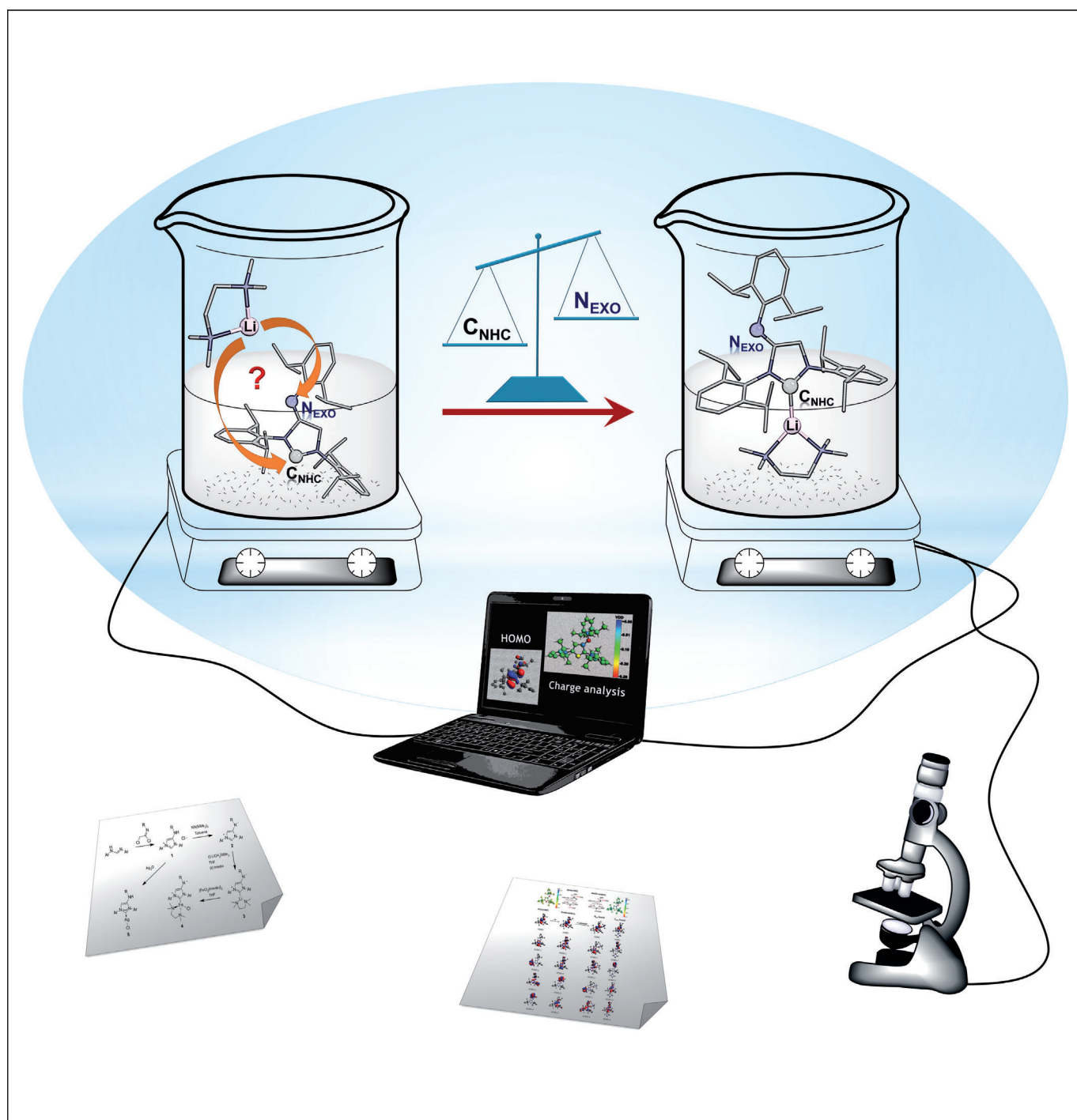


Anionic N-Heterocyclic Carbene Ligands from Mesoionic Imidazolium Precursors: Remote Backbone Arylimino Substitution Directs Carbene Coordination

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Dedicated to Professor Willie Motherwell on his retirement



