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Reactivity of Paramagnetic Fe\textsuperscript{II}–Bis(amidinate) Complexes

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Keywords: Iron / N ligands / Carbonylation / Lewis bases / Magnetic properties

Synthesis and characterisation of ether adducts of bis(amidinate) Fe\textsuperscript{II} complexes are described \{amidinate = 2,6-iPr\textsubscript{2}C\textsubscript{6}H\textsubscript{3}–NC(Ph)N–Ph\}. The isolation of these five-coordinate complexes contrasts with the homoleptic bis(amidinate) Fe complexes obtained previously with the sterically more demanding amidinate ligands 2,6-iPr\textsubscript{2}C\textsubscript{6}H\textsubscript{3}–NC(Ph)N–Ar (Ar = 2,6-iPr\textsubscript{2}C\textsubscript{6}H\textsubscript{3}, 2,6-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{3}) The more accessible ether adducts show enhanced reactivity towards Lewis bases and towards the π-acid carbon monoxide. Reaction with excess amounts of CO results in carbonyl insertion into the Fe–N bonds, thereby giving rise to a diamagnetic bis(CO) adduct supported by two carbamoyl ligands.

Introduction

Amidinates, [(RN)CR\textsubscript{11032}/H\textsubscript{11032}/H\textsubscript{11032}/H\textsubscript{11032}]–, have been used extensively as ligands for transition metals and lanthanides. With transition metals in particular, they show versatile binding modes (monodentate, bridging, chelating). The coordination mode is determined to a large extent by the nature of the C- and N-substituents. For chelating amidinate ligands, the size of the N-substituents can also influence the coordination geometry in complexes. This becomes especially apparent in homoleptic bis(amidinate)–metal complexes. In cases in which the electronic preference of the metal is not too strong, the steric demands of the ligands can actually outweigh the preference of the metal. The groups of Gambarotta and Winter have demonstrated this for Cr\textsuperscript{II} by using amidinates with simple alkyl or silyl substituents on the C and N atoms. For the bulkier N-substituents (CMe\textsubscript{3} or SiMe\textsubscript{3}), the geometry of these d\textsubscript{4} complexes deviates from the planar situation found with smaller substituents (R = Cy, iPr).

By using o-disubstituted aryls on the N-donor atoms, Boeré characterised a highly unusual planar Mg–bis(amidinate).\textsuperscript{[1,2]} This approach introduces steric protection above and below the NMN coordination plane. Our group has employed related amidinate ligands (Scheme 1) in the preparation of mono- and bis(amidinate) complexes of first-row transition metals and Fe\textsuperscript{II} in particular. Thus, using benzamidinate ligands [Dipp\textsubscript{2}L]– and [DippXyl\textsubscript{L}]–, homoleptic bis(amidinate complex)es were isolated with an unusual planar geometry (Scheme 2),\textsuperscript{[4]} whereas other structurally characterised homoleptic Fe\textsuperscript{II}–bis(amidinates) invariably exhibit tetrahedral geometries.\textsuperscript{[5–9]}

Although most studies on bis(amidinate) complexes have focussed on the relation between ligand steric bulk and coordination chemistry, interesting consequences may also be expected for the reactivity of such complexes. Particularly in mononuclear cases in which 2,6-disubstituted aryl groups are present on all four nitrogen atoms, the accessibility of the metal centre could be effectively limited. Thus, the cation [L\textsubscript{2}ZrMe\textsubscript{2}]\textsuperscript{+} has been reported not to interact with ethene for L = Dipp\textsubscript{2}L, whereas the analogous cation with L = DippXyl\textsubscript{L} induced slow olefin polymerisation.\textsuperscript{[10]} For first-row transition metals, such shielding effects are expected to be even more pronounced due to their smaller ionic radius.

In this contribution we investigate the reactivity of Fe\textsuperscript{II}–bis(amidinate) complexes toward σ-base as well as π-acid ligands as a function of gradual decrease in the steric demands of the amidinate ligand. To this end, the benzaamidinate [PhC(N-2,6-iPr\textsubscript{2}C\textsubscript{6}H\textsubscript{3})\textsubscript{2}(NPh)]− ([DippPh\textsubscript{L}]−, Scheme 1) is introduced. The reduced steric bulk of the latter is found to open up reactivity pathways unavailable to the more crowded analogues [Dipp\textsubscript{2}L]− and [DippXyl\textsubscript{L}]−.
Results and Discussion

Synthesis and Characterisation of Bis(amidinates) with [DippPhL]–

Amidine DippPhLH was synthesised by standard methodology[3] in 70% yield from N-(2,6-diisopropylphenyl)benzimidoyl chloride and aniline. The amidine crystallises as the Z-anti isomer as found by X-ray diffraction (see the Supporting Information). Also, in CDCl3, only one isomer is observed.

In situ deprotonation (nBuLi) and subsequent salt metathesis with FeCl2 in THF affords the new bis(amidinate) complex 1c·THF (Scheme 2) after removal of the reaction solvent in vacuo followed by extraction with hexanes. The isolation of a five-coordinate adduct contrasts with the previously reported base-free complexes 1a and 1b and seems a direct consequence of the reduction of ligand steric bulk.

