relative to TMS (0 ppm). The assignments of NMR resonances were aided by COSY and HMQC experiments using standard pulse sequences.

Mössbauer spectra were recorded with a ^{57}Co source in a Rh matrix using an alternating constant acceleration Wissel/Mössbauer spectrometer operated in the transmission mode and equipped with a Janis closed-cycle helium cryostat. Isomer shifts are given relative to iron metal at ambient temperature. Simulation of the experimental data was performed with the *Mfit* program: E. Bill, Max-Planck Institute for Chemical Energy Conversion, Mülheim/Ruhr, Germany.

Elemental analyses were performed by the analytical laboratory of the Institute of Inorganic Chemistry at the University of Göttingen using an Elementar Vario EL III instrument.

Cyclic Voltammetry was performed using a three-electrode setup with a silver wire pseudoreference electrode and a platinum disk working electrode (CHI102, CH Instruments; diameter = 2 mm). The platinum working electrode was polished before the experiment using an alumina slurry (0.05 μm), rinsed with distilled water, and subjected to brief ultrasonication to remove any adhered alumina microparticles. The electrodes were then dried in an oven at 75 °C overnight to remove any residual traces of water. The CV data were calibrated by adding decamethylferrocene at the end of the experiments. There is no indication that the addition of decamethylferrocene influences the electrochemical behaviour of the products. The potentials are reported vs $\text{Fc}^{+/0}$.²² All electrochemical measurements were performed at ambient temperatures under an inert N_2 atmosphere in THF or

DCE containing 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ as the supporting electrolyte. Data were recorded with *Autolab NOVA* software (version 2.0, 2.1 and 2.2).

Synthesis of $[\text{Bu}_4\text{N}][(\text{PhNNC}(p\text{-tol})\text{NNPh})\text{FeBr}_2]$ (3**).** To a solution of $\text{FeBr}_2(\text{THF})_2$ (50.0 mg, 1.0 eq, 0.14 mmol) in 5 mL of THF, tetrabutylammonium bromide (53.8 mg, 1.2 eq, 0.17 mmol) was added as a solid. A violet THF solution of $\text{K}[\text{PhNNC}(p\text{-tol})\text{NNPh}]\cdot 2\text{THF}$ (**LK**) (69.5 mg, 1.0 eq, 0.14 mmol) was added dropwise to the stirring reaction mixture (addition made in 15 minutes). After stirring at r.t. for 3 days the fuchsia solution was filtered through a 0.2-micron syringe filter. Slow diffusion of hexane into the THF solution at r.t. afforded 96.9 mg of dark purple crystals of **3** (12.6 mmol, 90 % yield).

^1H NMR (500 MHz, $\text{THF}-d_8$, 25 °C): δ 36.06 (3H, *p*-tolyl CH_3), 25.96 (4H, Ph *m*-CH), 25.11 (2H, *p*-tolyl *m*-CH), 2.74 (8H, NBu_4^+ CH_2), 1.59 (8H, NBu_4^+ CH_2), 1.39 (8H, NBu_4^+ CH_2), 0.74 (12H, NBu_4^+ CH_3), -7.27 (2H, *p*-tolyl *o*-CH), -8.30 (2H, Ph *p*-CH), -18.36 (br, 4H, Ph *o*-CH) ppm.

^{13}C NMR (126 MHz, $\text{THF}-d_8$, 25 °C) δ = 133.7, 77.3 (NBu_4^+ CH_2), 38.3 (NBu_4^+ CH_2), 24.4 (NBu_4^+ CH_2), 18.2 (NBu_4^+ CH_3), -0.5, -29.0, -42.1, -90.1 ppm.

Anal. calcd for $\text{C}_{36}\text{H}_{53}\text{N}_5\text{Br}_2\text{Fe}$: C 56.05, H 6.92, N 9.08; found: C 56.08, H 6.64, N 9.00.

Synthesis of $[\text{Bu}_4\text{N}][(\text{PhNNC}(p\text{-tol})\text{NNPh})\text{FeCl}_2]$ (4**).** To a solution of FeCl_2 (114.2 mg, 1.0 eq, 0.9 mmol) in 15 mL of THF, tetrabutylammonium chloride (300.2 mg, 1.2 eq, 1.1 mmol) was added as a solid. $\text{K}[\text{PhNNC}(p\text{-tol})\text{NNPh}]\cdot 2\text{THF}$ (**LK**) (447.0 mg, 1.0 eq, 0.9 mmol) was added in small portion as a solid and 15 mL of THF were used to wash the containing flask. After stirring at r.t. for 3 days the volatiles were removed under vacuum. The product was extracted in THF (2 x 10 mL) and slow diffusion of hexane into the fuchsia THF solution at -30 °C afforded **4** as crystalline purple solid (513.2 mg, 0.75 mmol, 84% yield).