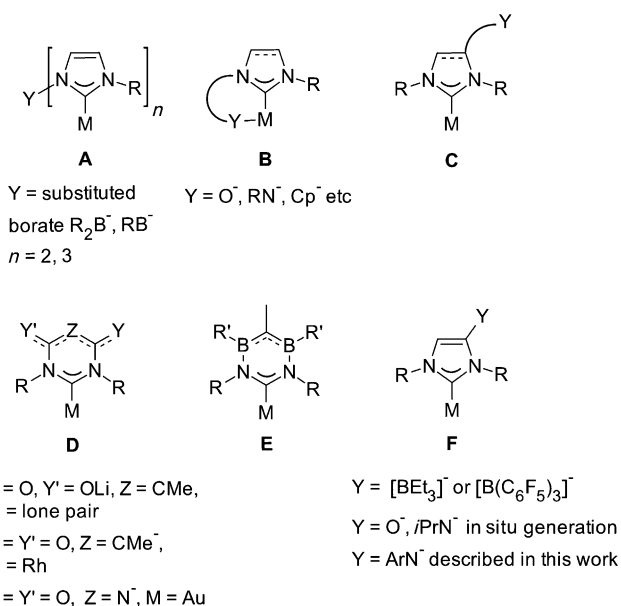
There is a rapidly growing interest in the chemistry of N-heterocyclic carbenes (NHC) bonded to early- and middle-transition metals, main-group elements, lanthanides, and actinides.^[1] This stems from intriguing observations on stabilisation of unusual coordination numbers, geometries, oxidation states, and bonding patterns^[2,3] and a number of still unsettled metal–NHC bonding issues.^[4,5] Anionic ligands confer higher stability to their complexes than neutral donors and this feature attracted us to anionic NHC ligands.^[6] Known and plausible approaches towards such ligands are summarised in Scheme 1. They include functional-

alities to one of the backbone atoms (remote from the C_{NHC} donor, structures **D–F**) facilitates interaction with the π -electron system of the heterocyclic ring and may lead to electronic tuning of the donor properties of the carbene function. It may also lead to “Janus-type” ligand coordination.^[9] However, only a limited number of formally anionic NHC and NHC related ligands are known, either type **D**, formally originating from pyrimidine betaine,^[10–12] type **E**, from diazadiborabenzene^[13] or type **F** from imidazolium mesoionic frameworks.^[14] Anionic NHC ligands of type **F** with Y = O[−] or *i*PrN[−] have been generated in situ but not fully characterised.^[15]

Relevant NHC-proligands (some of them being involved in tautomeric zwitterion–NHC equilibria)^[15b,16] and mesoionic NHC ligands have been recently prepared,^[17,18] and aspects of their coordination chemistry reported,^[9] they overall act as neutral ligands. The scarcity of information on the coordination behavior, scope, and tuning of anionic NHC ligands of type **F** (Y = anionic alkylamido or arylamido substituents) prompted our research in the area, with the long-term aim to access stable complexes without using chelating ligands as in type **B**. It is conceivable that a remote anionic amido functionality may incur an additional and/or competing metal-binding site (for similar behavior in pyrimidine betaine-derived anionic NHC ligands, see references [10–12]) leading to ligand polytopicity, ambidenticity or bimetallic coordination.^[9,12a,19] This potential extension is not anticipated in the boron backbone substituted ligands of type **F**.^[14]

Initially, attempts were made to establish the viability of well-defined, anionic NHC ligand-transfer reagents (type **F**, Y = ArN[−]; Ar = DiPP, 2,6-diisopropylphenyl) and, subsequently, to demonstrate their reactivity with metal precursors. *N*-arylamino functionalisation was chosen to take advantage of the steric and electronic tuning possibilities inherent to the aromatic ring substituent at the N_{exo}. Our results disclose the versatility of the ligand design and, with the help of density functional theory (DFT), provide an understanding of the scope associated with the choice of the remote N_{exo} substituent. Synthetic transformations are outlined in Scheme 2 and details are given in the Supporting Information.