To test whether a homoleptic complex (DippPhL)2Fe could be isolated, the complexation was also performed in the weaker donor solvent diethyl ether. Again, a five-coordinate adduct, [(DippPhL)2Fe(Et2O)] (1c·Et2O) was isolated. In this case, the poor solubility of the product in alkane solvents necessitated extraction with diethyl ether. Nevertheless, the ether ligand was not lost by drying in vacuo. Attempts to remove the ether molecule from 1c·Et2O by vacuum sublimation at 150 °C/200 mTorr led to decomposition of the complex and afforded the parent amidine and unidentified green/brown products. Preparation of base-free 1c by salt metathesis of Li[DippPhL] with FeCl2 in toluene was unsuccessful. Although initially a green colour reminiscent of that of (Dipp2L)2Fe was observed, no Fe complex was isolated.

The solid-state structures of 1c·THF[11] and 1c·Et2O (Figure 1 and Figure 2) display approximate (noncrystallographic) C2 symmetry with the C2 axis passing through the Fe–O vector. The complexes are best described as square pyramidal with the four nitrogen atoms forming the basal plane and the ether ligands as apexes (τ parameter[12] = 0.20 and 0.10 for 1c·THF and 1c·Et2O, respectively). In contrast, a trigonal bipyramidal geometry was reported for the tmdea adduct [(PhC(NSiMe3)(N-2,6-Me2C6H3))2Fe(tmeda)] (tmdea = Me2NCH2CH2NMMe2).[13] The iron centres in the adducts 1c are located somewhat above the N4 basal planes [0.107(1) Å for 1c·THF, 0.064(2) Å for 1c·Et2O] and the amidinate CN planes are slightly bent away from the ether ligands. The amidinates in the basal plane assume a mutual trans relation, thus avoiding steric interactions between 2,6-iPr2C6H3 groups from the two ligands. The Fe–O distance in 1c·Et2O is about 0.02 Å longer than that in 1c·THF, as expected for the weaker Lewis base. The Fe–N distances do not appear to be a direct function of the steric bulk on the nitrogen atoms, since for 1c·THF the NPh–Fe distance is larger than NDipp–Fe, whereas the situation is reversed for 1c·Et2O.

Magnetic susceptibility measurements show Curie–Weiss behaviour for 1c·THF and 1c·Et2O in the temperature range 50–300 K with θ = 2.1 K for 1c·THF and θ = 4.8 K for 1c·Et2O (Figure 3). The room-temperature magnetic moments of 5.3 and 5.0 μB, respectively, are consistent with high-spin (S = 2) FeII with four unpaired electrons. The effective magnetic moments are virtually temperature inde-
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Figure 2. Molecular structure of 1c·Et₂O (50% thermal ellipsoids). Selected bond lengths [Å] and angles [°]: Fe–O 2.0932(18), Fe–N1 2.164(2), Fe–N2 2.089(2), Fe–N3 2.157(2), Fe–N4 2.095(2), N1–C13 1.328(3), N2–C13 1.347(3), N3–C38 1.326(3), N4–C38 1.341(3); O–Fe–N1 108.26(7), O–Fe–N2 107.08(8), O–Fe–N3 102.76(7), O–Fe–N4 97.78(8), N1–Fe–N2 62.75(8), N1–Fe–N3 148.97(8), N1–Fe–N4 111.72(8), N2–Fe–N3 108.44(8), N2–Fe–N4 155.04(8), N3–Fe–N4 62.67(8).

Figure 3. μeff and χ⁻¹ (inset) versus T for 1c·THF (Δ) and 1c·Et₂O (○).

The paramagnetism of ether adducts 1c·THF and 1c·Et₂O is reflected in their ¹H NMR spectra in C₆D₆, which show broad, shifted resonances from around δ = +30 to −15 ppm (Figure 4). In spite of the paramagnetism of the iron complexes, their NMR spectra were found to be quite informative.

Assignment of the resonances was aided by comparison to the spectra of 1a and 1b. Complete assignment, however, is precluded by the fact that some sets of magnetically in-equivalent protons give rise to resonances with identical integrals and similar linewidths. The C₂ᵥ-symmetric spectra with only two iPr–Me and three m-H resonances suggest fast site exchange of ether ligands on the ¹H NMR spectroscopic timescale (Scheme 3).

Scheme 3.

Assignment of the resonances for coordinated THF (δ = 14.9 and 3.9 ppm) was confirmed by reaction with [D₈]THF (vide infra). Both adducts 1c are thermally stable for at least 24 h at 80 °C in C₆D₆.

Reactivity towards σ Bases

The reactivity of homoleptic 1a, 1b and ether adducts 1c towards σ donors was studied by ¹H NMR spectroscopy in C₆D₆. Addition of 1 equiv. [D₈]THF to 1a or 1b, however, does not affect their spectra. For the alkaline earth metals, the THF adducts [{HC(NAr)₂}₂M(THF)ₙ] (M = Ca, n = 1; M = Sr, Ba, n = 2; Ar = 2,6-iPr₂C₆H₃) have been structurally characterised. Although the shielding properties of the formamidinate resemble those of [Dipp₂L]⁻, the larger ionic radii of the divalent group II ions may enable accommodation of THF ligands.

