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N-tert-Alkyl-Substituted N-Heterocyclic Carbenes with a 1,1′-Ferrocenediyl Backbone

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1,1′-Diaminoferrocene (**1**) was converted to α-aminonitriles fc[NHC(CN)MeR′]$_2$ (fc = 1,1′-ferrocenediyl; **2a**: R′ = Me, **2b**: R′ = Ph, **2c**: R′ = *t*Bu) by reaction with ketones MeC(O)R′ in the presence of NaCN/HOAc or to the diimine fc(N=CPh$_2$)$_2$ (**3**) by condensation with Ph$_2$CO. Treatment of **2a–c** or **3** with MeLi furnished fc(NHR)$_2$ (**4a**: R = *t*Bu, **4b**: R = CMe$_2$Ph, **4c**: R = CMe$_2$*t*Bu, **4d**: R = CMePh$_2$) after aqueous work-up. The formylative cyclisation of **4a–d** to fc[(NR)$_2$CH][BF$_4$] (**5**H[BF$_4$]) was possible only for R = CMe$_3$ (**a**) and CMe$_2$Ph (**b**). The reaction of these formamidinium compounds with NaN(SiMe$_3$)$_2$ afforded the N-heterocyclic carbenes fc{[N(CMe$_3$)]$_2$C:} (**5a**) and fc{[N(CMe$_2$Ph)]$_2$C:} (**5b**). **5a** was converted to the thiourea derivative **5a**S with elemental sulfur. **5a** and **5b** slowly decompose in solution by alkene elimination, affording the respective formamidine fc(NRCH=N) (**6a**: R = CMe$_3$, **6b**: R = CMe$_2$Ph). **6a** was transformed to fc{[N(CMe$_3$)][N(CPh$_3$)]CH}[BF$_4$] (**5e**H[BF$_4$]) with Ph$_3$C[BF$_4$].

Introduction

The most popular N-heterocyclic carbenes (NHCs) are derived from five-membered heterocycles such as, for example, imidazole, imidazoline, and 1,2,4-triazole.[1] Expanded-ring N-heterocyclic carbenes (erNHCs),[2] which are based on heterocycles with ring sizes larger than five, are attracting increased attention.[3,4] The N–C–N angles of erNHCs are significantly larger than those of their five-membered ring counterparts (100–106°)[5] and similar to those observed for acyclic diaminocarbenes (ca. 121°).[6] This has important steric and electronic consequences. The *N*-substituents are pushed in the direction of the $C_{carbene}$ atom, causing an enhanced steric protection of coordinated metal centres, which is relevant for catalytic applications.[4a,c,e,f,7] The fact that erNHCs are bulkier than traditional NHCs is reflected by their comparatively higher %V_{bur} values.[4b,8] In terms of electronics, erNHCs are both more nucleophilic and more electrophilic than traditional NHCs. A widening of the carbene bond angle increases the p-character, and hence energy, of the carbene HOMO, causing an increase in σ-donicity and nucleophilicity. In turn, the increase in HOMO energy causes a decrease of the HOMO-LUMO gap, which correlates with the singlet-triplet energy separation (ΔE_{ST}),[9] and a low ΔE_{ST} value indicates a high electrophilicity of a singlet carbene.[10,11] Their comparatively pronounced ambiphilicity enables erNHCs to show reactivities unknown for traditional NHCs. For example, six-membered ring congeners have been reported to undergo C–H insertion with the methyl group of toluene.[12] The distinct differences in electronic properties of erNHCs vs. traditional NHCs are also relevant for catalytic applications, and electronic and steric cooperation associated with changes in ring size has been described in this context.[13]

N-heterocyclic carbenes with a 1,1′-ferrocenediyl (fc) backbone (fcNHCs, Figure 1) constitute a subclass of erNHCs, which, from a formal point of view, contain a six-membered ring and exhibit particularly fascinating properties.[14] Firstly, their ferrocene-based backbone can be utilized for redox-switching their electronic profile[15] and makes them suitable for redox-tunable catalysis.[16] Secondly, their ambiphilicity is sufficiently high to allow the activation of fundamentally important small molecules such as, for example, CO and NH$_3$.[17] Thermally stable congeners known to date contain bulky primary or secondary alkyl substituents at the N atoms, viz. 2-adamantyl and neopentyl.[17a,18,19] These fcNHCs were obtained by deprotonation of corresponding formamidinium salts (fcNHC–H[BF$_4$]), which were synthesized from the respective diaminoferrocene derivatives of the type fc(NHR)$_2$ and triethyl orthoformate in the presence of NH$_4$[BF$_4$].[20] We surmised that, owing to their bulkiness, tertiary alkyl groups will be even more beneficial for

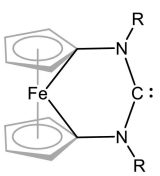

Figure 1. Structure of fcNHCs (drawn in a way that highlights the six-membered ring structure).

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the thermal stability of such fcNHCs. Different scales have been developed for the quantification of steric effects, which may lead to somewhat conflicting sequences concerning the steric size of substituents.[21] For example, while the steric impact of *tert*-butyl is higher than that of neopentyl on Beckhaus' S_f scale (3.82 vs. 2.29),[22] the situation is inverse on Charton's υ scale (1.24 vs. 1.34)[23] and Dubois' modified version of Taft's E_s scale (1.43 vs. 1.63).[24] The simplest tertiary alkyl group is *tert*-butyl (*t*Bu, CMe_3). Other tertiary alkyl groups targeted in our work in addition to CMe_3 are, in the order of increasing steric bulk,[25] CMe_2Ph, $CMePh_2$ and CMe_2*t*Bu. In view of the established synthetic access to fcNHCs described above, the synthesis of the corresponding diaminoferrocene derivatives $fc(NHR)_2$ (R = *t*Bu, CMe_2Ph, $CMePh_2$ and CMe_2*t*Bu) was desirable. The only ferrocene derivatives known to date containing an N-*tert*-alkyl moiety are the hydroxylamines FcN(OH)*t*Bu (Fc = ferrocenyl) and $fc[N(OH)tBu]_2$, which were synthesized by reacting *t*BuNO with FcLi and $fcLi_2$, respectively, followed by aqueous work-up.[26] Note that in the chemistry of aromatic organic compounds the synthesis of *N*-*tert*-alkylated anilines has traditionally been difficult to accomplish, frequently involving harsh reaction conditions and/or low yields.[27] It has only been recently that the Hartwig-Buchwald amination of aromatic halides with, for example, $tBuNH_2$ was established as an efficient method applicable under mild conditions in this context.[28] In ferrocene chemistry, Hartwig-Buchwald reactions have been described utilising aminoferrocene or 1,1′-diaminoferrocene together with aryl halides.[29] However, we are not aware of reports describing the C–N cross-coupling of a halogenated ferrocene derivative with an organic amine. Consequently, this approach to 1,1′-di(*tert*-alkylamino)ferrocenes does not appear to be promising. Other modern methods for the efficient synthesis of *N*-*tert*-alkylated anilines involve oxidative conditions (Bi^V, Cu^{II}, O_2),[30] which are generally not compatible with electron-rich ferrocene derivatives and thus do not seem to be particularly promising either. We therefore chose a distinctly different approach, which is based on a report by Hunter et al., who described the synthesis of *N*-*tert*-butylaniline by reacting methyllithium with *N*-phenylacetone imine and subsequent aqueous work-up.[31] This was later adopted by Cummins and co-workers for the synthesis of sterically more encumbered homologues based on 3,5-dimethylaniline and 2-fluoro-5-methylaniline.[32] A variation of the method relevant to our present work was published by Romero and co-workers, who reacted methyllithium not with aryl imines $ArN{=}CMe_2$, but with aryl α-aminonitriles $ArNHCMe_2CN$, which can be viewed as addition products of $ArN{=}CMe_2$ with HCN and are readily obtained from $ArNH_2$, acetone and Me_3SiCN in the presence of $ZnCl_2$.[33]

