Thermally stable potassium N-heterocyclic carbene complexes with alkoxide ligands, and a polymeric crystal structure with distorted, bridging carbenes†

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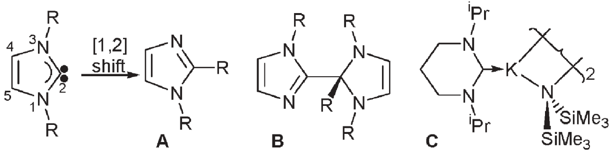
Alkoxide-functionalised N-heterocyclic carbenes (NHCs) stabilise the potassium-imidazole-2-ylidene fragment against 1,2 alkyl rearrangement reactions; this allows the first structural characterisation of a potassium NHC complex, which reveals distorted and unusual bonding interactions between the imidazole ring and the potassium cation.

The range of N-functionalised N-heterocyclic carbenes is expanding rapidly since a large and diverse range of homogeneous catalysts rely on NHC-based supporting ligands for steric and electronic control. The general synthetic route to most free carbene ligands involves the deprotonation of an imidazolium precursor at the C2 position with Group 1 bases, of which potassium *tert*-butoxide is the most commonly reported. As more N1- and N3-functional groups are incorporated into NHC ligands to tune the homogeneous catalysts, the opportunities for making NHC complexes in which the Group 1 metal cation is incorporated increases. In addition to enjoying widespread use for the *in situ* synthesis of NHC-based homogeneous catalysts,[4–6] potassium *tert*-butoxide is also used as an additive in many organic reactions that are catalysed by preformed palladium–NHC complexes.[7] Isolated Group 1 NHC salts are still rare,[1,2] but are now being shown to be effective and less costly transmetallation reagents than the labile silver(I) adducts also sometimes used as less air-sensitive vehicles for the NHC group. We have made lithium carbene complexes that are significantly more air-stable than the free carbenes, and used them to deliver the NHC group to copper(I), copper(II), and f-block cations.[2,3]



However, unlike their lithium counterparts, previously reported attempts to isolate potassium NHC complexes have resulted in the migration of an N-hydrocarbyl group to C2 to form cyclic imines **A** or amino-Claisen isomers **B**.[8–11] The only potassium diaminocarbene-type complex to have been isolated so far is that of a saturated, non-imidazole based system, $[K(C\{N(Pr^i)CH_2\}_2CH_2)(N\{SiMe_3\}_2)]$ **C**, which has been structurally characterised.

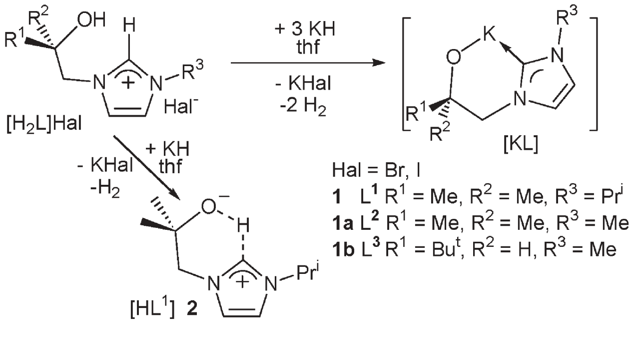
Thus, the reactivity, rearrangement, and even potential dimerisation[12] chemistry of even transiently formed potassium NHC complexes has potentially widespread significance in catalysis and organic chemistry.

Herein, we report how the use of O-functionalised N-alkyl arms on the imidazolium complexes allows a straightforward synthesis of the first thermally stable potassium salts of N-heterocyclic carbenes, and present the first crystal structure of a potassium NHC complex.

The reaction of the alcohol-functionalised imidazolium iodide $[H_2L^1]I$ with an excess of potassium hydride in thf affords the potassium alkoxide carbene $K[OCMe_2CH_2(1\text{-}C\{NCHCHNPr^i\})]$, KL^1, **1**, as a colourless powdery solid in high yield, Scheme 1 (see ESI†).‡ Related thermally stable potassium N-heterocyclic carbene complexes $[KOCR^1R^2CH_2(1\text{-}C\{NCHCHNR^3\})]$, **1a** and **1b**, are also readily made.

The ^1H NMR spectrum of a benzene-d_6 solution of **1**, isolated from thf, shows a single, symmetrical set of resonances assigned to deprotonated L^1, with no coordinated thf, and no resonance attributable to any rearranged product; the ^{13}C NMR spectrum shows a high-frequency $C_{carbene}$ chemical shift of 208.4 ppm.

The potassium salt KL^1 is very soluble in toluene and thf; single crystals suitable for X-ray analysis were grown from a thf solution by slow evaporation of solvent (96 h, 25 °C).§ The structure, Fig. 1, is polymeric, and based on a network of $[KL^1]_4$ tetramers with cube-shaped K_4O_4 cores. Ignoring the many close agostic-like potassium–hydrocarbyl contacts, each metal is four-coordinate—binding to three O atoms of L^1 and a carbene C2, except for one potassium in alternate cubes, which has an additional thf coordinated. All of the NHC groups bind to a potassium through



Hal = Br, I
1 L^1 R^1 = Me, R^2 = Me, R^3 = Pr^i
1a L^2 R^1 = Me, R^2 = Me, R^3 = Me
1b L^3 R^1 = Bu^t, R^2 = H, R^3 = Me

Scheme 1 Synthesis of potassium carbene complexes.