Whereas 1a and 1b do not coordinate THF, reaction with the stronger Lewis base pyridine differentiates between the accessibility of the metal centres in 1a and 1b. The most hindered complex 1a requires more than 1 equiv. of pyridine to observe a colour change from green to yellow. Only minor changes are visible in the ¹H NMR spectrum, even when an excess amount of pyridine is used, thereby suggesting that coordination of pyridine is weak. For the slightly more open complex 1b, this colour change is observed with equivalent protons give rise to resonances with identical integrals and similar linewidths. The C₂ᵥ-symmetric spectra with only two iPr–Me and three m-H resonances suggest fast site exchange of ether ligands on the ¹H NMR spectroscopic timescale (Scheme 3).

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Whereas 1a and 1b do not coordinate THF, reaction with the stronger Lewis base pyridine differentiates between the accessibility of the metal centres in 1a and 1b. The most hindered complex 1a requires more than 1 equiv. of pyridine to observe a colour change from green to yellow. Only minor changes are visible in the ¹H NMR spectrum, even when an excess amount of pyridine is used, thereby suggesting that coordination of pyridine is weak. For the slightly more open complex 1b, this colour change is observed with
only 1 equiv. of pyridine. The $^1$H NMR spectrum of the product, tentatively formulated as $1b\cdot py$, shows significant shifts and broadening of several resonances with respect to those of $1b$ (see the Supporting Information). Addition of more pyridine leads to coalescence of some lines and sharpening of others, thereby suggesting that $1b\cdot py$ undergoes site exchange like the ether adducts $1c$, but complete assignment of the spectra proved impossible.

The more accessible iron centres in the adducts $1c$ react even more readily with Lewis bases under replacement of the ether ligand. Thus, addition of $[\text{D}_8]\text{THF}$ to $1c\cdot\text{Et}_2\text{O}$ leads to clean formation of $1c\cdot[D_8]\text{THF}$ with liberation of diethyl ether. This experiment also permitted unambiguous assignment of the THF resonances in $1c\cdot\text{THF}$. Reaction of either $1c\cdot\text{THF}$ or $1c\cdot\text{Et}_2\text{O}$ with 1 equiv. pyridine leads to a sole product $1c\cdot py$ and is accompanied by a colour change from yellow to orange. The $^1$H NMR spectrum (Figure 5A) shows four separate resonances for the $i\text{Pr–Me}$ protons, which indicates magnetic inequivalence of the diastereotopic methyl groups above and below the $N_4$ plane. In addition, one of the $m$-aryl signals is significantly broadened. The $C_{2v}$-symmetric spectrum shows that site exchange for pyridine is slower than for THF on the NMR spectroscopic timescale. The fact that the pyridine ligand does exchange becomes apparent when more pyridine is added. Spectra that result from the addition of 2 equiv. and an excess amount of $[\text{D}_3]\text{pyridine}$ are shown in parts B and C of Figure 5. Significant broadening of the $i\text{Pr–Me}$ resonances is observed upon addition of 2 equiv. of pyridine, whereas one of the Ar–H$_m$ signals is sharpened. The fast exchange regime is reached with an excess amount of pyridine as evidenced by the $C_{2v}$-symmetric spectrum with only two diastereotopic $i\text{Pr–Me}$ resonances (Figure 5, C). Removal of all volatiles in vacuo and subsequent redissolution in $C_6D_6$ restores the spectrum of $1c\cdot py$, thereby indicating that only one pyridine is retained in the solid state. Preparative scale experiments in toluene afforded $1c\cdot py$ as an orange powder. Although analytically pure material could not be obtained,
the $^1$H NMR spectrum of the powder is identical to that obtained from the reaction on the scale of an NMR spectroscopy tube with 1 equiv. of pyridine.

With the chelating Lewis base 2,2'-bipyridine (bpy), 1c·Et$_2$O reacts in toluene to give the corresponding adduct. Dark green crystals of 1c·bpy could be isolated in 64% yield. The molecular structure (Figure 6) shows a pseudo-octahedral coordination environment with the nitrogen atoms bearing the N-2,6-iPr$_2$C$_6$H$_3$ substituents in a trans arrangement. Unfortunately, no crystals of sufficient quality were obtained, but the X-ray structure serves to confirm the connectivities of the non-hydrogen atoms. The asymmetric unit consists of one molecule of 1c·bpy and highly disordered toluene molecules.

Six-coordinate 1c·bpy is paramagnetic and magnetic measurements (superconducting quantum interference device, SQuID) indicate a room-temperature magnetic moment of 4.9 $\mu_B$, consistent with 4 unpaired electrons (high-spin Fe$^{II}$). The paramagnetic $^1$H NMR spectrum shows resonances from $\delta = +60$ to $-20$ ppm and tentative assignments were made (Figure 7). Most amidinate protons are observed around the shifts for the related adducts 1c·L ($L = \text{THF}, \text{Et}_2\text{O}, \text{py}$). Two characteristic resonances attributed to the bpy ligand are found further downfield at $\delta = 56.4$ and 43.6 ppm.

