Introduction

From an early stage, ligands with amine or imine functionality have played an important role in the field of coordination chemistry. After the remarkable discovery of the first stable and structurally characterised imidazol-2-ylidene by Anthony Joseph Arduengo, III, N-heterocyclic carbenes (NHCs) immediately became indispensable to developments in many diverse research areas, such as homogeneous catalysis, materials science and medicinal chemistry.

The enhanced electron-donating capacity and high nucleophilicity observed in these carbenes are indicative of the capability of the imidazolium ring to effectively stabilise a positive charge. An analogous principle can be applied to organic imidazol derivatives containing an exo-cyclic atom or an organic moiety X attached at the 2-position of the N-heterocycle such that, for species such as 2-methylene-, 2-imino-, 2-oxo- and 2-thioimidazolines (X = CH₂, NH, O, S), a strong contribution from the ylidic mesomeric form 1B may be considered (Chart 1).5,6

It was established that, due to the resulting build-up of negative charge at the X atom due to the mesomeric form 1B, the atom X possesses enhanced basicity and nucleophilicity. In recent years, Tamm and co-workers exploited this concept.
by providing access to a large variety of novel imidazolin-2-imines (ImNH, X = NH) that can be used for the preparation of imidazolin-2-iminato complexes of transition metals and rare earth elements, and, more recently, of actinide metals, in order to achieve very short M-N bonds. This has led to the probability of a multiple bonding character between M-N bonds. The M-N bond possesses a multiple bonding character – its reactivity is described as being very similar to a M=N imido bond. It has been observed that various metal complexes supported by imidazolin-2-iminato ligands display high activity in ethylene (co)polymerisation and in alkyne metathesis.

Lavoie et al. recently reported the preparation of urea and the thio-urea derivatives imidazol-2-ylidene-N′-p-tolyureate and imidazol-2-ylidene-N′-p-tolythioureate from imidazolin-2-imines and p-tolyl isocyanate and isothiocyanate, respectively. This family of neutral polyelectant ligands incorporates the imidazol-2-imine fragment in its fold. Lavoie et al. also introduced these urea- and thio-urea functionalised ligands into groups 4 and 10 in transition metal chemistry in order to explore their coordination behaviours. It was observed that these bis-dentate urea- and thio-urea functionalised ligands bound more electropositive metal ions (NiII and PdII) to be ligated through both the nitrogen atoms of the ligand. Nevertheless, their work was restricted to transition metal chemistry, and the structural aspects of alkali metal and alkaline earth metal complexes with these ligands have not been reported to date.

We earlier reported on phosphine-functionalised imidazol-2-imines, imidazol-2-ylidine-1,1-diphenylphosphine-amine and their chalcogenide derivatives (O, S, Se and Te). In our ongoing efforts to prepare functionalised imidazolin-2-imines, and with an interest to observe and record their coordination behaviour towards the main group organometallics, we prepared various alkali metal and alkaline earth metal complexes with imidazolin-2-imine urea derivatives.

It is in this context that herein we present the synthetic and structural details of two potassium complexes [k^5-(Im^BuNCONPh)K]_2 (2b) and [k^5-(Im^PPPNCNPh)K]_2(K[SiMe_3]_2)_2] (2c), one lithium complex (3a) and one calcium complex [k^5-(Im^BuNCONPh)Ca[N(SiMe_3)_2][K[SiMe_3]_2]_2] (4a) of imidazol-2-ylidene-N′-phenylureate ligand [Im^BuNCON(H)Ph] [(R = tBu (1a); Mes (1b) and Dipp (1c); Mes = mesityl, Dipp = 2,6-diisopropylphenyl]. We also report the molecular structures of an imidazol-2-ylidene-N′-phenylthiourate ligand (1d) and a siloxane incorporated calcium complex [k^5-(Im^BuNCONPh)CaK]_2(K[SiMe_3]_2)_2] (5a).

Results and discussion

Ligand synthesis

The imidazol-2-ylidene-N′-phenylureate and -thioureate ligands were prepared by an analogous method to that reported by Lavoie et al.11 Imidazol-2-imines (Im^N=NH) with three different substituents over nitrogen atoms were charged with a slight excess of phenyl isocyanate (5% excess) at ambient temperature to give the corresponding imidazol-2-ylidene-N′-phenylureate [Im^NCON(H)Ph] (R = tBu) (1a); Mes (1b) and Dipp (1c) (Scheme 1). The analogous thioureate ligand [Im^NCONCSN(H)Ph] (1d) was isolated by the reaction of [Im^BuN] with phenyl isothiocyanate in toluene (Scheme 1). All the ligands were characterised using standard analytical and spectroscopic techniques. The solid-state structures of 1a and 1d were established by single-crystal X-ray diffraction analysis.