The 4-(2,6-diisopropylphenyl)-substituted imidazolium chloride **1** was obtained in one step and selectively mono-deprotonated with one equivalent of KN(SiMe₃)₂ in toluene to give the light yellow zwitterion **2** (see Supporting Information for their crystallographic data).^[27] Importantly, the ¹H NMR spectrum of **2** exhibits two sharp doublets at room temperature at δ = 6.00 and 4.92 ppm assignable to the NCHN and NCHC protons of the heterocyclic ring and three septets and six doublets due to the isopropyl groups of the DiPPs. The appearance of the ¹H NMR spectrum provides evidence that, in solution, a single zwitterionic tautomer is present, and this is to be contrasted to the tautomeric equilibrium between the amino–NHC and the zwitterion tautomers observed when R = *i*Pr.^[15b] (Scheme 3). Compound **2** does not exhibit any sensitivity to moisture, in fact it can be crystallised from wet toluene as the monohydrate.

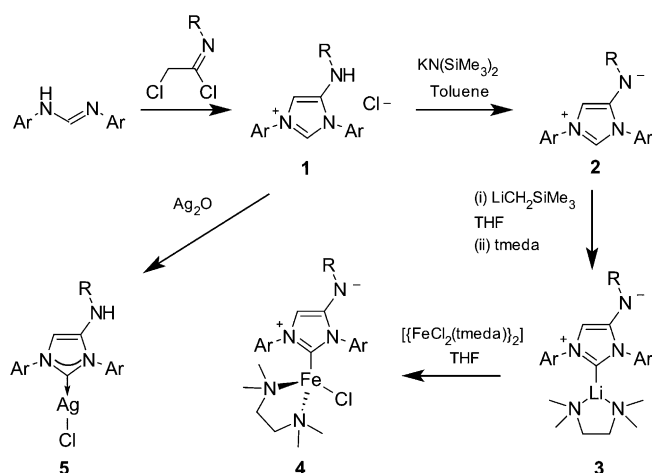


Scheme 1. Schematic summary of anionic ligands with NHC donors.

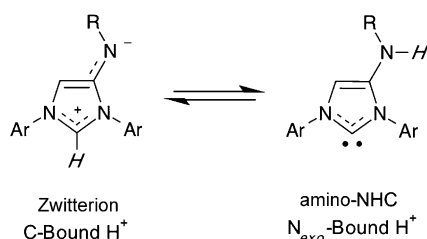
isation of the heterocyclic ring by an anionic group attached to one nitrogen atom either directly (type **A**) or through a linker (type **B**) or to one carbon backbone atom (type **C**). Furthermore, the negative charge could be delocalised over the backbone atoms of the heterocycle (types **D** and **E**). Currently, the most established approach comprises ligands of type **B**, in which hard anionic donors (e.g., RO[−], R₂N[−] etc.) participate in the formation of multi-dentate chelating architectures.^[6,7] Attachment of two or three NHCs to an anionic non-coordinating boron centre leads to ligands of type **A** (analogous to di- and tris-pyrazolylborates) that can coordinate to the metal solely through the 2e donor NHC(s).^[8] In contrast, direct attachment of anionic function-

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Scheme 2. The synthesis of the anionic NHC proligands and complexes with arylamino/arylimino remote backbone substituent; Ar and R = DiPP. Canonical forms with localised π systems are shown for simplicity, even though the anionic charge is delocalized over the ligand framework. The metallated-zwitterionic heterocycles in **3** and **4** are anionic ligands, bound to Li^+ and Fe^{2+} , respectively.



Scheme 3. Possible tautomeric equilibrium involving the meso-ionic and the amino NHC species.^[15b] For **2** (Ar, R = DiPP) only the zwitterionic form is detected by ^1H NMR spectroscopy.

Aiming to access an anionic ligand, we reacted **2** with $\text{LiCH}_2\text{SiMe}_3$ in THF which cleanly afforded an orange microcrystalline, extremely sensitive solid that after the addition of tmeda gave crystals of **3**- C_7H_8 from toluene (tmeda = *N, N, N', N'*-tetramethylethylenediamine).