Reactivity towards $\pi$ Acids

To probe the reactivity of the bis(amidinate) complexes 1 towards $\pi$-acid ligands, their reactivity towards carbon monoxide was studied. Exhaustive carbonylation often converts paramagnetic bis(amidinate)-Fe$^{II}$ complexes into the corresponding 18-electron bis-CO adducts.$^{[8,9,16,17]}$ On account of their diamagnetism, these are amenable to NMR spectroscopic structure analysis. The sterically encumbered complexes 1a or 1b, however, fail to react with an excess amount of carbon monoxide (1 atm.) in C$_6$D$_6$, possibly due to the inaccessibility of the iron centres. Incomplete carbonylation due to inaccessibility of the Fe centre has been reported previously for Kawaguchi’s bis(amidinate)-diiron complex.$^{[9]}$ In this dimer, only one of the two iron centres was found to react with CO as a result of a more sterically hindered conformation induced by carbonylation of the first Fe centre.

The influence of steric bulk in 1a and 1b becomes apparent when the ether adducts of 1c are treated with CO under the same conditions. The more accessible Fe centres in 1c·THF and 1c·Et$_2$O react rapidly, as indicated by a colour change from greenish yellow to red. After three days the colour changes to yellow again and the diamagnetic compound 2 is formed quantitatively (Scheme 4).

On a preparative scale, the final product 2 can be isolated in 33% yield as a yellow powder. It was characterised by standard spectroscopic methods and combustion analysis. An X-ray structure confirmed the formulation of 2 as a bis(carbamoyl) complex that results from the uptake of 4 equiv. of CO. In addition to the two terminal carbonyl ligands, two more CO molecules are inserted into the amidinate Fe–N bonds. Carbonyl insertion is relatively common for Fe and Co amidinates with bulky substituents.$^{[16,18,19]}$ The regiochemistry seems to be determined by steric factors as insertion usually occurs next to the nitrogen that carries the most sterically demanding substituent.$^{[17]}$ Attempts to characterise the red intermediate {presumably the bis-CO adduct [(DippPh$_2$L)$_2$Fe(CO)$_2$]} were unsuccessful. Treatment of 1c·Et$_2$O with 2 equiv. CO in C$_6$D$_6$ generated a red solution, but $^1$H NMR spectroscopic analysis showed no other species than unreacted 1c·Et$_2$O and 2.

The solid-state structure of 2 (Figure 8) shows a pseudo-octahedrally coordinated iron centre ligated by two κ$^2$-N,C-carbamoyl ligands and two terminal CO ligands in a cis configuration. The structure has approximate (noncrystallographic) C$_2$ symmetry with the C$_2$ axis bisecting the angle between the two terminal carbonyls. In contrast to
the parent ether adducts, in which identical C–N distances were observed in the amidinate ligands (ca. 1.33 Å), these distances differ significantly in the carbamoyl moieties in 2 (ca. 1.36 and 1.30 Å). However, the (near) planarity of all carbon and nitrogen atoms in the carbamoyl rings (sum of angles around C = 360°, sum of angles around N = 357.6–359.6°) indicates significant conjugation. The bite angle of the carbamoyl chelate is approximately 82°, comparable to the FeII–carbamoyl chloride complex \([\text{[FeCl(CO)}_2\text{C}(\text{Ph})\text{N(Ar)}\text{C(O)}]}\text{2}]\) (ca. 85°).[17] The Fe–N bond lengths [Å] and angles [°]: Fe–N2 1.961(3), Fe–N4 1.960(3), Fe–C51 1.953(3), Fe–C52 1.958(3), Fe–C53 1.810(4), Fe–C54 1.809(4), O1–C51 2.190(4), O2–C52 2.111(4), O3–C53 1.142(5), O4–C54 1.144(5); N2–Fe–N4 169.03(10), N2–Fe–C51 81.53(13), N2–Fe–C53 91.20(15), C53–Fe–C54 81.58(13), N4–Fe–C53 94.74(14), N4–Fe–C54 94.29(13), C51–Fe–C52 82.83(14), C51–Fe–C53 90.24(13), C51–Fe–C54 173.31(15), C52–Fe–C53 175.09(15), C52–Fe–C54 91.20(15), C53–Fe–C54 92.31(17).

**Conclusion**

The use of o-disubstituted aryls 2,6-R\_2C\_6H\_3 as nitrogen substituents in bis(benzamidinate)–FeII complexes can render the metal centre virtually inaccessible to Lewis bases. Stepwise reduction of the size of R, however, gradually exposes the FeII nucleus and restores much of the reactivity common to more open FeII–amidinate complexes. Thus, five- and six-coordinate Lewis base adducts can be obtained as well as a bis(carbamoyl) complex that results from carbonyl insertion. The accommodation of a fifth ligand, however, is also a function of the strength of the added Lewis base.

**Experimental Section**

**General:** All manipulations, except for amidine synthesis, were carried out under a dry nitrogen atmosphere using standard glovebox, Schlenk and vacuum-line techniques. Pentane, hexanes and toluene were passed over columns of Al2O3 (Fluka), BASF-R-3-11-supported Cu oxygen scavenger and molecular sieves (Alirdich, 4 Å). THF and Et3O (Alrich, anhydrous, 99.8%) were dried by percolation with Al2O3 (Fluka). [D6]THF and CD2Cl2 were distilled from Na/K. [D6]Pyridine (Acros) was used as received.

**Starting Materials:** Pyridine (Merck) was distilled from calcium hydroxide. 2,2'-Bipyridine (Merck, 99.5%), aniline, triethylamine, nBuLi (2.5 m in hexanes (Acros) and CO (Praxair, 99.997%) were used as received. FeCl2,[20] [Dipp2FeL]FeCl(CO)2 (1a)[16,17] and [DippN\_2L]Fe (1b)[16,17] were prepared according to literature procedures.