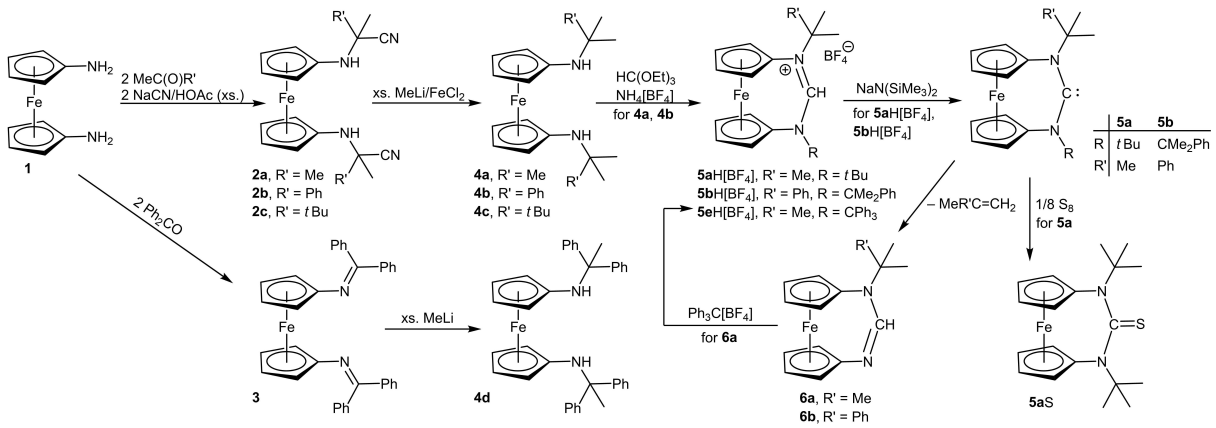
Results and Discussion

Synthesis

The synthesis of the diaminoferrocene derivatives $fc(NHR)_2$ of this study is outlined in Scheme 1.

The sequence starts from 1,1′-diaminoferrocene (**1**), which was converted to an α-aminonitrile $fc[NHC(CN)MeR']_2$ (**2a–c**; R′ = Me, Ph and *t*Bu, respectively) by reaction with a ketone MeC(O)R′ in the presence of NaCN/HOAc or to the diimine $fc(N{=}CPh_2)_2$ (**3**) by condensation with benzophenone. **2b** and **2c** each exhibit two chiral centres and were obtained as approximately equimolar mixtures of the *rac*- and *meso*-diastereomers according to ^1H and $^{13}C\{^1H\}$ NMR spectroscopy (two sets of signals, ratio ca. 1:1). Subsequent treatment of the α-aminonitriles **2a–c** with an excess of MeLi (10 equiv. per α-aminonitrile unit) in the presence of $FeCl_2$ (used to "mop up" cyanide by complexation) furnished the diaminoferrocene derivatives $fc(NHR)_2$ (**4a–c**; R = *t*Bu, CMe_2Ph, and CMe_2*t*Bu, respectively) in high yields of up to 92% after standard aqueous work-up. The synthesis of $fc(NHCMePh_2)_2$ (**4d**) was achieved by reacting the diimine **3** with an excess of MeLi (10 equiv. per imine unit), followed by aqueous work-up, which afforded the product in 87% yield.

With the diaminoferrocene derivatives **4a–d** in hand, their formylative cyclisation to the corresponding formamidinium tetrafluoroborates **5a**H[BF_4]–**5d**H[BF_4] was attempted with triethyl orthoformate and ammonium tetrafluoroborate



Scheme 1. Synthesis and follow-up chemistry of the diaminoferrocene derivatives $fc(NHR)_2$ (**4a**: R = *t*Bu, **4b**: CMe_2Ph, **4c**: CMe_2*t*Bu, **4d**: $CMePh_2$) investigated in this work.

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(Scheme 1). This reaction was successful in the case of R = *t*Bu and CMe_2Ph, affording **5a**H[BF_4] and **5b**H[BF_4] in isolated yields of 51% and 52%, respectively, which is in the usual range reported for compounds of this type.[15a,c,18] Despite many attempts, the desired formamidinium compounds could not be isolated with the two bulkier substituents (R = $CMePh_2$, CMe_2*t*Bu), since only intractable mixtures were obtained, irrespective of the reaction conditions (solvent, temperature, time). This finding is in concert with the observation reported already more than a decade ago by Bielawski and co-workers that 1,1′-diaminoferrocene derivatives of type **4** bearing bulky *N*-substituents such as, for example, $CHPh_2$ are reluctant to undergo such formylative cyclisation reactions.[15c]

The free fcNHCs **5a** and **5b** were easily generated from **5a**H[BF_4] and **5b**H[BF_4], respectively, by reaction with $NaN(SiMe_3)_2$ in toluene or benzene (Scheme 1). The $C_{carbene}$ atom gives rise to a characteristic low-field ^{13}C NMR signal located at $\delta \approx 261$ ppm (C_6D_6) in each case, which is essentially identical to the values reported for the persistent *i*Bu and the thermally stable 2-adamantyl homologue.[15c,18c] The *t*Bu homologue **5a** undergoes a specific decomposition to isobutene and formamidine **6a** in solution (Scheme 1), which is sufficiently slow at room temperature to allow the isolation of **5a** in 91% yield as a yellow microcrystalline solid after immediate and rapid work-up. This decomposition is accelerated by $NaN(SiMe_3)_2$. Consequently, an excess of this reagent should be avoided. The sterically more encumbered homologue **5b** undergoes an analogous, but significantly faster, decomposition to α-methylstyrol and formamidine **6b** (Scheme 1), which prevented the isolation of this fcNHC in pure form. The decomposition of **5a** and **5b** is strongly reminiscent of the β-fragmentation reactions previously reported by us for the iconic "Alder carbene" (iPr$_2$N)$_2$C and related acyclic diaminocarbenes.[34] A closely related process involving the loss of isobutene has been reported for the cyclic diazenium salt [(*o*-C_6H_4)(N*t*Bu)$NCPh_2$][BF_4].[35] We also note the Hofmann-like elimination reactions shown by sterically highly encumbered tertiary amines in this context, where particularly bulky *tert*-alkyl groups can give rise to the formation of a secondary amine by loss of an alkene (for example, *t*Bu*i*PrNCMe_2CH_2*t*Bu decomposes to *t*Bu*i*PrNH and $H_2C{=}CMeCH_2$*t*Bu).[36]

Not surprisingly, the new fcNHCs are extremely sensitive towards air and moisture, and hydrolysis by trace amounts of adventitious moisture could not be completely avoided even under our best inert conditions. In one instance a few crystals of fc(N*t*Bu–CHO)(NH*t*Bu) (**7**, not shown in Scheme 1), i.e. the hydrolysis product of **5a**, were serendipitously obtained, which allowed the structural characterisation of this formamide by X-ray diffraction (see below).

Despite its bulkiness, **5a** reacted cleanly and swiftly with elemental sulfur (S_8) under mild conditions, affording the corresponding cyclic thiourea derivative **5a**S in an isolated yield of 90% (Scheme 1). The analogous reaction of **5b** was too sluggish in comparison with its thermal decomposition to formamidine **6b**. No reaction was observed for **5a** and **5b** with elemental selenium; only decomposition to the formamidines **6a** and **6b** occurred. Attempts to synthesize **5a**Se and **5b**Se by reacting the respective fcNHC with the Se atom transfer reagent $(Me_2N)_3PSe$ failed, too, due to inertness.[37]

Formamidine **6a**, which was obtained by the specific thermal decomposition of the corresponding fcNHC **5a**, was easily converted to formamidinium salt **5e**H[BF_4] by reaction with $Ph_3C[BF_4]$ (Scheme 1). Attempts to react **5e**H[BF_4] with $NaN(SiMe_3)_2$ or similar bases in order to generate the corresponding fcNHC **5e**, whose steric bulk would rival that of Rivard's 1,3-bis(trityl)imidazolin-2-ylidene (ITr),[38] were not successful. This may be due to the extremely poor solubility of this particular formamidinium salt even in THF. There was no indication for a formamidine, which might have formed together with isobutene from **5e**. Only intractable material was obtained. **5e**H[BF_4] was found to hydrolyse readily with trace amounts of water, affording Ph_3COH and **6a**H[BF_4].