Characteristically, in the ^1H NMR spectrum of **3**, the two doublets mentioned previously for **2** have given way to one singlet, indicating that further overall deprotonation had occurred on the ring. The presence of Li in solution was supported by ^7Li NMR spectroscopy; however, in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum a signal assignable to C_{NHC} was not observable. The structure of **3** was unequivocally established crystallographically (Figure 1, Scheme 4).^[27]

As seen in Figure 1, the $\text{Li}(\text{tmeda})$ moiety is bound to the heterocycle through the C_{NHC} . Based on the asymmetric unit contents and the experimental location of relevant hydrogen atoms of the molecule, the ligand is described as mono-anionic (cf. Me in MeLi). The $\text{C}_{\text{NHC}}-\text{N}$, the backbone $\text{C}2-\text{C}3$ and the $\text{C}3-\text{N}3$ bonds have partial double-bond character ($\text{C}1-\text{N}1$ 1.3511(18), $\text{C}1-\text{N}2$ 1.3840(18) Å). The rather short $\text{C}28-\text{N}_{\text{exo}}$ bond is indicative of electron delocalisation over the DiPP ring. The $\text{Li}-\text{C}_{\text{NHC}}$ bond length (2.093(3) Å) is close to the recently reported values (2.092(2)/2.094(3) Å)

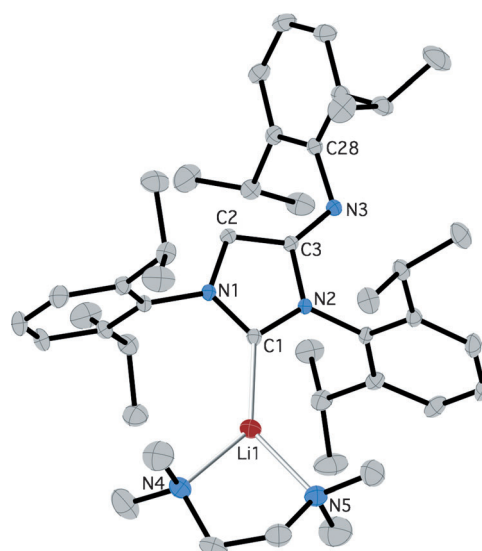
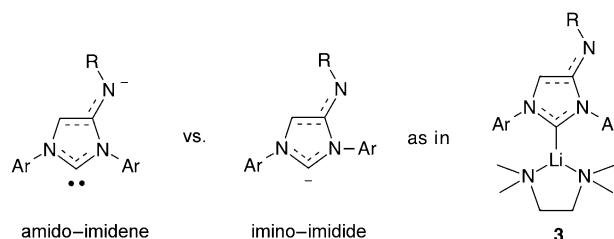


Figure 1. The molecular structure of **3**; ellipsoids are at 30% probability level. One molecule of toluene in the asymmetric unit is omitted for clarity. Selected bond lengths [Å] and angles [°]. $\text{Li}1-\text{C}1$ 2.093(3), $\text{C}1-\text{N}1$ 1.3511(18), $\text{C}1-\text{N}2$ 1.3840(18), $\text{C}2-\text{N}1$ 1.3964(18), $\text{C}3-\text{N}2$ 1.4256(17), $\text{C}2-\text{C}3$ 1.384(2), $\text{C}3-\text{N}3$ 1.3257(18), $\text{C}28-\text{N}3$ 1.4085(19); $\text{C}3-\text{N}3-\text{C}28$ 116.19(12), $\text{N}1-\text{C}1-\text{N}2$ 102.08(11), $\text{N}1-\text{C}1-\text{Li}1$ 129.47(13), $\text{N}2-\text{C}1-\text{Li}1$ 128.45(13).



Scheme 4. The anionic NHC ligand and its valence isomeric amido carbene (Ar, R = DiPP).

for complexes of type **F** (Scheme 1) with $\text{Y} = \text{B}(\text{Et}_3)$, $\text{B}(\text{C}_6\text{F}_5)_3$, $\text{M} = \text{Li}(\text{tmeda})$ or $\text{Li}(\text{thf})_2$, respectively,^[14] and consistent with three-coordinate $\text{Li}-\text{tmeda}$ alkyls^[20] (average 2.122 Å). Thus, **3** can be viewed as being composed of an anionic NHC ring functionalised in the backbone position by an arylimino group or as a neutral NHC with an anionic amido substituent at a backbone position. Considering the observed metrical data, **3** could also be described as a one-heteroatom-substituted diamino Alder-type carbene^[21] linked through two $\text{C}-\text{N}$ single bonds to an anionic azaallyl structure (see below for the discussion comparing metrical data).