**Instrumentation:** 1H and 13C{1H} NMR spectra were recorded at ambient temperature with a Varian VXR 300 spectrometer operating at 299.968 MHz (H) and a Mercury Plus 400 operating at 100.573 MHz (13C{1H}) and 399.931 MHz (1H). NMR spectra were referenced internally using the residual solvent resonances (CHCl3, δ = 7.26 ppm; CD3OH, δ = 7.15 ppm) relative to Si(CH3)4 (δ = 0 ppm). Proton NMR spectroscopic data for paramagnetic compounds are listed as δ [ppm] (Av, [Hz], integral, tentative assignment). IR spectra were recorded with a 4020 Mattson Instruments FTIR spectrophotometer using nujol mulls between KBr discs. Elemental analyses were performed at the Microanalytical Department of the University of Groningen or by H. Kolbe, Mikroanalytisches Laboratorium, Mülheim an der Ruhr. Reported values are the average of two independent determinations. MS spectra were obtained with a Jeol JMS-600 spectrometer in electron ionisation (EI) mode.

**N-Phenyln-1,3-C(1H)-benzamidinyl chloride (DippLH):** A solution of aniline (2.46 mL, 27 mmol), triethylamine (3.0 mL) and benzamidoxychloride (3.2 g, 27 mmol) in toluene (100 mL) was heated at reflux for 24 h. The mixture was washed with water (3×) and with a saturated solution of NaCl. Toluene was removed in vacuo. The solid was dissolved in ethanol and dried in vacuo to remove residual toluene. After recrystallisation from ethanol/water, white crystals were obtained (6.70 g, 91–10096, 70 %). 1H NMR (200 MHz, CDCl3, 298 K): δ = 7.63–6.27 (m, 13 H, Ar–H), 3.16–3.23 (sept., J = 6.6 Hz, 12 H, Ar–CH), 2.39–2.52 ppm (2×Ar–CH3) ppm. 13C{1H} NMR (75 MHz, CDCl3, 298 K): δ = 153.75, 140.11, 139.06, 135.03, 129.73, 128.86, 128.71, 128.26, 123.57, 122.48, 28.16 (2×Ar–CH3) ppm. IR (KBr): ν = 3359 (s, N–H), 3026 (m), 3055 (m), 3044 (m), 2921 (s), 2910 (s), 1669 (w), 1637 (s), 1597 (s), 1587 (s), 1579 (s), 1496 (s), 1488 (s), 1436 (m), 1414 (m), 1359 (m), 1343 (s), 1329 (s), 1303 (m), 1289 (m), 1261 (w), 1253 (m), 1244 (m), 1234 (m), 1194 (m), 1178 (w), 1109 (w), 1093 (m), 1075 (m), 1059 (w), 1043 (w), 1028 (w), 959 (w), 936 (w), 902 (m), 834 (w), 809 (w), 803 (w), 788 (w), 768 (s), 758 (s), 737 (s), 702 (s), 692 (s), 558 (w), 509 (w), 490 (m) cm–1. HRMS (EI): calcd: for C25H28N2: 356.2252; found 356.2240.

**N-Phenyln-1,3-C(1H)-benzamidinyl chloride (DippN\_2L):** A solution of aniline (2.46 mL, 27 mmol), triethylamine (3.0 mL) and benzamidoxychloride (3.2 g, 27 mmol) in toluene (100 mL) was heated at reflux for 24 h. The mixture was washed with water (3×) and with a saturated solution of NaCl. Toluene was removed in vacuo. The solid was dissolved in ethanol and dried in vacuo to remove residual toluene. After recrystallisation from ethanol/water, white crystals were obtained (6.70 g, 91–10096, 70 %). 1H NMR (200 MHz, CDCl3, 298 K): δ = 7.63–6.27 (m, 13 H, Ar–H), 3.16–3.23 (sept., J = 6.6 Hz, 12 H, Ar–CH), 2.39–2.52 ppm (2×Ar–CH3) ppm. 13C{1H} NMR (75 MHz, CDCl3, 298 K): δ = 153.75, 140.11, 139.06, 135.03, 129.73, 128.86, 128.71, 128.26, 123.57, 122.48, 28.16 (2×Ar–CH3) ppm. IR (KBr): ν = 3359 (s, N–H), 3026 (m), 3055 (m), 3044 (m), 2921 (s), 2910 (s), 1669 (w), 1637 (s), 1597 (s), 1587 (s), 1579 (s), 1496 (s), 1488 (s), 1436 (m), 1414 (m), 1359 (m), 1343 (s), 1329 (s), 1303 (m), 1289 (m), 1261 (w), 1253 (m), 1244 (m), 1234 (m), 1194 (m), 1178 (w), 1109 (w), 1093 (m), 1075 (m), 1059 (w), 1043 (w), 1028 (w), 959 (w), 936 (w), 902 (m), 834 (w), 809 (w), 803 (w), 788 (w), 768 (s), 758 (s), 737 (s), 702 (s), 692 (s), 558 (w), 509 (w), 490 (m) cm–1. HRMS (EI): calcd: for C25H28N2: 356.2252; found 356.2240.
Preparation of Li[DippPhL]: N-Phenyl-N’-(2,6-diisopropylphenyl)benzamidin (1.10 g, 2.74 mmol) was treated with n-butyllithium (1.1 mL, 2.5 m in hexanes, 2.8 mmol) in diethyl ether. After stirring for 0.5 h at room temperature, the solvent was removed in vacuo. The product was suspended in pentane and subsequently dried in vacuo to remove residual pentane; yield 0.96 g (2.64 mmol, 96%).