The 1H NMR spectra measured in C_6D_6 for the compounds 1a–c and CDCl_3 (1d) are similar and show a characteristic singlet resonance [δ 6.18 (1a), 5.80 (1b), 6.10 (1c) and 6.22 (1d) ppm] for imidazolium backbone olefinic protons. These can be observed as a downfield shift from that of the respective imidazol-2-imines [δ 5.96 (tBu); 5.71 (Mes); 5.87 (Dipp) ppm]. The resonances for 18 protons from the six methyl groups in 1a appeared as singlets at δ 1.43 ppm, whereas two singlets at δ 2.26 and 2.05 ppm could be assigned to the o- and p-methyl protons, respectively, in the mesityl groups. The distinct septet signal at δ 3.21 ppm, and the two doublet resonances with a coupling constant 6.8 Hz each, appeared at δ 1.45 and 1.16 ppm, respectively, due to the –CH hydrogen and isopropyl methyl hydrogen atoms of the ligand 1c. The C=O stretching frequencies [ν 1627 (1a), 1647 (1b), 1650 cm⁻¹] were considerably lower than that of the starting isocyanate (2170 cm⁻¹), indicating a marked reduction in C=O strength upon formation of the urea. As the observed stretching frequencies were also slightly lower than those commonly observed in organic amides – a manifestation of the electron

![Scheme 1](image-url)
delocalisation from the imidazole ring to the acyl group – a further decrease of the C–O bond order can be realised. The resonance for the tert-butyl methyl protons in compound 1d could be detected as a sharp singlet at δ 1.65 ppm. The strong absorption band at 1400–1600 cm⁻¹ in the FT-IR spectrum of 1d indicated the presence of a C=S group. However, the exact band was difficult to identify due to the mixing of the other vibration modes.¹⁴

Single crystals of 1a and 1d were obtained from the concentrated toluene solution of the respective compounds at ambient temperature. Compound 1a crystallised in the monoclinic space group P2₁/c with four molecules in the unit cell. In contrast, the thiourea derivative 1d crystallised in the trigonal space group R₃ with 18 molecules in the unit cell. The details of the structural parameters are given in Table TS1 in the ESI.† The solid-state structure of complex 1a is shown in Fig. 1, whereas Fig. S1 in the ESI† represents the solid-state structure of 1d. The C1–N1 bond distance of 1.346(3) Å in 1a is elongated, compared to Im[NH][1.295(2) Å];¹⁵ presumably due to enhanced electron donation to the imino nitrogen atom from the imidazolium ring. A slight elongation of the carbonyl C12–O1 bond [1.236(3) Å] was observed due to the delocalisation of electrons from imino nitrogen to the oxygen atom of the isocyanate building block. The slightly shorter N1–C12 bond [1.339 (3) Å], compared to the N4–C12 bond [1.389(3) Å], is also supportive of the above delocalisation over the N1–C12–O1 unit on ligand 1a. Short hydrogen bonding between the electronnegative oxygen atom and hydrogen atoms from adjacent methyl groups, O1⋯H5a (2.706 Å) and O1⋯H9c (2.541 Å), is also observed (Fig. 1).

Potassium complexes

In the recent past, we reported the syntheses and structural studies of highly reactive alkali metal complexes in order to apply them well-defined precursors for various salt metathesis reactions.¹⁶ To gain an additional insight into the structure-reactivity relationships of alkali metal complexes of imidazol-2-ylidene-N'-phenylureate ligands, we studied this chemistry further. The mesityl derivative of the ligand (1b) was reacted with potassium bis(trimethylsilyl)amide in a 1 : 1 molar ratio and at ambient temperature in toluene to afford the tetranuclear structure 2b in a good yield (Scheme 2). The ligand 1d was reacted in a similar fashion with alkali and alkaline earth metal precursors; however, we could not isolate any of the corresponding alkali metal or alkaline earth metal complexes, probably due to the soft nature of the sulfur atom which did not have a preference for the hard metal ions. The polymeric potassium complex 2c was isolated in a good yield by the reaction of 1c and potassium bis(trimethylsilyl)amide in a 1 : 2 molar ratio in toluene at room temperature (Scheme 3). The air- and moisture-sensitive compounds 2b and 2c were characterised using ¹H and ¹³C{¹H} NMR spectroscopy, and the solid-state structures of complexes 2b and 2c were established by single-crystal X-ray diffraction analysis.