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† Electronic supplementary information (ESI) available: Full synthetic details for complexes and crystallographic data for **1**. See http://www.rsc.org/suppdata/cc/b4/b418302a/

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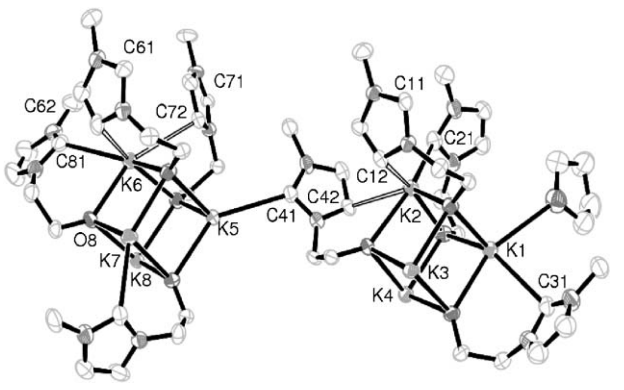


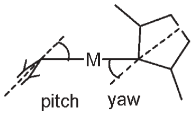
Fig. 1 Thermal ellipsoid drawing of **1** (50% probability). Methyl groups and H omitted for clarity. Selected distances (Å) :K(1)–C(31) 2.984(5), K(2)–C(21) 3.053(5), K(3)–C(71) 3.128(4), K(4)–C(11) 3.157(4), K(5)–C(41) 3.068(4), K(6)–C(81) 2.947(5), K(7)–C(51) 2.991(5), K(8)–C(61) 3.055(4), K(1)–O(1) 2.656(3), K(1)–O(100) 2.984(4).

the 'normal' C2 carbon. Additionally, some of the C4 and C5 carbon atoms display close, potentially bonding contacts with other potassium cations. In addition, four L^1 ligands bind to more than one cube using both the alkoxide and carbene C2 donors, completing the network. To the best of our knowledge, this is the first example of a neutral NHC-based organometallic polymer.

The carbene heterocycles display a wide range of K–CN_2 geometries other than the anticipated trigonal planar carbon. The range of pitch angles, measured as the vertical angle between M–C and the NCN plane are between 9 and 52°, Fig. 2, distortions previously unseen in late metal carbene complexes.

Previously, we reported severe M–CN_2 distortions (a pitch angle of 20°) in a lithium NHC complex $[Li\{N(Bu^t)CH_2CH_2(1\text{-}C\{NCHCHNBu^t\})\}]_2$, and the lithium salt of **1b** [LiL^3·LiI], which also crystallises as a Li_4 tetramer, and has a pitch of 19° and a yaw (horizontal distortion) angle of 22°.[2,13] The average K–C2 bond length is 3.048 Å, (*cf* 3.00 Å in **C**) and importantly here, there is no apparent correlation between the angle of the distortion and the bond distance. The binding of even a distorted NHC in preference to thf again supports the dominance of electrostatic effects in the bonding between the hard metal cations and soft polarisable NHCs.

The ligands based on C10, C40, and C60 bridge the cubes. In these the C2 carbene geometries are now closer to trigonal planar, but interestingly, the backbone C4 and C5 atoms also display unprecedented close contacts with the adjacent potassium cation. These interactions are reminiscent of the increasing number of 'wrong carbene' adducts being reported as (unanticipated) products arising from a [1,4] H shift in which one backbone carbon, C4 or C5 is deprotonated and binds as a donor instead of C2.[14] This H rearrangement has even been observed to occur when a 'normal' free carbene $[\{1,1,1\text{-}(C\{NCHCHN(Bu^t)\})CH_2\}_3CMe]$, is complexed by Cu(I) to yield a bis(carbene) alkenyl complex[15] and recently IR studies on Ir(III) complexes have suggested that the C5-bound carbene is a better donor than the C2-bound.[16] In the crystal structure of **1**, three of the close contacts with other NHC ring carbons are within the sum of the potassium and carbon covalent radii: The closest backbone C interactions are K2–C42 3.083(4) Å, K6–C62 3.135(5) Å, and K6–C72 3.161(4) Å. For comparison, the average K–C distance in potassium cyclopentadienide complexes is 3.10 Å.[17] Close contacts with arene, phenol, and pyrrole ligands are increasingly reported in the organometallic literature, since often the additional reducing electrons provided by incorporated potassium affords unusual reduced dinitrogen and carbon dioxide adducts of the most electropositive metals.[18–20] In these complexes, K–C distances of about 3.3 Å are reported.



metal:	K4	K5	K8	K3	K6	K1	K2	K7
pitch(°):	9	13	17	21	36	41	43	52
yaw(°):	5	7	3	7	6	10	7	12
M-C(Å):	3.16	3.07	3.06	3.13	2.95	2.98	3.05	2.99

Fig. 2 Potassium carbene fragment metrics ordered by pitch angle.