The deprotonation of **2** could also be achieved by using $\text{KN}(\text{SiMe}_3)_2$ in $[\text{D}_8]\text{THF}$. The ^1H NMR spectrum of the product was very similar to that of **3**; however, in this case the C_{NHC} signal in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum was observed at $\delta = 202.3$ ppm. We cannot yet conclude whether the K^+ is coordinated to the C_{NHC} (in analogy with the Li in **3**) or is involved in a solvent-separated ion pair with the anionic NHC ligand or, less likely, coordinated to the *exo*-nitrogen atom. Further work in this direction is in progress.

The consequences of the deprotonation and metallation of **2** to give **3** (Scheme 4) and the influence of the R substituent at N_{exo} on possible tautomeric equilibria (Scheme 3)^[15b] were explored by DFT calculations at the BP86/TZ2P level. In particular, it was desirable to establish possible influence of the N_{exo} substituent R on the preference for the formation of C-bound versus N_{exo} -bound H^+ and $Li(tmeda)^+$. The study of the electronic and steric effects of R involved: 1) the optimisation of the structures of the corresponding C and N_{exo} valence-bond- and regioisomers and tautomers; 2) the calculation of their relative (ΔE_{rel}) and bond dissociation (D_e) energies for R=Me, *i*Pr, *t*Bu, Ph, and DiPP; 3) the probing of any steric effects inherent to the $Li(tmeda)^+$ fragment, by employing “naked” Li^+ in place of $Li(tmeda)^+$ (see Schemes S1–S4, Supporting Information and discussion on computational methodology). As a result, for all R substituents we observed that H^+ prefers to be C-bound by approximately 18–30 kJ mol⁻¹ when R=Me, *i*Pr and approximately 43–53 kJ mol⁻¹ when R=Ph, DiPP (Scheme S1 in the Supporting Information). This is in agreement with our experimental observations (see also Scheme 3). In contrast, Li^+ prefers to be N_{exo} -bound by approximately 50 kJ mol⁻¹ when R=Me and *i*Pr and approximately 45 kJ mol⁻¹ when R=Ph and DiPP (Scheme S2 in the Supporting Information), although in the latter case additional stabilising interactions with adjacent aromatic rings were also detected in the optimised structures (Scheme S3 in the Supporting Information). The observed H^+ and Li^+ site preference is consistent with the high affinity of H^+ for C_{NHC} ^[22] and carbanions, and of Li^+ for amide (NH_2^- ; Tables S3 and S4 in the Supporting Information).

Interestingly, $Li(tmeda)^+$ is calculated to prefer N_{exo} binding by approximately 4–13 kJ mol⁻¹ when R=Me and *i*Pr, but C_{NHC} binding by approximately 4–20 kJ mol⁻¹ when R=Ph, DiPP and *t*Bu (Scheme S4 in the Supporting Information). Here, inter-

linked steric and electronic factors are at work as detailed below.

Steric effects associated with complexation of $Li(tmeda)^+$ to N_{exo} of the anionic NHC ligands were evaluated as a function of R by calculation of the % V_{bur} ^[23] for the optimised structures of 1) the amido–imidene anions (i.e., no $Li(tmeda)^+$ coordination) and 2) the amido–imidene– $Li(tmeda)$ complexes (for more details, see Figures S12 and S13 in the Supporting Information). In the amido–imidene anions and the amido–imidene– $Li(tmeda)$ complexes, the values of % V_{bur} fall in the range 56–69 and 47–57%, and increase in the order Me < *i*Pr < Ph < DiPP < *t*Bu and Me < Ph < DiPP < *i*Pr < *t*Bu, respectively. In contrast, the C_{NHC} binding site is sterically more open in the anionic NHC ligands, with a