The ¹H NMR spectra of complexes 2b and 2c, measured in C₄D₄, revealed one set of signals in each case. The two olefinic protons of the imidazole backbone resonated at δ 5.80 (2b) and 5.95 ppm (2c), respectively. These in a similar range to those of the starting urea ligands (5.80 ppm for 1b and 6.10 ppm for 1c). The methyl protons of the mesityl groups in 2b were observed to resonate at δ 2.26 and 2.06 ppm as two sharp singlets. Furthermore, in complex 2c, a broad signal at δ 3.16 ppm and two doublet resonances with a coupling constant of 8.4 Hz each appeared at δ 1.29 and 1.19 ppm, respectively, due to the –CH hydrogen and isopropyl methyl hydrogen atoms of the imidazolin-2-imine fragment of ligand 1c. A sharp singlet at δ 0.09 ppm was also observed for the trimethylsilyl group present in complex 2c. In the ¹³C{¹H} NMR spectra of 2b and 2c, the chemical shift of the central imidazole carbon was observed at 149.6 ppm for 2b (versus 144.7 ppm for 1b) and at 147.5 ppm for 2c (versus 150.5 ppm for 1c).

Potassium complex 1a was isolated in a good yield by the reaction of potassium bis(trimethylsilyl)amide in a 1 : 1 molar ratio with the corresponding alkali metal or alkaline earth metal precursors; however, we could not isolate any of the corresponding alkali metal or alkaline earth metal complexes, probably due to the soft nature of the sulfur atom which did not have a preference for the hard metal ions. The polymeric potassium complex 2c was isolated in a good yield by the reaction of 1c and potassium bis(trimethylsilyl)amide in a 1 : 2 molar ratio in toluene at room temperature (Scheme 3). The air- and moisture-sensitive compounds 2b and 2c were characterised using ¹H and ¹³C{¹H} NMR spectroscopy, and the solid-state structures of complexes 2b and 2c were established by single-crystal X-ray diffraction analysis.
for 1c), while the carbonyl carbon nucleus resonated at δ 158.2 ppm for 2b (versus 154.2 ppm 1b) and at 165.2 ppm for 2c (versus 157.2 ppm for 1c). The decrease in the C=O stretching frequency (ν_{CO} = 1623 cm\(^{-1}\) for 2b and 1620 cm\(^{-1}\) for 2c) compared to that of the urea ligands 1b (ν_{CO} = 1647 cm\(^{-1}\)) and 1c (ν_{CO} = 1647 cm\(^{-1}\)) also supported coordination through the oxygen atom.

X-ray quality crystals of complex 2b were grown at −35 °C by the slow liquid diffusion of THF into a concentrated toluene solution, while single crystals of 2c were obtained at −35 °C from a concentrated solution of toluene. Complex 2b crystallised in the tetragonal space group P4\(_2\)\(_1\)c, with two molecules of complex 2b and two THF solvent molecules in the unit cell. In contrast, complex 2c crystallised in the monoclinic space group P2\(_1\)\(_1\)c, with four molecules of 2c in the unit cell.

Complex 2b is tetra-nuclear monomeric, whereas complex 2c is polymeric in nature. Details of the structural parameters are given in Table TS1 in the ESI.\(^1\) The solid-state structure of complex 2b is shown in Fig. 2. This solid-state structure of the tetra-nuclear potassium complex 2b confirmed the κ\(^2\)-coordination mode of each ligand fragment forming four times four-membered metallacycles. Each potassium is ligated with the imidazolium-2-iminato nitrogen and the oxygen atom of the isocyanoate building block. Four potassium and four oxygen atoms formed a heterocubane structure, with an average K-O distance of 2.659–2.709 Å and a K-O-K angle between 80.37(8) and 89.15(8)°, thus confirming the distorted nature of the heterocubane motif, which can be best described as a K\(_4\) tetrahedron consisting of four oxygen atoms capping the four triangular faces (Fig. 3). Significant electron donation from the imidazolium ring to the ureate group is evident from the unusual elongation of the N1–C27 (1.411(5) Å) and N1–C1 [1.285(5) Å] bonds. In addition, both the bond lengths C27–O1 [1.279(4) Å] and C27–N4 [1.309(5) Å] are between those of carbon–oxygen and carbon–nitrogen single bonds and double bonds, respectively, thus indicating extensive electron delocalisation over N1–C27–O1. A similar observation was reported in [CpTiCl\(_2\)\{Im\(_{Me}N\)CNO\}][Tol = p-tolyl] by Lavoie et al.\(^1\) They, however, reported a bi-dentate mode of coordination of the ureate ligand through the oxygen and nitrogen atoms of the isocyanoate building block, while leaving the imidazolium-2-imine fragment uncoordinated. To the best of our knowledge, complex 2b is the first reported ureate–potassium complex where the mono-anionic ligand is coordinated through the oxygen atom of the ureate group and the nitrogen atom from the imidazolium-2-imine fragment. An even similar pattern of bonding was discussed by Snaith et al., although it must be noted that such a heterocubane structural motif, derived using an ureate ligand in alkali metal chemistry, has not been reported so far.\(^1\)

