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'Janus-type' Organopotassium Chemistry by Deprotonation of Mesoionic Imidazolium Aminides and Amino N-Heterocyclic Carbenes: Coordination and Organometallic Polymers

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The first direct observation of the tautomeric equilibrium between mesoionic *I*midazolium *A*minides (*IA*) and *A*mino NH*C*s (*AC*) shows its dependence on the aminide substituent. A potassium (imidazol-2-ylidenyl)(anilide), an ion-pair with the 'free' anionic NHC, and potassium organometallic polymers, with the repeat unit exhibiting 'Janus-type' coordination, are reported.

There is considerable and general interest in the study of novel, 'unconventional' carbene- and carbenoid-species, in which the heteroatom stabilisation of the divalent carbon atom participating in the heterocyclic ring is diminished, resulting in more reactive chemical entities.¹ The objective is to uncover novel bonding patterns and reactivity with applications in coordination chemistry and in catalysis with metal-based or metal-free systems. Mesoionic carbenes (MIC) have emerged as a new, broad class of N-heterocyclic carbenes (NHCs).²⁻⁴ They are reactive, usually transient species, generated *in situ* in the presence of metals.

Tautomeric equilibria between mesoionic azolium compounds (a sub-class of mesomeric betaines)⁵ bearing a remote aminide (i.e. amido) substituent and (non-mesoionic) remote amino NHCs have been recently postulated in two cases.⁶ This was based on the 'carbene-like' reactivity of the mesoionic azolium compound, albeit the corresponding carbene partner has only been implicated. We have now directly observed the equilibrium between *I*midazolium *A*minides (*IA*), imidazolium-4-aminides, and their tautomeric *A*mino-NHCs (*AC*), 4-aminoimidazol-2-ylidenes (Scheme 1) and isolated key derivatives of general relevance. Deprotonation of any of the tautomers in this equilibrium would give an *overall anionic* NHC (Scheme 2).

Recently, we obtained computational evidence that the nature of the R group at the exocyclic aminide N atom (N_{exo}) influences the position of the equilibrium (Scheme 1) and the coordination behaviour of the anionic NHC (Scheme 2).⁷ In view of the more pronounced ionic character of the potassium organometallics, compared *e.g.* to the lithium analogues,^{8a} and the widely recognised property of potassium not to be involved in adduct formation with NHCs,^{2-3,8b-d} we used benzyl potassium (KBz) as a base to access anionic NHCs.



Scheme 1. Equilibrium between (*IA*) and (*AC*) tautomers. In the text a tautomer is designated as n(IA) or n(AC) and an equilibrium mixture as $n(IA \leftrightarrows AC)$, n = 1 - 6.

We now demonstrate *experimentally* that by suitable selection of R we can: (i) observe the equilibrium of Scheme 1 by NMR spectroscopies; (ii) isolate and characterise one monomeric potassium (imidazol-2-ylidenyl)(anilide), and one '*free' anionic* NHC (accompanied by the non-interacting cation [K(18-crown-6)]⁺), and (iii) obtain (co)polymeric organometallics in which anionic NHC repeat units act as ambidentate, 'Janus-type' ligands⁹ (Scheme 3). The only related *anionic* NHCs are with B-, P- or (*t*-Bu)₂Znremote substitution and the anionic dicarbenes (carbanionic carbenes).¹⁰



Scheme 2. Resonance forms of (*IA*) (top) and of the anionic NHC derived thereof (bottom).

Even though the (*IA*) form was exclusively present in solution and the solid state when R = mesityl and 4-*t*-Bu-phenyl, the position of the tautomeric equilibrium was shifted toward the (*AC*) form for R = t-Bu, especially in aromatic solvents at room temperature. The ¹H- and ¹³C-NMR data (see ESI) provided unequivocal evidence for an equilibrium in favor of the (*AC*) form ($K_{RT} = 1.5$). Lowering the temperature in toluene to -60 °C shifted the equilibrium to K = 0.9, while in THF there was no significant temperature dependence. Importantly, attempts to crystallise **6**(*AC*) from pentane at -40 °C gave only crystals of **6**(*IA*) (crystal structure in the ESI), which on redissolving in toluene restored the original equilibrium mixture. For **n**(*IA* \equiv *AC*), n = 4, 5, $K_{RT} \approx 0.25$ in toluene. The mechanism by which the *t*-Bu influences the position of the equilibrium is not clear. Plausible explanations may invoke the reduced electronegativity of *t*-Bu compared to *i*-Pr and Cy¹¹ leading to destabilisation of **6**(*IA*) (ESI) does not reveal any significant differences. DFT calculations are in progress.