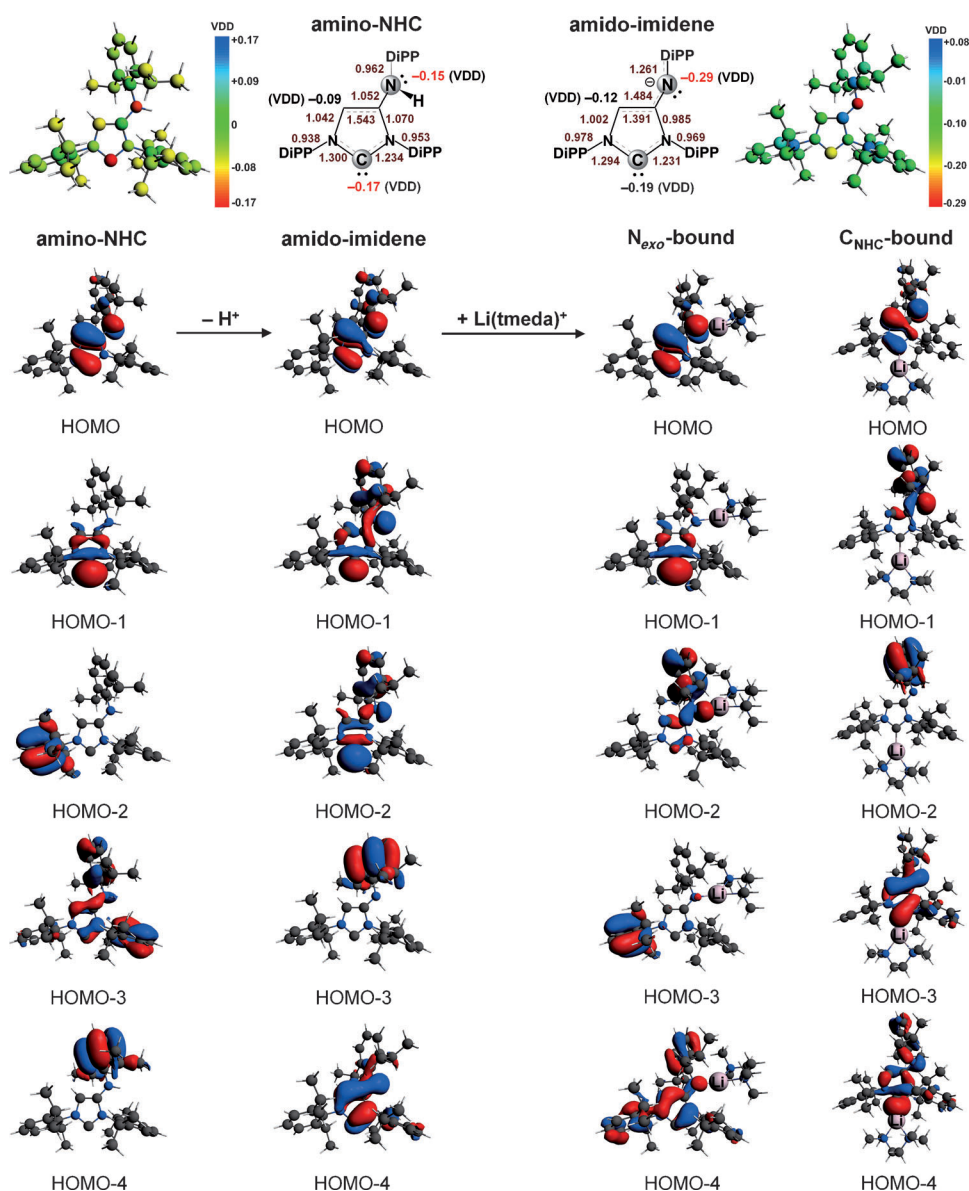


Figure 2. Distribution of the Voronoi deformation density (VDD) atomic charges, Mayer bond orders and relevant highest occupied molecular orbitals (± 0.03 isosurface value) of the amino-NHC, the anionic amido-imidene ligand, and the N_{exo} - and C_{NHC} -bound $Li(tmeda)$ complexes for R=DiPP showing the orbital evolutionment when going left to right.^[24]