Crystal Structures

Most new compounds were structurally characterised by single-crystal X-ray diffraction. The molecular structures of the α-aminonitriles **2a** and **2c** are shown in Figure 2 and Figure 3.

The molecules are aggregated in the solid state due to intermolecular N–H···N≡C hydrogen bonds (indicated by dashed lines in Figure 2 and Figure 3).[39] **2a** exhibits crystallographically imposed molecular C_i symmetry. Its C≡N bond length of 1.134(7) Å is typical for carbon-nitrogen triple bonds and the two other carbon-nitrogen bond lengths of 1.415(6) and 1.460(6) Å are typical for C(sp^2)–N(sp^3) and C(sp^3)–N(sp^3) single bonds, respectively.[40] The aggregation of neighbouring molecules by hydrogen bonding is reflected by an H···N distance of 2.34 Å and an N–H···N angle of 178°. **2c** exhibits crystallographically imposed molecular C_2 symmetry. Due to a disorder of the methyl and the nitrile group at C6, the metric parameters

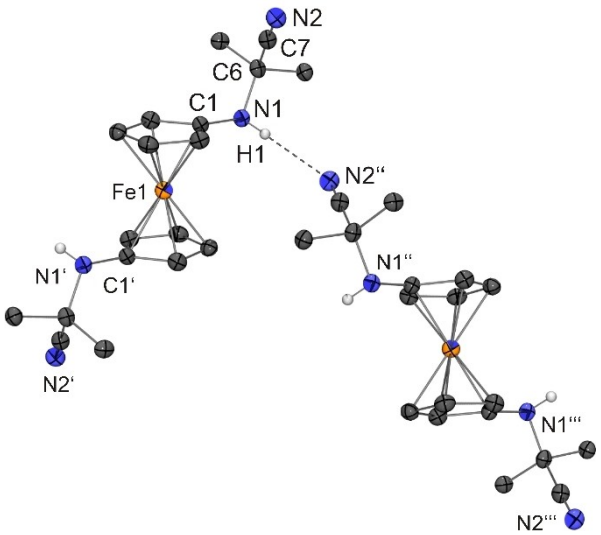

Figure 2. Molecular structure and aggregation of **2a** in the crystal (ORTEP with 30% probability ellipsoid, C-bonded H atoms omitted for clarity). Selected interatomic distances (Å) and angles (°): C1–N1 1.416(6), C6–N1 1.462(6), C6–C7 1.505(7), C7–N2 1.135(7); C6–C7–N2 178.2(6).

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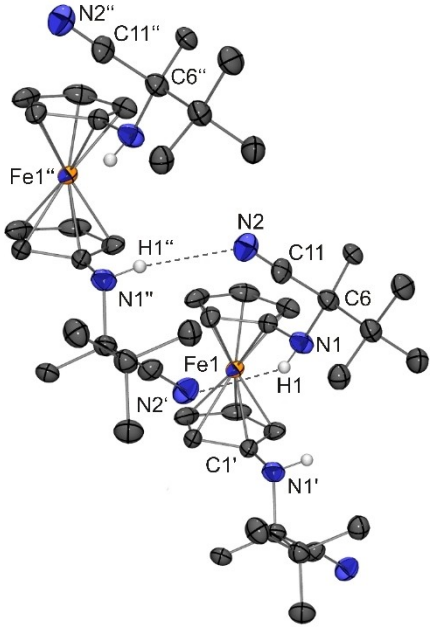

Figure 3. Molecular structure and aggregation of **2c** in the crystal (ORTEP with 30% probability ellipsoid, C-bonded H atoms omitted for clarity). Selected interatomic distances (Å) and angles (°): C1–N1 1.422(4), C6–N1 1.479(4), C6–C11 1.54(3), C11–N2 1.15(3); C6–C11–N2 178(3).

of the C–C≡N moiety show comparatively large estimated standard deviations, which makes a detailed discussion of the hydrogen bonds not meaningful.

The molecular structure of the diimine **3** is shown in Figure 4.

The molecule has an approximate non-crystallographic C_2 symmetry about an axis that passes through the Fe atom and bisects the vector linking the N atoms. The N–C_{ipso}–C_{ipso}–N torsion angle is 19.9°. Each N atom exhibits two distinctly different C–N bond lengths of ca. 1.29 and 1.40 Å, respectively, which are in accord with a double and single bond between sp^2-hybridised carbon and nitrogen atoms. Similar structural features have been observed for closely related compounds such as, for example, fc(N=CH-*p*-C_6H_4-OMe)$_2$.[41]

Figure 5 and Figure 6 show the molecular structures of the diaminoferrocenes **4b** and **4d**. Note that the structures, but not the synthesis, of **4a** and **4c** had already been reported by us previously.[29,42]

Similar to **4a**,[42] the molecules of **4b** and **4d** exhibit a synperiplanar conformation of the cyclopentadienyl rings with fairly small N–C_{ipso}–C_{ipso}–N torsion angles below ca. 12° and rather short intramolecular N···N distances between ca. 3.04 and 3.11 Å, which is more than 0.20 Å below the interplanar distance between the Cp rings in ferrocene. Together with intramolecular H···N distances and N–H···N angles of approximately 2.4 Å and 140°, respectively, these structural data suggest the presence of weak intramolecular N–H···N hydrogen

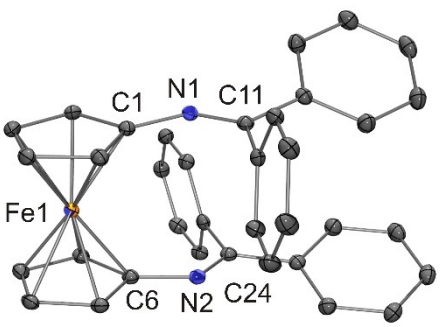

Figure 4. Molecular structure of **3** in the crystal (ORTEP with 30% probability ellipsoid, H atoms omitted for clarity). Selected interatomic distances (Å) and angles (°): C1–N1 1.399(2), C6–N2 1.400(2), C11–N1 1.286(2), C24–N2 1.284(2); C1–N1–C11 125.85(14), C6–N2–C24 125.98(14).

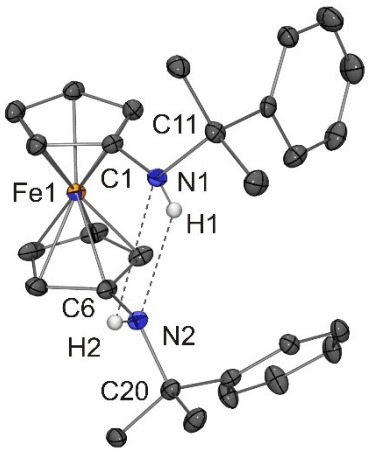

Figure 5. Molecular structure of **4b** in the crystal (ORTEP with 30% probability ellipsoid, C-bonded H atoms omitted for clarity). Only one of the two independent molecules is shown. Selected interatomic distances (Å): C1–N1 1.423(7), C6–N2 1.425(7), C11–N1 1.485(7), C20–N2 1.499(7); C1–N1–C11 117.2(4), C6–N2–C20 116.0(4).

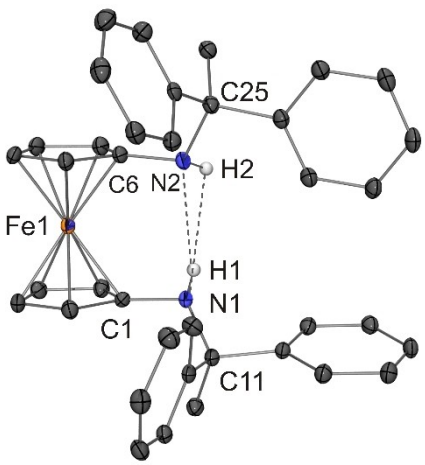

Figure 6. Molecular structure of **4d**·$^1/_2$ C_6H_6 in the crystal (ORTEP with 30% probability ellipsoid, C-bonded H atoms and solvent molecule omitted for clarity). Selected interatomic distances (Å) and angles (°): C1–N1 1.429(3), C6–N2 1.431(3), C11–N1 1.485(4), C25–N2 1.492(3); C1–N1–C11 116.5(2), C6–N2–C25 115.8(2).