1H NMR (300 MHz, [D6]THF/C6D6, 298 K): δ = 7.23–6.55 (m, 13 H, Ar-H), 3.55 (septet, J = 7.0 Hz, 2 H, i-Pr-CH3), 1.17 (d, J = 7.0 Hz, 6 H, i-Pr-CH3), 1.03 (d, J = 7.0 Hz, 6 H, i-Pr-CH3) ppm. 13C{1H} NMR (75 MHz, [D6]THF/C6D6, 298 K): δ = 178.10 (NCN), 160.85, 155.13, 140.97, 137.27, 131.02, 128.36, 127.46, 127.31, 126.73, 121.58, 116.94, 28.39 (i-Pr-CH3), 25.30, 23.03 (2×i-Pr-CH3) ppm.

Preparation of [Dipp2L]2Fe(THF) (1c·THF): nBuLi (2.1 mL, 2.5 m in hexane, 5.2 mmol) was added dropwise over 30 min at room temperature to a solution of N-phenyl-N’-(2,6-diisopropylphenyl)benzamidin (1.86 g, 5.2 mmol) in 30% THF/pentane. The solvents were removed in vacuo and the product was dissolved in pentane (30 mL). The obtained brown solution was decanted from the yellow/green precipitate. The mixture was stirred for 2 h. The solvents were removed and the residue was dissolved in THF. The mixture was stirred for 16 h. The solid was extracted with hexane (25 mL). The solvent was removed in vacuo and the remainder was dissolved in pentane and subsequently dried in vacuo.

Preparation of [Dipp2L]2Fe(THF) (1c·THF): 25 mL of a 4% solution in THF was treated with excess amount of pyridine. The solution changed to yellow immediately. 1H NMR spectrum of [Dipp2L]2Fe(11 mg, 0.01 mmol) in C6D6 (ca. 0.4 mL) was reacted with pyridine (1 equiv., 1 mg, 0.01 mmol). No colour change was observed. The colour of the solution changed to yellow upon addition of a second equivalent. The colour remained yellow after subsequent addition of a few drops (excess amount) of pyridine. 1H NMR (300 MHz, C6D6, 1 equiv. pyridine, 298 K): δ = 56.4 (887), 31.6 (45, 4 H), 22.1 (44, 4 H), 16.8 (22, 4 H), 14.6 (141, 2 H), 8.3 (30, 4 H), 7.6 (9, 6.9 ppm), 6.9 (6, 6.5 ppm), 6.4 (100, 1 H), 3.8 (107, 1 H), 2.0 (23, 2 H), –5.1 (58, 2 H), –6.2 (29, 2 H), –9.0 (249, 12 H) ppm. 1H NMR (300 MHz, C6D6, 2 equiv. pyridine, 298 K): δ = 55.8 (857), 31.6 (45, 4 H), 22.1 (44, 4 H), 16.8 (25, 4 H), 14.5 (150, 12 H), 12.3 (383, 4 H), 7.7, 7.3, 6.9 (pyridine), 6.5 (6, 107, 1 H), 3.8 (107, 1 H), –1.9 (26, 2 H), –5.0 (64, 2 H), –6.3 (31, 4 H), –28.9 (261, 12 H) ppm. 1H NMR (300 MHz, C6D6, excess amount of pyridine, 298 K): δ = 36.1 (679), 27.8 (62, 4 H), 22.2 (50, 4 H), 17.9 (22, 4 H), 11.2 (130), 9.6–6.6 (br., pyridine and C6D5 H), 3.6 (97, 12 H), 2.0 (23, 2 H), –1.7 (75, 12 H), –7.2 (27, 4 H), –14.7 (928), –24.6 (225, 12 H) ppm.

Reactions of [Dipp2L]2Fe (1a) with Pyridine: A solution of [Dipp2L]2Fe (12 mg, 0.01 mmol) in C6D6 (ca. 0.4 mL) was treated successively with 1 equiv. (1 mg, 0.01 mmol), 2 equiv. and an excess amount of pyridine. The colour of the solution changed to yellow immediately after the first equivalent of pyridine was added. 1H NMR (300 MHz, C6D6, 1 equiv. pyridine, 298 K): δ (νa, Hz) = 63.0 (br), 29.3 (1827), 26.2 (972), 19.8 (27), 17.6 (168), 12.5 (395), 4.2 (40), 1.1 (60), –9.5 (30), –14.0 (90), –16.8 (179) ppm. 1H NMR (300 MHz, C6D6, 2 equiv. pyridine, 298 K): δ (νa, Hz) = 25.9 (1128), 20.6 (23), 19.8 (73), 10.5 (256), 5.3 (21), 1.3 (70), –9.5 (30), –15.1 (36), –18.6 (66) ppm. 1H NMR (300 MHz, C6D6, excess amount of pyridine, 298 K): δ (νa, Hz) = 25.9 (998), 20.4 (28), 20.2 (169), 12.1–4.4 (br., overlapping with pyridine and C6D5 H), 5.4 (44), 1.3 (95), –9.6 (37), –15.3 (39), –18.9 (76) ppm.