Scheme 3. Synthesis of potassium derivatives (localised K-C, K-N and K-O bonds are represented as solid, cation- π interactions as dotted, bonding interactions of neighboring polymer repeat units as dashed lines); Ar = 2,6-*i*-Pr₂-C₆H₄, DiPP: (i) 1.25 equiv. KBz, 1.20 equiv. 18-crown-6 in THF; (ii) 1.25 equiv. KBz, in THF; (iii) 1.20 equiv. KBz in THF; (iv) 1.70 equiv. KBz in THF.

Deprotonation of **1**(*IA*) with KBz in slight excess (1.2 fold) in THF gave highly air sensitive **7** after crystallisation at -40 °C. Complex **7** (Fig. 1) can be considered as *formally* arising from deprotonation of **1**(*AC*) by KBz; the K⁺ coordination sphere comprises one aminide group bound *via* the planar N_{exo} , and three THF molecules. Additional stabilisation is provided by interaction with the π -system of the proximal DiPP; there is no close contact involving the C_{NHC} . The deprotonation was evidenced by the disappearance of the two doublets due to the two ring Hs of **1**(*IA*) at δ 6.00 and 4.92 and the appearance of a singlet at δ 4.76, due to the only H left on the heterocycle. In solution in THF the K⁺- π -aromatic system interaction is non-rigid as evidenced by the broadness of the *i*-Pr and the aromatic proton signals associated with this particular ring, and by variable-temperature NMR spectroscopy. Deprotonation with KN(SiMe₃)₂ gave the same product less cleanly.

Reaction of 1(IA) with one equiv. KBz in the presence of 18crown-6 afforded the extremely air sensitive **8** which was structurally characterised (Fig. 2). It comprises a pair of wellseparated discrete ions: the cation [K(18-crown-6)]⁺ and the 'free' deprotonated NHC. The heterocyclic ring, the N_{exo} and the C_{ipso} atoms of all three DiPP substituents are coplanar, in support of extensive electronic delocalisation (ESI). The reduction of the angle at the C_{NHC} points to increased s-character in the σ -lone pair compared to the C-H σ -bonding orbital of the imidazolium. This is a recurring observation with other imidazolium-NHC conjugate acid-base pairs. Spectroscopically, the deprotonation was evidenced by the disappearance of the two doublets associated with the two ring protons of 1(IA) at δ 6.00 and 4.92 and the appearance of a singlet at δ 4.76 (see also above for 7), however in **8** there is no evidence of fluxionality at room temperature.



Figure 1. Structure of 7.

Deprotonation of the less bulky 3(IA) and $4(IA \leftrightarrows AC)$ with 1.2 equiv. of KBz gave good yields of the polymeric complexes 9 and 10 shown in Figures 3 and 4, respectively.



Figure 2. Structure of the anion in 8; the [K(18-crown-6)]⁺ is omitted.

Unexpected results were obtained on attempted second deprotonation from n(IA), n = 1-3. Thus, reaction of 1(IA) with at least 1.70 equiv. of KBz in THF afforded the new organometallic species 12 as orange, extremely air sensitive crystals of limited solution stability at ambient temperature (see ESI).



Figure 3. Structure of 9; four consecutive repeat units (one in red) are shown.

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The structure of **12** (Fig. 5) revealed the formation of an organometallic copolymer, the repeat unit of which comprised two metallated anionic NHCs bound through their N_{exo} to one potassium cation and through the C_{NHC} to another potassium cation; the latter is also interacting with a bridging μ - η^6 -anionic benzylic group bound to a third potassium cation; the coordination sphere of the two potassium cation bound to C_{NHC} is completed by THF molecules.

The K2-C1 bond length falls into the short end of the range for the number of K-C bonds that have been structurally characterised (average 3.183 Å) but are typical of other K- $C_{\rm NHC}$ bonds (see also above).



Figure 4. Structure of 10; four consecutive repeat units (one in red) are shown.



Figure 5. Structure of copolymer 12; one repeat unit is shown in red; due to symmetry the $KCH_2C_6H_5$ (C51) has half-occupancy

In conclusion, the choice of the N_{exo} substituent allows tuning of the (*IA*) vs. (*AC*) equilibrium and influences the nature of the anionic products obtained by deprotonation of the equilibrium partners. The study of these parameters for the synthesis of metal complexes are in progress. Exploration of any effect that the organic substituent at the N_{exo} has on the coordination modes adopted by the anionic NHC, could lead to novel organometallics.

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Notes and references

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