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bond interactions (indicated by dashed lines in Figure 5 and Figure 6).[39]

The molecular structures of the cations of **5a**H[BF_4], **5b**H[BF_4] and **5e**H[BF_4] are shown in Figure 7, Figure 8 and Figure 9.

The three formamidinium cations share a number of characteristic structural features. The bonding environment of the N atoms is trigonal planar in each case. The N–C–N angle is ca. 131° and the C–N bond lengths in this unit are ca. 1.32 Å. These values are in accord with those of other ferrocene-based formamidinium cations.[18,19]

The molecular structures of fcNHC **5a** and the corresponding thiourea **5a**S are shown in Figure 10 and Figure 11.

In comparison with the formamidinium cations discussed above, the N–C–N angles of the free fcNHC **5a** and its thiourea derivative **5a**S are more acute (by ca. 10°) and the C–N bonds in this unit are elongated. The structural data suggest that the

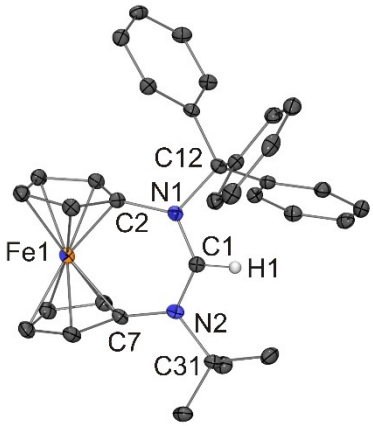

Figure 9. Molecular structure of **5e**H[BF_4] in the crystal (ORTEP with 30% probability ellipsoid, anion and H atoms except that at C1 omitted for clarity). Selected interatomic distances (Å) and angles (°): C1–N1 1.324(4), C1–N2 1.317(4), C2–N1 1.440(4), C7–N2 1.433(4), C12–N1 1.540(4), C31–N2 1.529(4); N2–C1–N1 131.7(3).

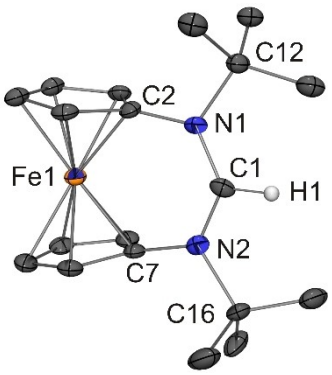

Figure 7. Molecular structure of **5a**H[BF_4] in the crystal (ORTEP with 30% probability ellipsoid, anion and H atoms except that at C1 omitted for clarity). Only one of the two independent molecules is shown. Selected interatomic distances (Å) and angles (°): C1–N1 1.326(11), C1–N2 1.321(11), C2–N1 1.443(11), C7–N2 1.444(11), C12–N1 1.523(11), C16–N2 1.541(11); N2–C1–N1 130.8(9).

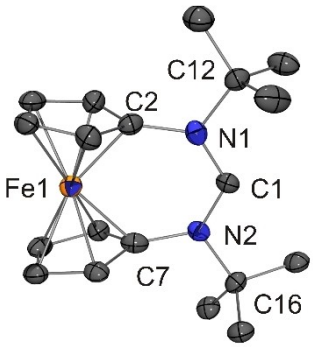

Figure 10. Molecular structure of **5a** in the crystal (ORTEP with 30% probability ellipsoid, H atoms omitted for clarity). Selected interatomic distances (Å) and angles (°): C1–N1 1.360(11), C1–N2 1.344(11), C2–N1 1.427(12), C7–N2 1.456(13), C12–N1 1.522(12), C16–N2 1.502(11); N1–C1–N2 121.6(8).

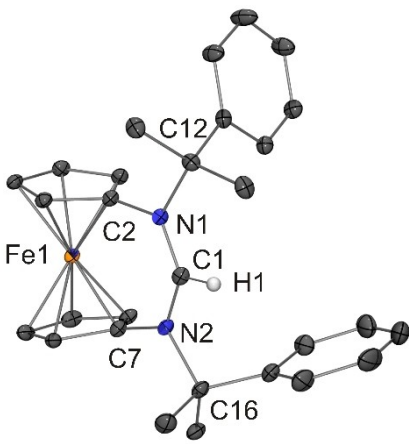

Figure 8. Molecular structure of **5b**H[BF_4] in the crystal (ORTEP with 30% probability ellipsoid, anion and H atoms except that at C1 omitted for clarity). Selected interatomic distances (Å) and angles (°): C1–N1 1.310(4), C1–N2 1.323(4), C2–N1 1.433(4), C7–N2 1.434(4), C12–N1 1.523(4), N2–C21 1.536(4); N1–C1–N2 131.4(3).

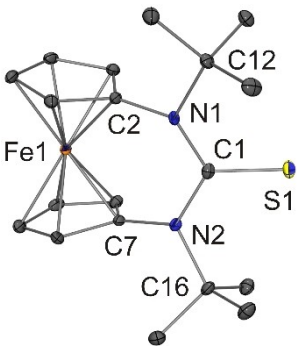

Figure 11. Molecular structure of **5a**S in the crystal (ORTEP with 30% probability ellipsoid, H atoms omitted for clarity). Selected interatomic distances (Å) and angles (°): C1–S1 1.685(3), C1–N1 1.395(3), C1–N2 1.392(3), C2–N1 1.434(3), C7–N2 1.430(3), N1–C12 1.534(3), N2–C16 1.531(3); N1–C1–N2 119.9(2).

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degree of π-delocalisation in the N_2C unit is highest in the formamidinium cations and lowest, but still significant, in the thiourea derivative. **5a**S exhibits a C–S bond length of 1.685(3) Å, which is considerably longer than carbon-sulfur double bonds in thioketones (ca. 1.62 Å),[43] and very similar to the corresponding value of 1.688(3) Å published for the thiourea derivative of 1,3-di-*tert*-butylimidazolin-2-ylidene.[44] Such elongated bonds are typical for thioureas in general,[39] in line with a significant contribution of zwitterionic canonical structures N_2C^+–S^- featuring single dative bonds.[45]

The formamidines **6a** and **6b** did not afford single crystals suitable for X-ray diffraction studies. However, **6a** could be structurally characterised in protonated form as **6a**H[BF_4] (obtained from **5e**H[BF_4] by hydrolysis with adventitious moisture; vide supra); the molecular structure of the cation is shown in Figure 12. Formamidine **6b** was structurally characterised as iron(II) complex [$FeCl_2$(**6b**)$_2$] (Figure 13), which was obtained by serendipity.

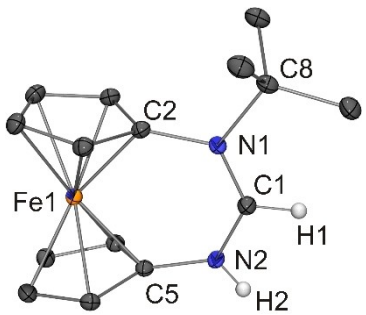


Figure 12. Molecular structure of **6a**H[BF_4] in the crystal (ORTEP with 30% probability ellipsoid, anion and C-bonded H atoms except that at C1 omitted for clarity). Selected interatomic distances (Å) and angles (°): C1–N1 1.313(3), C1–N2 1.318(3), C2–N1 1.439(3), C5–N2 1.422(3), C8–N1 1.531(3); N1–C1–N2 129.4(2).