^1H NMR (500 MHz, $\text{THF}-d_8$, 25 °C): δ 34.19 (3H, *p*-tolyl CH_3), 25.05 (2H, *p*-tolyl *m*-CH), 22.77 (4H, Ph *m*-CH), 3.76 (8H, NBu_4^+ CH_2), 2.35 (8H, NBu_4^+ CH_2), 1.61 (8H, NBu_4^+ CH_2), 0.86 (12H, NBu_4^+ CH_3), -6.26 (2H, *p*-tolyl *o*-CH), -7.66 (2H, Ph *p*-CH), -25.69 (br, 4H, Ph *o*-CH) ppm.

Synthesis of $[(\text{PhNNC}(p\text{-tol})\text{NNPh})\text{Fe}(\text{CNC}_6\text{H}_4(p\text{-OMe})_4)[\text{Br}]$ (5**).** In a schlenk reactor **3** (79.4 mg, 1.0 eq, 0.103 mmol) was mixed together with 4-methoxyphenyl isocyanide (63.6 mg, 4.5 eq 0.46 mmol) in THF (10 mL). The reaction mixture was stirred at r.t. for 2 h obtaining a green solution, which was opened at the air. Slow diffusion of pentane into the THF solution at r.t. for 3 days afforded a green crystalline solid, which was washed with toluene and pentane and dried (110.2 mg). The solid was proved by NMR to be a mixture of **5** and Bu_4NBr in ratio respectively 1:1.4.

^1H NMR (600 MHz, CD_2Cl_2 , 25 °C): δ 7.87 (d, J = 8.2 Hz, 2H, *p*-tolyl *o*-CH), 7.81 (d, J = 7.6 Hz, 4H, Ph *o*-CH), 7.48 (t, J = 8.4 Hz, 4H, Ph *m*-CH), 7.35 (t, J = 7.3 Hz, 2H, Ph *p*-CH), 7.23 (d, J = 8.2 Hz, 2H, *p*-tolyl *m*-CH), 7.21 (d, J = 9.0 Hz, CN-Ar), 7.07 (d, J = 9.0 Hz, CN-Ar'), 6.90 (d, J = 9.0 Hz, CN-Ar'), 6.87 (d, J = 9.0 Hz, CN-

Ar), 3.83 (s, CN-Ar', *p*-OCH₃), 3.82 (s, CNC_6H_4 (s, CN-Ar, *p*-OCH₃), 3.68 (m, THF)*, 3.33-3.30 (m, NBu_4^+ CH_2), 2.40 (s, 3H, *p*-tolyl CH_3), 1.82 (m, THF), 1.71-1.65 (m, NBu_4^+ CH_2), 1.48-1.42 (m, NBu_4^+ CH_2), 1.02 (t, NBu_4^+ CH_3) ppm.

* Crystals of **5** contain 4 THF per iron complex, but drying results in loss of part of the THF solvate molecules.

^{13}C NMR (151 MHz, $\text{THF}-d_8$, 25 °C) δ = 161.5 (CN-Ar C $\equiv$ N), 161.2 (CN-Ar' C $\equiv$ N), 159.8 (CN-Ar *ipso*-C-OCH₃), 159.7 (CN-Ar' *ipso*-C-OCH₃), 159.2 (Ph *ipso*-C), 151.2 (NCN), 137.8 (*p*-tolyl *ipso*-CCH₃), 135.5 (*p*-tolyl *ipso*-C), 129.8 (*p*-tolyl *m*-CH), 129.7 (Ph *m*-CH), 128.5 (CN-Ar *o*-CH), 128.3 (CN-Ar' *o*-CH), 127.6 (Ph *p*-CH), 124.5 (Ph *o*-CH), 124.4 (*p*-tolyl *o*-CH), 120.7 (CN-Ar' *ipso*-C), 119.9 (CN-Ar *ipso*-C), 115.5 (CN-Ar *m*-CH), 115.4 (CN-Ar' *m*-CH), 68.3 (THF), 59.7 (NBu_4^+ CH_2), 56.4 ((CN-Ar and CN-Ar' *p*-OCH₃), 26.1 (THF), 24.7 (NBu_4^+ CH_2), 21.5 (*p*-tolyl CH_3), 20.4 (NBu_4^+ CH_2), 14.00 (NBu_4^+ CH_3) ppm.

IR: ν_{max} = 2171 cm^{-1} (stretch C $\equiv$ N), 2152 cm^{-1} (stretch C $\equiv$ N).

Conflicts of interest

There are no conflicts to declare.

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