Reactions of [Dipp2L]2Fe (1c·Et2O) with Pyridine: A solution of [Dipp2L]2Fe (12 mg, 0.01 mmol) in C6D6 (ca. 0.4 mL) was treated with pyridine (4 mg, 0.04 mmol). A solution of [Dipp2L]2Fe (18 mg, 0.02 mmol) in C6D6 (ca. 0.4 mL) was treated with pyridine (1 mg, 0.01 mmol), 2 equiv. and an excess amount of pyridine. The colour of the solution changed to yellow immediately after the first equivalent of pyridine was added. 1H NMR (300 MHz, C6D6, 1 equiv. pyridine, 298 K): δ (νa, Hz) = 63.0 (br), 29.3 (1827), 26.2 (972), 19.8 (27), 17.6 (168), 12.5 (395), 4.2 (40), 1.1 (60), –9.5 (30), –14.0 (90), –16.8 (179) ppm. 1H NMR (300 MHz, C6D6, 2 equiv. pyridine, 298 K): δ (νa, Hz) = 25.9 (1128), 20.6 (23), 19.8 (73), 10.5 (256), 5.3 (21), 1.3 (70), –9.5 (30), –15.1 (36), –18.6 (66) ppm. 1H NMR (300 MHz, C6D6, excess amount of pyridine, 298 K): δ (νa, Hz) = 25.9 (998), 20.4 (28), 20.2 (169), 12.1–4.4 (br., overlapping with pyridine and C6D5 H), 5.4 (44), 1.3 (95), –9.6 (37), –15.3 (39), –18.9 (76) ppm.
A few drops of [D₃]pyridine were added to a solution of [DippPhL]₂Fe(THF) (14 mg, 0.01) in C₅D₅ (ca. 0.4 mL). The colour of the solution immediately changed to yellow. ¹H NMR (300 MHz, C₆D₆/C₅D₅N, 298 K): δ = 23.9 (20, 4 H, Ar-H₃). Add 2,4 H, Ar-H₄), 40.2 (3, 4 H, Ar-H₄), 7.8 (4, 4 H, Ar-H₄), 5.4 (36, 4 H, Ar-H₄), 4.4 (3, 4 H, Ar-H₄), 4.2 (24, 4 H, Ar-H₄), 3.8 (4, 4 H, Ar-H₄), 3.6 (s, THF), 1.4 (s, THF), 1.3 (32, 2 H, Ar-H₄), 0.6 (390, 12 H, Pyr-CH₃), 5.8 (21, 2 H, Ar-H₄), –10.2 (384, 12 H, Pyr-CH₃), –15.7 (21, 2 H, Ar-H₄) ppm.

Pyridine (8 µL, 0.12 mmol) was added to a solution of [DippPhL]₂Fe(THF) (24.6 mg, 0.029 mmol) in C₅D₅ (ca. 0.4 mL). The colour of the solution changed from brown to light/overlap yellow. ¹H NMR (300 MHz, C₅D₅, 298 K): δ = 23.9 (34, 4 H, Ar-H₃), 17.0 (37, 4 H, Ar-H₄), 14.0 (40, 4 H, Ar-H₄), 11.6–7.7 (br., C₅D₅H and pyridine obscuring paramagnetic signals), 6.3, 3.6 (THF), 1.4 (THF), 5.8 (32, 2 H, Ar-H₄), –10.2 (384, 12 H, Pyr-CH₃), –15.7 (30, 2 H, Ar-H₄) ppm. Removal of the volatiles and redissolution in C₅D₅ resulted in a ¹H NMR spectrum identical to that obtained from reaction of 1c·THF with 1 equiv. of pyridine.

Preparation of [DippPhL]₂Fe(pyridine) (1c·py): Pyridine (0.1 mL, 1.23 mmol) was added to a brown solution of 1c·Et₂O (0.36 g, 0.43 mmol) in toluene (15 mL). The colour changed to orange/light brown. The reaction mixture was stored at -80 °C for one day and the product could be isolated as an orange powder (0.2 g, 60%). The ¹H NMR spectrum in C₅D₅ is identical to that obtained from the reaction of 1c·THF with 1 equiv. pyridine as described above.