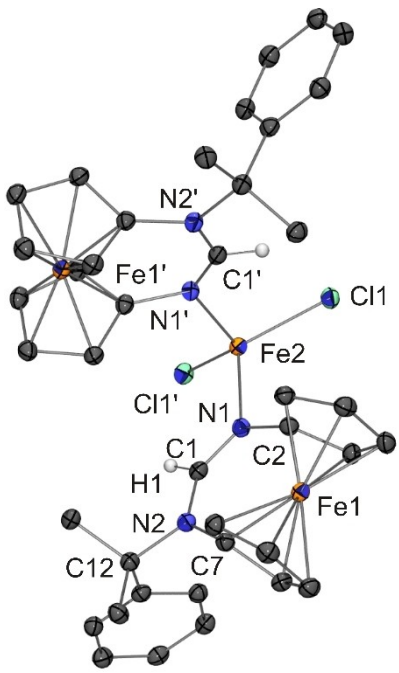
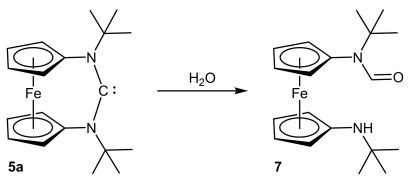


Figure 13. Molecular structure of [$FeCl_2$(**6b**)$_2$] in the crystal (ORTEP with 30% probability ellipsoid, H atoms except that at C1 omitted for clarity). Selected interatomic distances (Å) and angles (°): Fe2–Cl1 2.2766(6), Fe2–N1 2.082(2), C1–N1 1.298(3), C1–N2 1.353(3), C2–N1 1.425(3), C7–N2 1.432(3), C12–N2 1.508(3); Cl1–Fe2–Cl1 120.34(4), N1–Fe2–N1 97.39(11), N1–C1–N2 132.1(2).

Not surprisingly, protonation (in the case of **6a**) or metal coordination (in the case of **6b**) of the N_{imine} atom leads to a formamidinium-type N_2C unit with a large N–C–N angle (average value 131°) and rather short C–N bonds (average value 1.32 Å), similar to what was observed for **5a**H[BF_4], **5b**H[BF_4] and **5e**H[BF_4] (vide supra). The tetracoordinate Fe^{II} atom of [$FeCl_2$(**6b**)$_2$] resides in a distorted pseudotetrahedral bonding environment, exhibiting bond lengths and angles similar to those of closely related complexes.[46]

In line with results from our previous work,[17a,18] the N–C–N bridge present in the structurally characterised diaza-[3]ferrocenophane derivatives of this study (Figures 7–13) is not sufficiently long to allow a coplanar arrangement of the cyclopentadienyl rings, causing ring tilt angles in the range from 14.3–17.5°. The resulting ring strain is rather small, as is indicated by only marginal deviations of the N atoms from their respective cyclopentadienyl ring plane in the direction of the Fe atom; the N–C_{ipso}–cg (cg = cyclopentadienyl ring centroid) angles lie in the range from 177.2 to 179.5°. Not surprisingly, the largest tilt angles are observed for **5a** (17.2°) and **5a**S (17.5°), whose N–C–N angles are more acute (by ca. 10°) than those of the other compounds. The cyclopentadienyl rings adopt an eclipsed conformation in all cases, as is indicated by very small N–C_{ipso}–C_{ipso}–N torsion angles ≤2.1°. The only slight exception is the sterically most encumbered congener **5e**H[BF_4], whose torsion angle is 5.6° due to steric repulsion between the trityl and *tert*-butyl groups. For comparison, pristine [3]ferrocenophane has a tilt angle of 10.3°, an H_2C–C_{ipso}–C_{ipso}–CH_2 torsion angle of 1.9° and H_2C–C_{ipso}–cg angles of 175.9 and 176.5°.[47]

The molecular structure of **7** (obtained from **5a** by hydrolysis with adventitious moisture; Scheme 2) is shown in Figure 14. It resembles that of the closely related neopentyl homologue [Fe{η^5-C_5H_4[N(CHO)CH_2tBu]}{η^5-C_5H_4(NHCH_2tBu)}].[17a] The partial double bond character of the formamide carbon-nitrogen bond is reflected by a length of ca. 1.35 Å. The lengths of the two Me_3C–N bonds of **7** are significantly different, viz. 1.510(6) vs. 1.461(6) Å, with that involving the $N_{formamide}$ atom being 0.05 Å longer than the other one involving the N_{amine} atom. There appears to be no obvious reason for this structural feature. Note that the Me_3CCH_2–N bond lengths of the neopentyl homologue, viz. 1.475(5) and 1.449(6) Å, differ only



Scheme 2. Formation of **7** from **5a** by hydrolysis with adventitious moisture.

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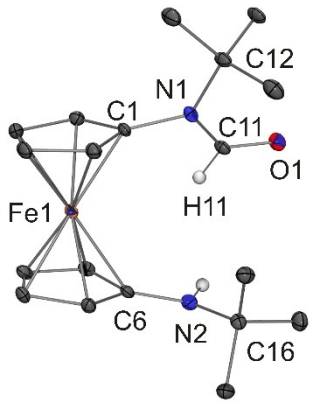

Figure 14. Molecular structure of **7** in the crystal (ORTEP with 30% probability ellipsoid, C-bonded H atoms except that at C11 omitted for clarity). Selected interatomic distances (Å) and angles (°): C1–N1 1.435(5), C6–N2 1.371(6), C11–O1 1.231(5), C11–N1 1.346(6), C12–N1 1.510(6), C16–N2 1.461(6); O1–C11–N1 126.4(4).

marginally[17a] and that the $Me_3C–N_{formamide}$ and $Me_3C–N_{amine}$ bond lengths of *t*BuN(CHO)CH_2CH_2NH*t*Bu are almost equal, their values being 1.494(2) and 1.483(2) Å.[48]

Conclusion

We have demonstrated that *N-tert*-alkyl-substituted 1,1′-diaminoferrocenes fc$(NHR)_2$ (R = CMe_2*t*Bu and CMe_nPh_{3-n}, *n* = 1–3) are efficiently accessible on a multigram scale in two steps from 1,1′-diaminoferrocene. Their formylative cyclisation to ferrocene-based formamidinium compounds fc[$(NR)_2$CH][BF_4] was possible for R = CMe_3 and CMe_2Ph, but not for the bulkier substituents $CMePh_2$ and CMe_2*t*Bu. The corresponding N-heterocyclic carbenes fc{[$N(CMe_3)$]$_2$C:} and fc{[$N(CMe_2Ph)$]$_2$C:} were synthesised from their formamidinium precursors under routine conditions by reaction with $NaN(SiMe_3)_2$, but proved to be unstable in solution under ambient conditions due to their specific decomposition by alkene elimination, leading to the respective formamidine fc(NRCH=N) (R = CMe_3, CMe_2Ph). The *tert*-butyl congener was transformed to the unsymmetrical formamidinium compound fc{[$N(CMe_3)$][$N(CPh_3)$]CH}[BF_4] by reaction with $Ph_3C[BF_4]$. Attempts to utilise this compound for the synthesis of the very bulky N-heterocyclic carbene fc{[$N(CMe_3)$][$N(CPh_3)$]C:} were severely hampered by the very poor solubility of this particular formamidinium salt. We surmise that higher solubilities may result by applying tritylium salts with larger anions such as, for example, $[B(C_6F_5)_4]^-$[49] or $[Al\{OC(CF_3)_3\}_4]^-$.[50] We expect that fc{[$N(CMe_3)$][$N(CPh_3)$]C:} will undergo isobutene elimination, thus affording fc[$N(CPh_3)$CH=N], which might be transformed to the extremely bulky N-heterocyclic carbene fc{[$N(CPh_3)$]$_2$C:}. Further work in this direction is underway. We envisage that very bulky fcNHCs can be employed for the synthesis of linear dicoordinate metal complexes with interesting and useful properties. For example, it has been shown in this context that the photoluminescence properties of copper(I) carbene complexes are significantly improved by increased steric encumbrance of the carbene ligand[38b,51] and that the catalytic activity of hydridocopper(I) carbene complexes in hydrosilylation reactions depends critically on the steric encumbrance of the carbene, because very bulky carbenes favour the formation of the catalytically active monomer [CuH(NHC)] from the corresponding dimer dominant in solution.[52]

Experimental Section

General considerations: All reactions involving air-sensitive compounds were performed in an inert atmosphere (argon or dinitrogen) by using standard Schlenk techniques or a conventional glovebox. Starting materials were procured from standard commercial sources and used as received. 1,1′-Diaminoferrocene was synthesised according to a published procedure.[53] NMR spectra were recorded at ambient temperature with Varian NMRS-500 and MR-400 spectrometers operating at 500 and 400 MHz, respectively, for ^{1}H. High-resolution (HR) ESI mass spectra were obtained with a micrOTOF time-of-flight mass spectrometer (Bruker Daltonics, Bremen, Germany) using an Apollo™ "ion funnel" ESI source. Mass calibration was performed immediately prior to the measurement with ESI Tune Mix Standard (Agilent, Waldbronn, Germany). Elemental analyses were carried out with a HEKAtech Euro EA-CHNS elemental analyser at the Institute of Chemistry.