While it is possible that these backbone carbon atoms could be considered sp^3 hybridised to bond with the potassium ions, this seems unlikely since the heterocycle NC and CC distances are still short, and upon redissolution the ^1H NMR spectrum of **1** is regenerated.

The elemental analysis data fit (within the 0.4% criterion) for both the formulation KL^1 measured by ^1H NMR spectroscopy, and for $[KL]_8$thf measured crystallographically. The solution spectroscopic data suggest that the polymeric, polynuclear structure of **1** is not retained in solution, but the observation of low-mass fragments based on $[K(NHC)_2]^+$ in the EI mass spectrum suggest the clusters do not readily separate into simple KL monomers or dimers upon volatilisation from the solid.

We also note that treatment of the imidazolium iodide $[H_2L^1]I$ with just one equivalent of KH in thf affords a zwitterionic, toluene-soluble, imidazolium alkoxide $[OCMe_2CH_2(1\text{-}HC\{NCHCHNPr^i\})]$ HL^1, **2** that can be isolated as a very hygroscopic pale cream powder in excellent yield. The approximate pK_as of *N*,*N′*-dimethyl imidazolium salts and *tert*-butanol are 23 and 15, respectively, but the acidic C2 proton appears to bridge the two functional groups. A ^1H chemical shift of reasonably high frequency, but broadened (fwhm 37 Hz), appropriate for an imidazolium salt is measured, but a (slightly broadened) ^{13}C chemical shift, appropriate for a C2-carbene, is also measured in the NMR spectra of **2** in benzene, pyridine, and thf. Thus, **2** appears to contain a proton-bridged six-membered ring; an intermediate between a carbene alcohol and a zwitterionic imidazolium alkoxide. Interestingly, while **1** decomposes upon vacuum sublimation, **2** sublimes in quantitative yield (80 °C, 10^{-6} mbar), giving further support to a neutral formulation for **2**.

In conclusion, the potassium(I)-facilitated [1,2] rearrangement of NHC N-hydrocarbyl groups is avoided by the incorporation of an additional alkoxide ligand. Perhaps in the same manner, in potassium *tert*-butoxide mediated *in situ* deprotonations, the alkoxide group stabilises potassium carbene systems that are inert to rearrangement. Spectroscopic analysis of an imidazolium alkoxide suggests an intermediate structure in which the acidic proton bridges the alkoxide and carbene groups.

This alkoxide ligand has allowed the first crystallographic characterisation of a potassium N-heterocyclic carbene complex, which forms K–$C_{carbene}$ bonds with a range of distorted geometries, even in the presence of thf, and generates a polymeric solid-state structure through close contacts to other NHC ring carbon atoms. The isolation of these thermally stable potassium NHC complexes may have implications in the design of functionalised NHC ligands for use in *in situu*, or additive-enhanced homogeneous catalysis.

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Notes and references

‡ Data for **1**. Anal. Calcd. for $C_{10}H_{17}N_2OK$: C 54.51, H 7.78, N 12.71. Found C 54.77, H 7.93, N 12.59. Calcd. for $[C_{10}H_{17}N_2OK]_8[thf]$: C 54.98, H 7.91, N 12.21. (EI)MS *m/z*: 284 ($[K(CN(CH_2)N(Pr^i)CHCH)_2]^+$, 16%), 226 ($[K(C\{N(CH_2)CH\}_2)_2]^+$, 8%). Data for **2**. Anal. Calcd. for $C_{10}H_{18}N_2O\cdot0.25H_2O$: C 64.30, H 9.98, N 14.99. Found C 64.21, H 9.94, N 14.91. ^1H-NMR (C_6D_6, 300 MHz): δ ppm 7.77 (br s, fwhm 37 Hz, 1H, NC*H*N) (thf, 300 MHz): δ ppm 6.75 (s, 1H, NC*H*N) $^{13}C\{^1H\}$-NMR (C_6D_6, 75 MHz): δ ppm 198.7.0 (NCN) (thf, 75 MHz): δ ppm 202.4 (NCN). MS (ES): *m/z* 182 ($[M]^+$, 100%).

§ Crystal data for **1**. $C_{84}H_{144}K_8N_{16}O_{93}$ Plate, colourless $M_r = 1834.96$ Triclinic, $P1$ $a = 10.675(3)$ $b = 13.281(3)$ $c = 19.726(5)$ Å $\alpha = 101.281(4)$ $\beta = 97.104(4)$ $\gamma = 102.741(4)^\circ$ $V = 2634.1(12)$ Å^3 $\mu = 0.38$ mm^{-1} $Z = 1$ $D_x = 1.157$ Mg m^{-3} 20405 independent reflections. Final R_1 [15243 $F > 4\sigma(F)$] = 0.057 and wR (all F^2) was 0.142. CCDC 258267. See http://www.rsc.org/suppdata/cc/b4/b418302a/ for crystallographic data in .cif or other electronic format.

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