<table>
<thead>
<tr>
<th>Table 1. Crystal collection and refinement data.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
</tr>
<tr>
<td><strong>Mₙ</strong></td>
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<tr>
<td><strong>Dimensions [mm]</strong></td>
</tr>
<tr>
<td><strong>Colour, Habit</strong></td>
</tr>
<tr>
<td><strong>Crystal System</strong></td>
</tr>
<tr>
<td><strong>Space Group</strong></td>
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<tr>
<td><strong>a [Å]</strong></td>
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<tr>
<td><strong>b [Å]</strong></td>
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<td><strong>c [Å]</strong></td>
</tr>
<tr>
<td><strong>β [°]</strong></td>
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<tr>
<td><strong>Z</strong></td>
</tr>
<tr>
<td><strong>V [Å³]</strong></td>
</tr>
<tr>
<td><strong>ρ/calcd. [g/cm³]</strong></td>
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<tr>
<td><strong>θ range [°]</strong></td>
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<tr>
<td><strong>Lσ/Lo-Ka</strong></td>
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<tr>
<td><strong>T [K]</strong></td>
</tr>
<tr>
<td><strong>Collection time [h]</strong></td>
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<tr>
<td><strong>Measured reflections</strong></td>
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<tr>
<td><strong>Unique reflections</strong></td>
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<tr>
<td><strong>M [cm⁻³]</strong></td>
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<tr>
<td><strong>Parameters</strong></td>
</tr>
<tr>
<td><strong>Weighting scheme a, [h]</strong></td>
</tr>
<tr>
<td><strong>R(F) for Fₑ ≥ 3σ(Fₑ) [h]</strong></td>
</tr>
<tr>
<td><strong>wR(F) [h]</strong></td>
</tr>
<tr>
<td><strong>Residual el. density [e Å⁻³]</strong></td>
</tr>
<tr>
<td><strong>GoFcalcd [h]</strong></td>
</tr>
</tbody>
</table>

[a] w = \frac{1}{\sigma(FH)} + (\sigma P)^2 + bP P = \text{max}(F₀,F₀ + 2F₀/3). [b] R(F) = \frac{\sum|F₀| - |F₁|}{\sum|F₀|}. [c] wR(F) = \frac{\sum w(F₀ - F₁)^2/\sum w(F₀)^2}{\sum w(F₀)^2}. [d] GoFcalcd = \frac{\sum w(F₀ - F₁)^2/\sum w(F₀)^2/n = \text{number of reflections}, p = \text{number of parameters refined}.}
solution. The brown solution was decanted and the remaining yellow powder was dried in vacuo; yield 107 mg (0.12 mmol, 33%). The yield was not optimised. 1H NMR (300 MHz, C6D6, 298 K): δ = 7.97 (d, J = 7.7 Hz, 2 H, Ar-CH), 7.07–6.45 (m, 24 H, Ar-CH), 3.64 (septet, J = 6.7 Hz, 2 H, ipr-CH), 3.40 (septet, J = 6.7 Hz, 2 H, ipr-CH), 1.63 (d, J = 6.6 Hz, 6 H, ipr-CH3), 1.45 (d, J = 7.0 Hz, 6 H, ipr-CH3), 1.27 (d, J = 7.0 Hz, 6 H, ipr-CH3). 11 (d, J = 6.6 Hz, 6 H, ipr-CH3) ppm. 13C(1H) NMR (75 MHz, C6D6, 298 K): δ = 219.9 (C=O), 209.5 (C=O), 167.0 (NCN), 152.8, 148.7, 146.9, 135.0, 130.8 (5 x ipr-CH), 129.3, 129.1, 129.0, 128.4, 127.3, 126.0, 125.6, 124.4, 124.2, 123.4 (10 x CAr), 3 resonances obscured by C6D6). 29.8, 28.9 (2 x ipr-CH), 27.2, 26.8, 23.4, 22.8 (4 x ipr-CH) ppm. IR (KBr): ν = 3601 (w), 3023 (w), 2020 (s, C=O), 1961 (s, C=O), 1937 (w), 1659 (s, C=O), 1592 (m), 1584 (m), 1494 (w), 1321 (w), 1277 (w), 1186 (w), 1173 (w), 1102 (w), 1073 (w), 1040 (w), 1027 (w), 1003 (w), 989 (m), 930 (w), 898 (w), 796 (m), 761 (w), 743 (w), 693 (m), 652 (w), 598 (w), 579 (w), 544 (w), 533 (w), 470 (w), 449 (w) cm⁻¹. C6H8N4O4Fe (878.89): calcd. C 73.80, H 6.19, N 6.37; found C 73.71, H 6.13, N 6.44.

**X-ray Diffraction:** Crystals suitable for X-ray analysis were obtained at room temperature by layering a concentrated THF solution with hexanes (1c·THF), by layering a concentrated Et2O solution with pentane (1c·Et2O) or by recrystallisation from toluene (2). Crystals were picked from the mother liquor and covered with inert oil to avoid deterioration due to loss of solvent from the crystal lattice. For 2, the scattering power of the crystals was very weak: around 1/1000 of the crystals was very weak: around 1/1000 of the observed susceptibility to the following Equation (3). [26]

\[
\chi = \frac{N g^2 e^2}{3 k T} \left( \frac{2 \pi^2 h^2}{3} \right)^{1/2} \left( X - 1 \right) \left( T - T_0 \right)
\]

(1)

Effective magnetic moments were calculated as Equation (2).

\[
\mu_{eff} = 2.828 \sqrt{JMT}, \quad g = 2.00
\]

(2)

Zero-field splitting parameters were obtained by least-squares fitting of the observed susceptibility to the following Equation (3).[26]

\[
\chi = \frac{N g^2 e^2}{3 k T} \left( \frac{2 \pi^2 h^2}{3} \right)^{1/2} \left( X - 1 \right) \left( T - T_0 \right)
\]

(3)

**Supporting Information** (see also the footnote on the first page of this article): X-ray structure of amidine DippPh2NH, 1H NMR spectra for reactions of 1b with pyridine and magnetic susceptibility data for 1c·bpy.

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[11] The adduct 1c·THF crystallises with two independent molecules in the asymmetric unit. In view of their geometric similarity, only one of these is discussed here.


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