Synthesis of 2a: A suspension of 1,1′-diaminoferrocene (3.06 g, 14.2 mmol) in acetone (21 mL) was cooled to 0 °C with an ice bath. Acetic acid (9 mL) was added, followed by sodium cyanide (3.00 g, 61 mmol). The mixture was stirred at 0 °C for 3 h and was subsequently stored at −20 °C for 18 h without stirring. The product was precipitated by addition of ice-cold water (300 mL). The precipitate was isolated by filtration, washed with ice-cold water (3×100 mL) and finally dried under vacuum. This afforded the product as a voluminous yellow solid. Yield 3.97 g (80%). Single crystals suitable for XRD were obtained by vapour phase diffusion of diethyl ether into a dichloromethane solution. $C_{18}H_{22}FeN_4$ (350.24): calcd. C 61.73, H 6.33, N 16.00%; found C 61.72, H 6.33, N 15.85%. HRMS/ESI (+): *m/z* = 350.1193 $[M]^+$, 350.1194 calcd. for $[C_{18}H_{22}FeN_4]^+$. ^{1}H NMR (500 MHz, C_6D_6): δ = 1.08 (s, 12 H, Me), 3.03 (br., 2 H, NH), 3.87, 4.17 (2 m, 2×4 H, cyclopentadienyl H). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ = 27.5 (Me), 50.9 (CMe_2), 65.0, 66.0 (2× cyclopentadienyl CH), 100.9 (C_{ipso}), 123.6 (C≡N).

Synthesis of 2b: A suspension of 1,1′-diaminoferrocene (1.02 g, 4.7 mmol) in acetophenone (7 mL) was cooled to 0 °C with an ice bath. Acetic acid (3 mL) was added, followed by sodium cyanide (1.03 g, 21 mmol). The mixture was stirred at 0 °C for 2 h and was subsequently stored at −20 °C for 18 h without stirring. Volatile components were removed under vacuum at ambient temperature. Toluene (150 mL) was added to the residue. Insoluble material was removed by filtration. Volatile components were removed from the filtrate under vacuum with gentle warming (final bath temperature 50 °C, 18 h). This afforded the product as a red solid (1:1 mixture of *rac*- and *meso*-**2b**). Yield 1.60 g (72%). HRMS/ESI (+): *m/z* = 474.1486 $[M]^+$, 474.1507 calcd. for $[C_{28}H_{26}FeN_4]^+$. ^{1}H NMR (400 MHz, C_6D_6): δ = 1.16, 2.13 (2 s, 2×3 H, Me), 3.66, 3.78, 4.00, 4.05, 4.31, 4.41, 4.52, 4.58 (8 m, 8×1 H, cyclopentadienyl H), 4.42 (m, 2 H, NH), 6.95, 7.10, (2 m, 2×3 H, phenyl H), 7.60, 7.90 (2 m, 2×2 H, phenyl H). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ = 18.3, 32.0 (2×Me), 58.6 (*C*MePh), 63.7, 64.6, 65.9, 66.0 (4×cyclopentadienyl CH), 66.7 (*C*MePh), 67.0, 67.2, 67.6, 67.6 (4×cyclopentadienyl CH), 100.8, 103.3 (2×cyclopentadienyl C_{ipso}), 123.0 (C≡N), 125.8, 127.2, 127.3 128.6, 128.9, 130.0 (6×phenyl CH), 141.2, 141.3 (2× phenyl C_{ipso}).

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Synthesis of 2c: A suspension of 1,1′-diaminoferrocene (2.07 g, 9.6 mmol) in pinacolone (27 mL) was cooled to 0 °C with an ice bath. Acetic acid (14 mL) was added, followed by sodium cyanide (2.01 g, 41 mmol). The mixture was stirred at 0 °C for 4 h and was subsequently stored at −20 °C for 18 h without stirring. Volatile components were removed under vacuum at ambient temperature. Toluene (150 mL) was added to the residue. Insoluble material was removed by filtration. Volatile components were removed from the filtrate under vacuum with gentle warming (final bath temperature 40 °C, 6 h). This afforded the product as a waxy orange solid. Yield 4.05 g (97%). Single crystals suitable for XRD were obtained by slow evaporation of a toluene solution. HRMS/ESI (+): m/z = 434.2119 $[M]^+$, 434.2133 calcd. for $[C_{24}H_{34}FeN_4]^+$. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.94, 0.95 (s, 2×9 H, CMe_3), 1.02, 1.06 (2 s, 2×3 H CMeCN), 3.06, 3.11 (2 br., 2×1 H, NH), 3.81, 3.87, 3.90, 3.96 (4 m, 4×1 H, cyclopentadienyl H), 3.99 (m, 2 H, cyclopentadienyl H), 4.50, 4.51 (2 m, 2×1 H, cyclopentadienyl H). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ = 19.4, 19.5 (2×*C*MeCN) 25.0, 25.1 (2×*CMe*$_3$), 37.4, 37.5 (2×*C*Me$_3$), 63.2, 63.6 (2×*C*MeCN), 66.0, 66.1, 66.2, 66.3 67.0, 67.1, 67.5, 68.7 (8× cyclopentadienyl CH), 101.0, 101.8 (2×C_{ipso}), 122.8, 125.7 (2×C≡N).

Synthesis of 3: Acetic acid (0.88 g, 14.7 mmol) was added to a stirred solution of 1,1′-diaminoferrocene (1.50 g, 6.9 mmol) and benzophenone (3.79 g, 20.8 mmol) in THF (50 mL). Stirring was continued for 24 h. Volatile components were removed under vacuum. Toluene (50 mL) was added to the residue. Insoluble material was removed by filtration through a short pad of Celite. The solvent was removed from the filtrate under vacuum. The crude product was subjected to purification first by column chromatography (silica gel, *n*-hexane-ethyl acetate 7:3) and finally by sublimation (10^{-2} mbar, 100 °C). This afforded the product as a dark red crystalline solid, which contained single crystals suitable for XRD. Yield 0.85 g (22%). $C_{36}H_{28}FeN_2$ (544.47): calcd. C 79.41, H 5.18, N 5.15%; found C 79.43, H 5.14, N 4.86%. HRMS/ESI (+): m/z = 545.1610 $[M+H]^+$, 545.1680 calcd. for $[C_{36}H_{29}FeN_2]^+$. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 3.87, 4.04 (2 m, 2×4 H, cyclopentadienyl H), 7.18, 7.24 (2 m, 2×4 H, phenyl H), 7.36 (m, 2 H, phenyl H), 7.42 (m, 6 H, phenyl H), 7.59 (m, 4 H, phenyl H). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ = 67.9, 68.7 (2×cyclopentadienyl CH), 104.0 (cyclopentadienyl C_{ipso}), 128.5, 128.8 (two closely spaced signals), 129.0, 129.1, 130.1 (6×phenyl CH), 139.2, 141.0 (2×phenyl C_{ipso}), 165.6 (N=*C*).

Synthesis of 4a: $FeCl_2$ (0.76 g, 6.0 mmol) was added to a solution of **2a** (3.51 g, 10.0 mmol) in toluene (100 mL). The stirred mixture was cooled to −80 °C and then slowly added via cannula to a stirred mixture of toluene (60 mL) and MeLi (1.6 M in diethyl ether, 125 mL, 200 mmol) kept at −80 °C. Stirring was continued at this temperature for 2 h. The cooling bath was subsequently removed. Stirring was continued for 18 h, after which time water (100 mL) was slowly added. Volatile components were removed under vacuum. Toluene (200 mL) was added to the residue. Insoluble material was removed by filtration through a short pad of Celite. The filtrate was reduced to dryness under vacuum. This afforded the product as a sticky orange-brown semi-solid. After many attempts, a few single crystals suitable for XRD were obtained by slow evaporation of a toluene solution. Yield 2.30 g (70%). HRMS/ESI (+): m/z = 329.2487 $[M+H]^+$, 329.1680 calcd. for $[C_{18}H_{28}FeN_2]^+$. ^{1}H NMR (500 MHz, C_6D_6): δ = 1.08 (s, 18 H, Me), 2.34 (br., 2 H, NH), 3.92, 4.00 (2 m, 2×4 H, cyclopentadienyl H). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ = 30.0 (*CMe*$_3$), 51.6 (*C*Me$_3$), 65.8, 67.1 (2×cyclopentadienyl CH), 101.5 (C_{ipso}).