minor influence of R ($\% V_{\text{bur}} = \text{ca. } 43\text{--}50\%$, $\text{Me} \approx i\text{Pr} \approx t\text{Bu} < \text{Ph} < \text{DiPP}$). This is also the case for C_{NHC} after $\text{Li}(\text{tmeda})^+$ coordination ($\% V_{\text{bur}} = \text{ca. } 39\text{--}43\%$, $\text{Ph} < t\text{Bu} \approx \text{Me} \approx i\text{Pr} < \text{DiPP}$). The comparison between the sterics around N_{exo} and C_{NHC} binding sites explains the preference of $\text{Li}(\text{tmeda})^+$ to bind to C_{NHC} rather than to N_{exo} on replacing $\text{R} = \text{Me}$ or $i\text{Pr}$ with $t\text{Bu}$ because of unfavorable deformations of steric origin in the latter. In the $t\text{Bu}$ case, even nonsymmetrical Li-tmeda chelates are observed (see $\Delta(\text{Li-N})_{\text{tmeda}}$ in Figure S12 and calculated deformation energies, ΔE_{def} , in Table S5 of the Supporting Information).

The differences in the relative energies for $\text{R} = \text{Ph}$, DiPP , and $i\text{Pr}$ should be ascribed to the contribution of steric and electronic factors to the deformation energies of the amido-imidene fragment upon coordination. The fact that $\text{Li}(\text{tmeda})^+$ complexation results in the reversal of the order of $\% V_{\text{bur}}$ as a function of R points to a substantial readjustment of metrical parameters in order to accommodate the metal fragment with its energetic consequences. Conformational changes involving the aromatic ring at the N_{exo} (for example, but not exclusively, the torsional angle formed by the $\text{C3-N}_{\text{exo}}\text{-C28}$ plane and the DiPP ring) are indeed expected to influence the π delocalisation on the ring and the remaining ligand framework. Extensive π -electronic delocalisation over the whole amido-imidene framework is consistent with metrical data for the optimised and experimental structures (see Figure 2 for frontier MOs and Mayer bond orders for $\text{R} = \text{DiPP}$ and Figures S7 and S8 in the Supporting Information). This, in combination with the reduced electrophilicity of $\text{Li}(\text{tmeda})^+$ compared to Li^+ (compare VDD charges of +0.33 and +1.00, respectively) results in a weaker Li-N_{exo} -amido bond that cannot compensate for the energy demands of the conformational changes implied above (see calculated bond dissociation energies, D_e , in Table S6 of the Supporting Information).

The idea of using **3** as a ligand-transfer reagent was also examined. In view of the current high interest in iron chemistry, **3** was reacted with $[\{\text{Fe}(\mu\text{-Cl})\text{Cl}(\text{tmeda})\}_2]$ to access novel Fe-NHC complexes of catalytic potential (Scheme 2). Extremely air- and moisture-sensitive green crystals of **4**·THF were obtained and characterised by spectroscopic and diffraction methods (see Figure 3 and the Supporting Information).^[27]

The tetrahedral Fe^{II} is bound through C_{NHC} to the anionic heterocyclic ligand and additionally to a chloride. Interestingly, the Fe-C_{NHC} bond is shorter than in other Fe^{II} monodentate NHC complexes of Fe (2.122(2)–2.177(3) Å) and other anionic alkyls and aryls on tetrahedral Fe (2.111(3)–2.168(3) Å), but slightly longer than in alkyls of three-coordinate Fe (2.056(2)–2.063(3) Å).^[2,25] Compared to the metrical data of the ligand framework in **3**, there is elongation of the $C_{\text{NHC}}\text{-N}$ bonds in **4**, possibly implying reduced π donation to the C_{NHC} p_z orbital and increased interaction of the p_z orbital with Fe d_{π} orbitals. Consistent with the predominantly single-bond character of N1-C2 and N2-C3 , the metrical data of the azaallyl-type backbone moiety of the ligand are virtually identical in **3** and **4**.