Synthesis of 4b: The product was obtained as a sticky red semi-solid by a procedure essentially identical to that described above for **4a** from $FeCl_2$ (0.25 g, 2.0 mmol), **2b** (1.57 g, 3.3 mmol) and MeLi (1.6 M in diethyl ether, 41 mL, 66 mmol). After many attempts, a few single crystals suitable for XRD were obtained by slow evaporation of a toluene solution. Yield 1.58 g (85%). HRMS/ESI (+): m/z = 452.1962 $[M]^+$, 452.1915 calcd. for $[C_{28}H_{32}FeN_2]^+$. ^{1}H NMR (500 MHz, C_6D_6): δ = 1.39 (s, 12 H, Me), 2.65 (s, 2 H, NH), 3.65, 3.71 (2 m, 2×4 H, cyclopentadienyl H), 7.12 (m, 2 H, phenyl H), 7.23, 7.54 (2 m, 2×4 H, phenyl H). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ = 30.2 (*CMe*$_2$), 56.9 (*C*Me$_2$), 65.3, 64.3 (2×cyclopentadienyl CH), 126.5, 126.6, 128.4 (3×phenyl CH), 149.1 (phenyl C_{ipso}); cyclopentadienyl C_{ipso} not detected.

Synthesis of 4c: The product was obtained as a sticky red semi-solid by a procedure essentially identical to that described above for **4a** from $FeCl_2$ (0.73 g, 5.8 mmol), **2c** (4.17 g, 9.6 mmol) and MeLi (1.6 M in diethyl ether, 120 mL, 192 mmol). After many attempts, a few single crystals suitable for XRD were obtained by slow evaporation of a toluene solution. Yield 3.64 g (92%). HRMS/ESI (+): m/z = 412.2526 $[M]^+$, 412.2541 calcd. for $[C_{28}H_{32}FeN_2]^+$. ^{1}H NMR (500 MHz, C_6D_6): δ = 0.99 (s, 12 H, CMe_2) 1.01 (s, 18 H, CMe_3), 2.39 (br., 2 H, NH), 3.90, 4.00 (2 m, 2×4 H, cyclopentadienyl H). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ = 22.9 (*CMe*$_2$), 26.0 (*CMe*$_3$), 37.7 (*C*Me$_3$), 59.0 (*C*Me$_2$), 65.7, 68.4 (2×cyclopentadienyl CH), 103.1 (C_{ipso}).

Synthesis of 4d: A stirred solution of **3** (0.76 g, 1.4 mmol) in toluene (30 mL) was cooled to −80 °C and then slowly added via cannula to a stirred mixture of toluene (30 mL) and MeLi (1.6 M in diethyl ether, 17 mL, 27 mmol) kept at −80 °C. Stirring was continued at this temperature for 1 h. The cooling bath was subsequently removed. Stirring was continued for 18 h, after which time water (10 mL) was slowly added. Volatile components were removed under vacuum. Toluene (80 mL) was added to the residue. Insoluble material was removed by filtration through a short pad of Celite. The filtrate was reduced to dryness under vacuum. This afforded the product as an orange crystalline solid. Yield 0.70 g (87%). $C_{38}H_{36}FeN_2$ (576.55): calcd. C 79.16, H 6.29, N 4.86%; found C 79.15, H 6.23, N 4.73%. HRMS/ESI (+): m/z = 576.2204 $[M]^+$, 576.2228 calcd. for $[C_{38}H_{36}FeN_2]^+$. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.79 (s, 6 H, Me), 3.62, 3.72 (2 m, 2×4 H, cyclopentadienyl H), 7.26 (m, 12 H, phenyl H), 7.41 (m, 8 H, phenyl H). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ = 27.6 (Me), 64.1 (*C*MePh$_2$), 65.4, 66.0 (2×cyclopentadienyl CH), 102.9 (cyclopentadienyl C_{ipso}), 126.9, 127.6, 128.5 (3×phenyl CH), 149.3 (phenyl C_{ipso}).

Synthesis of 5aH[BF_4]: A stirred mixture of **4a** (1.25 g, 3.8 mmol), $NH_4[BF_4]$ (0.79 g, 7.6 mmol) and triethyl orthoformate (2.26 g, 15.2 mmol) in toluene (25 mL) was heated to reflux for 3 h and was then allowed to cool to ambient temperature. Its volume was subsequently reduced to ca. 5 mL under vacuum. Diethyl ether (20 mL) was added. Stirring was continued for 10 min. The dark brown solid was filtered off and subjected to purification by column chromatography (silica gel, ethyl acetate). This afforded the product as a bright yellow microcrystalline solid. Single crystals suitable for XRD were obtained by slow evaporation of an ethyl acetate solution. Yield 0.67 g (51%). HRMS/ESI (+): m/z = 339.1483 $[M-BF_4]^+$, 339.1524 calcd. for $[C_{19}H_{27}FeN_2]^+$. $C_{19}H_{27}N_2BF_4Fe$ (426.08): calcd. C 53.56, H 6.39, N 6.57%; found C 53.13, H 6.42, N 46.37%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.51 (s, 18 H, Me), 4.46, 4.52 (2 m, 2×4 H, cyclopentadienyl H), 8.24 (s, 1 H, N_2CH). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ = 29.4 (*CMe*$_3$), 66.1 (*C*Me$_3$), 70.0, 73.1 (2×cyclopentadienyl CH), 90.7 (C_{ipso}), 155.9 (N_2CH).

Synthesis of 5bH[BF_4]: Acetic acid (6 drops) was added to a stirred mixture of **4b** (386 mg, 0.85 mmol), $NH_4[BF_4]$ (179 mg, 1.71 mmol) and triethyl orthoformate (1.00 g, 6.7 mmol) in toluene (10 mL). The mixture was heated to reflux for 3 h and was then allowed to cool to ambient temperature. Its volume was subsequently reduced to ca. 3 mL under vacuum. Diethyl ether (40 mL) was added. Stirring was discontinued after 10 min. The mixture was stored at −40 °C for 14 h. The brown solid was isolated by filtration and then taken up in dichloromethane (10 mL). The solution was passed through a short pad of Celite. Volatile components were subsequently

removed under vacuum. This afforded the product as a brownish microcrystalline solid. Single crystals suitable for XRD were obtained by slow evaporation of a dichloromethane solution. Yield 245 mg (52%). HRMS/ESI (+): m/z = 463.2809 $[M–BF_4]^+$, 463.1837 calcd. for $[C_{29}H_{31}FeN_2]^+$. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.58 (s, 12 H, Me), 4.52, 4.68 (2 m, 2×4 H, cyclopentadienyl H), 7.37 (m, 10 H, phenyl H), 7.55 (s, 1 H, N_2CH). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6): δ = 28.1 (CMe_2), 69.3 (CMe_2), 69.0, 72.4 (2×cyclopentadienyl CH), 90.4 (cyclopentadienyl C_{ipso}), 126.1, 128.6, 129.0 (3×phenyl CH), 142.2 (phenyl C_{ipso}), 159.0 (N_2CH).

Synthesis of 5eH[BF$_4$]: $Ph_3C[BF_4]$ (109 mg, 0.33 mmol) was added to a solution of **6a** (vide infra) in dichloromethane (0.5 mL). The mixture was shaken for 3 min and then stored for 12 h. The supernatant was decanted off. The remaining solid was washed with diethyl ether (2×1 mL) and was subsequently dried under vacuum. This afforded the product as a yellow microcrystalline solid. Single crystals suitable for XRD were obtained by vapour phase diffusion of diethyl ether into a dichloromethane solution at −20 °C. Yield 84 mg (46%). $C_{34}H_{33}N_2BF_4Fe$ (612.29): calcd. C 66.69, H 5.43, N 4.58%; found C 65.67, H 5.53, N 4.29%. HRMS/ESI (+): m/z = 525.0919 $[M–BF_4]^+$, 525.1993 calcd. for $[C_{34}H_{33}FeN_2]^+$. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.20 (s, 9 H, Me), 4.26, 4.29, 4.46, 4.70, (4 m, 4×2 H, cyclopentadienyl H), 7.13–7.25 (m, 6 H, phenyl CH), 7.41–7.43 (m, 9 H, phenyl CH), 8.09 (s, 1 H, N_2CH). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ = 29.4 (CMe_3), 66.8 (CMe_3), 69.7, 70.1, 73.4, 73.5 (4× cyclopentadienyl CH), 86.3 (CPh_3), 90.9, 92.7 (2×cyclopentadienyl C_{ipso}), 129.1, 129.7, 131.2 (3×phenyl CH), 140.8 (phenyl C_{ipso}), 161.4 (N_2CH).

Synthesis of 5a: Toluene (5 mL) was added to $NaN(SiMe_3)_3$ (7.9 mg, 0.043 mmol) and **5a**H[BF_4] (20.5 mg, 0.048 mmol). The mixture was stirred for 30 min. Insoluble material was removed by filtration through a short pad of celite. The filtrate was reduced to dryness under vacuum. This afforded the product as a yellow microcrystalline solid. Single crystals suitable for XRD were obtained by slow evaporation of a toluene solution. Yield 13.2 mg (91%). ^{1}H NMR (500 MHz, C_6D_6): δ = 1.54 (s, 18 H, Me), 3.79, 3.96 (2 m, 2×4 H, cyclopentadienyl H). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ = 31.7 (CMe_3), 60.8 (CMe_3), 68.7, 69.6 (2×cyclopentadienyl CH), 100.3 (C_{ipso}), 260.9 ($C_{carbene}$).

Synthesis of 5b: $NaN(SiMe_3)_3$ (7.5 mg, 0.041 mmol) was added to a stirred suspension of **5b**H[BF_4] (25.0 mg, 0.045 mmol) in C_6D_6 (3 mL) cooled to 5 °C. The mixture was stirred at this temperature for 5 min. Insoluble material was removed with a syringe filter. The filtrate was subjected to immediate NMR spectroscopic analysis. ^{1}H NMR (400 MHz, C_6D_6): δ = 1.93 (s, 12 H, Me), 3.46, 3.74 (2 m, 2×4 H, cyclopentadienyl H), 7.14 (m, 2 H, phenyl H), 7.46, 7.57 (2 m, 2×4 H, phenyl H). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ = 31.4 (CMe_2), 65.7 (CMe_2), 68.4, 69.3 (2×cyclopentadienyl CH), 100.1 (cyclopentadienyl C_{ipso}), 126.5, 126.9, 127.9 (3×phenyl CH), 149.2 (phenyl C_{ipso}), 261.3 ($C_{carbene}$).

Synthesis of 5aS: Toluene (5 mL) was added to $NaN(SiMe_3)_3$ (8.0 mg, 0.044 mmol) and **5a**H[BF_4] (20.0 mg, 0.047 mmol). The mixture was stirred for 15 min. Sulfur (1.5 mg, 0.047 mmol S) was added. Stirring was continued for 45 min. Insoluble material was removed by filtration through a short pad of Celite. The filtrate was reduced to dryness under vacuum. This afforded the product as a light orange solid. Single crystals suitable for XRD were obtained by slow evaporation of an *n*-hexane solution. Yield 14.6 mg (90%) HRMS/ESI (+): m/z = 371.2213 $[M+H]^+$, 371.1244 cald. for $[C_{19}H_{27}FeN_2S]^+$. ^{1}H NMR (400 MHz, C_6D_6): δ = 1.68 (s, 18 H, Me), 3.90, 3.96 (2 m, 2×4 H, cyclopentadienyl H). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ = 29.7 (CMe_3), 61.8 (CMe_3), 69.9, 70.5 (2×cyclopentadienyl CH), 90.8 (C_{ipso}), 167.0 (CS).

Synthesis of 6a: Toluene (15 mL) was added to $NaN(SiMe_3)_3$ (72 mg, 0.39 mmol) and **5a**H[BF_4] (160 mg, 0.38 mmol). The stirred mixture was heated to 60 °C for 12 h and was then allowed to cool to ambient temperature. Volatile components were removed under vacuum. The residue was extracted with *n*-hexane (3×5 mL). The extracts were combined. Small amounts of insoluble material were removed by filtration. The filtrate was reduced to dryness under vacuum. This afforded the product as a bright yellow microcrystalline solid. Single crystals suitable for XRD were obtained by slow evaporation of a benzene solution. Yield 93 mg (92%). $C_{15}H_{18}N_2Fe$ (268.16): calcd. C 63.85, H 6.43, N 9.93%; found C 63.43, H 6.68, N 9.35%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.36 (s, 9 H, Me), 3.76, 3.90, 4.06, 4.18 (4 m, 4×2 H, cyclopentadienyl H), 7.56 (s, 1 H, N_2CH). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ = 30.7 (CMe_3), 57.6 (CMe_3), 60.4, 69.2, 69.9, 70.1 (4×cyclopentadienyl CH), 88.2, 107.9 (2×C_{ipso}), 151.6 (N_2CH).

Synthesis of 6b: Toluene (5 mL) was added to $NaN(SiMe_3)_3$ (6.7 mg, 0.037 mmol) and **5b**H[BF_4] (20.0 mg, 0.36 mmol). The stirred mixture was heated to 60 °C for 3 h and was then allowed to cool to ambient temperature. Insoluble material was removed by filtration. The filtrate was reduced to dryness under vacuum. This afforded the crude product as a sticky brownish solid. Further purification by crystallisation or chromatography was not attempted. Yield 12.4 mg (99%). HRMS/ESI (+): m/z = 345.1045 $[M+H]^+$, cald. 345.1054 for $[C_{20}H_{21}FeN_2]^+$. ^{1}H NMR (400 MHz, C_6D_6): δ = 1.33 (s, 6 H, Me), 3.76, 3.89, 4.05, 4.09 (4 m, 4×2 H, cyclopentadienyl H), 7.14 (m, 2 H, phenyl H), 7.22 (m, 3 H, phenyl H), 7.36 (s, 1 H, N_2CH). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ = 30.3 (CMe_2), 62.0 (CMe_2), 64.0, 69.3, 69.4, 70.2 (4×cyclopentadienyl CH), 87.6, 108.4 (2× cyclopentadienyl C_{ipso}), 126.2, 127.3, 128.9 (3×phenyl CH), 147.9 (phenyl C_{ipso}), 152.8 (N_2CH).

X-ray Crystallography: For each data collection a single crystal was mounted on a micro-mount at 100(2) K and all geometric and intensity data were taken from this sample. Data collections were carried out on a Stoe IPDS2 diffractometer equipped with a 2-circle goniometer and an area detector or a Stoe StadiVari diffractometer equipped with a 4-circle goniometer and a DECTRIS Pilatus 200 K detector. The data sets were corrected for absorption, Lorentz and polarisation effects. The structures were solved by direct methods (SHELXT) and refined using alternating cycles of least-squares refinements against F^2 (SHELXL2014/7).[54] C-bonded H atoms were included in the models in calculated positions, heteroatom-bonded H atoms have been found in the difference Fourier lists. All H atoms were treated with the 1.2 fold or 1.5 fold isotropic displacement parameter of their bonding partner. Experimental details for each diffraction experiment are given in Table S1 in the Supporting Information.

Supporting Information (see footnote on the first page of this article): Crystallographic data, plots of NMR spectra.

Deposition Numbers 2124099 (for **2a**), 2124100 (for **2c**), 2124101 (for **3**), 2124102 (for **4b**), 2124103 (for **4d**·$^1/_2$ C_6H_6), 2124104 (for **5a**H[BF_4]), 2124105 (for **5b**H[BF_4]), 2124106 (for **5e**H[BF_4]), 2124107 (for **5a**), 2124108 (for **5a**S), 2124109 (for **6a**H[BF_4]), 2124110 (for [$FeCl_2$(**6b**)$_2$]), and 2124111 (for **7**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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