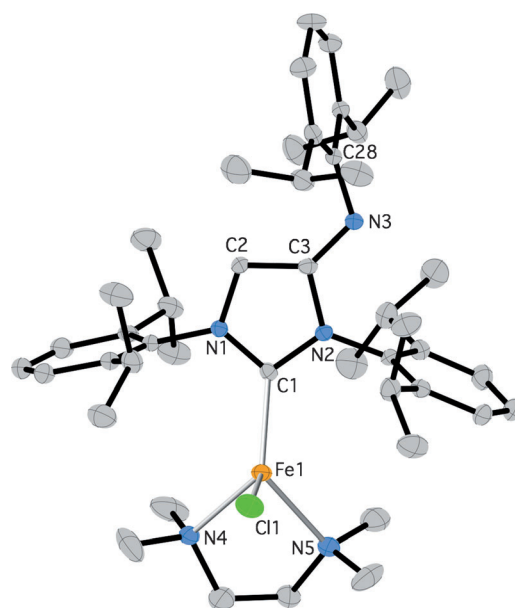


Figure 3. The molecular structure of **4**; ellipsoids are at 30% probability level; one THF molecule in the asymmetric unit is omitted. Selected bond lengths [Å] and angles [°]. C1-Fe1 2.090(2), N4-Fe1 2.1775(19), N5-Fe1 2.209(3), Cl1-Fe1 2.2682(8), C1-N1 1.339(3), C1-N2 1.396(3), C2-N1 1.389(3), C3-N2 1.413(3), C2-C3 1.390(3), C3-N3 1.327(3), C28-N3 1.412(3); N1-C1-N2 103.09(19), C1-Fe1-Cl1 115.17(7), N4-Fe1-Cl1 99.59(6), N5-Fe1-Cl1 102.96(8), C1-Fe1-N4 124.91(9), C1-Fe1-N5 125.85(10), N4-Fe1-N5 81.44(8), C3-N3-C28 117.7(2).

In order to compare the structures of the anionic imino-imidide moieties in **3** and **4** with that of a neutral amino-NHC moiety, we prepared the Ag^{I} complex **5** by the reaction of Ag_2O with **1** (Scheme 2).

Complex **5** (Figure 4) comprises a linear two-coordinate Ag centre with a typical Ag-C_{NHC} bond length.^[26] The dif-

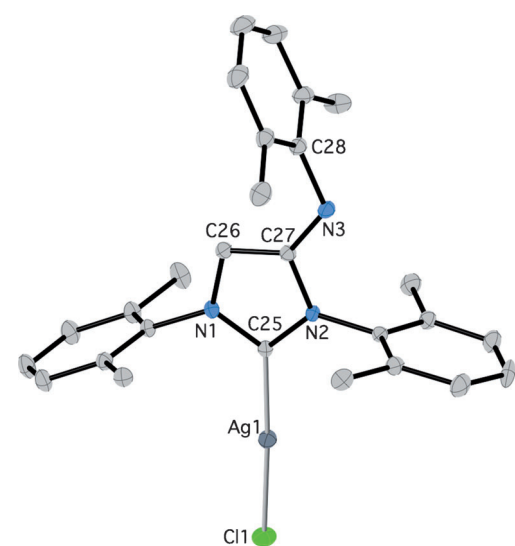


Figure 4. The molecular structure of **5**; ellipsoids are at 30% probability level. The N3-H and the methyls of DiPP groups are omitted. Selected bond lengths [Å] and angles [°]. C28-N3 1.4085(19), C25-N1 1.347(2), C25-N2 1.368(2), C25-Ag1 2.0735(16), C27-N3 1.375(2), C26-C27 1.355(2); C25-Ag1-Cl1 175.65(4), N1-C25-N2 104.09(13).

ferences between the amino–NHC form in **5** and the imino–imide form in **3** and **4** manifest themselves in the C–N_{exo} and the C–C lengths of the heterocycle, which are shorter and longer in **3** and **4** respectively, relative to **5**, in accordance with an azallylic character in **3** and **4** as opposed to an enamine in **5**.

In conclusion, we have demonstrated through a combined experimental and computational study the versatility, and potential tunability of the anionic 4-arylimino-substituted-imidazole-based NHC ligands and showed their transferability to transition metals. Although the nitrogen versus carbon binding affinity may depend on the metal–complex fragments and other subtle effects, it is evident that the remote backbone substitution offers a versatile way to develop novel anionic NHC ligands. This is currently being explored in our laboratory by experimental and computational methods.

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Keywords: imidazolium • iron • lithium • N-heterocyclic carbenes • silver

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