The effect of a substituent over the imidazol ring is very significant. The solid-state structure of complex 2c was found to be polymeric in nature, due to the use of two equivalents of potassium precursor in its preparation compared to one equivalent used for the synthesis of 2b. The asymmetric unit of complex 2c is shown in Fig. 4. The molecular structure of 2c confirms the κ\(^3\) coordination of the ureate ligand towards potassium. It further reveals that two molecules [KNSiMe\(_3\)]\(_2\) are also present in the asymmetric unit in order to stabilise the complex 2c. The nitrogen atoms from the imidazolium-2-imine and the ureate fragments bond with the potassium ion K1, whereas the third donor atom oxygen is also ligated to another adjacent potassium ion that is attached to the bis(trimethyl)silyl amide group. Two four-membered metallacycles, N1–K1–N4–C28 and N7–K4–N10–C71, are formed by the chelation of two nitrogen atoms of each ureate ligand with the potassium ion, while two six-membered metallacycles, N4–C28–O1–K3–C30–C29 and N10–C71–O2–K2–C37–C72, are observed by the ligation of an oxygen atom and a phenyl carbon of each ureate.
Fig. 4 Solid-state structure of complex 2c. The hydrogen atoms are omitted for clarity. The secondary interactions of the potassium atoms and methyl carbon atoms are shown. Selected bond lengths [Å] and bond angles [°]: K1–N1 2.734(4), K1–N4 2.726(4), K1–N5 2.769(4), N1–C28 1.417(5), N4–C28 1.327(6), N4–C29 1.401(5), C28–O1 1.248(5), N1–C1 1.290(5), K2–O2 2.507(3), K2–N5 2.801(4), K2–C34 3.358(7), K3–N6 2.841(4), K3–O1 2.528(3), K3–C30 3.293(6), N5–Si1 1.670(4), N5–Si2 1.666(4), N1–C28–N4 111.2(4), N1–C28–O1 121.4(4), N4–C28–O1 127.2(4), C1–N1–C28 124.8(4), C28–N4 117.9(4), N1–K1–N4 49.02(10), K1–N5–K2 40.61(8), O1–K3–N6 170.44(13), N5–K2–O2 160.99(14), Si1–N5–Si2 133.2(2).

As the ureate ligand has multiple donor atoms, as observed (Scheme 4). Complex 3a was characterised using $^1$H, $^{13}$C($^1$H) NMR and combustion analysis, while its solid-state structure was established using single-crystal X-ray crystallography.

In the $^1$H NMR spectra of complex 3a measured in C$_6$D$_{6}$, the characteristic singlet at δ 6.28 ppm could be assigned to the olefinic protons of the imidazol backbone, which was in the same region (6.22 ppm) as that of ligand 1a. The tert-buty1 methyl protons of the imidazol scaffold resonated at 1.46 ppm, whereas the ‘Bu protons from the phenoxy ring were displayed as sharp singlets at 1.30 ppm. Additional singlet resonance at 2.10 ppm was obtained for the methyl protons located at position 4 of the phenox moiety. In the $^{13}$C spectra, resonances at 165.5 ppm for ipso carbon, 157.0 ppm for carbonyl carbon and 149.9 ppm for NCN group were observed for complex 3a.

Crystals of 3a were grown from a concentrated solution of toluene at –35 °C. Complex 3a crystallised in the asymmetric unit in the monoclinic space group P2/c along with a molecule of 1a. Details of the structural parameters are given in Table 4S in the ESI.† The solid-state structure of the lithium fragment of complex 3a is shown in Fig. 5. The molecular structure clearly indicates that the neutral urea ligand 1a coordinated to the lithium ion in a $\kappa^3$ mode through the oxygen atom of the isocyanate building block of the ligand. A four-membered Li$_2$O$_2$ diamond core was formed by the bridging coordination of two oxygen atoms from two phenoxy ligands. The terminal Li1–O1 bond distance [1.835(9) Å] where the oxygen atom is neutral is slightly shorter than the bridging Li1–O2 bond (1.863(9) Å) where the oxygen atom is anionic.

Lithium complex

As the ureate ligand has multiple donor atoms, as observed (κ$^2$ and κ$^3$) from the above potassium complexes 2b and 2c, multidentate coordination was expected from two nitrogen and oxygen atoms. We were interested in exploring the coordination behaviour of monoanionic ureate ligands towards lithium, a smaller alkali metal. As several attempts to crystallise the lithium complex did not succeed, we reacted the lithium complex prepared from 1a and LiCH$_3$SiMe$_3$ in a 1:1 molar ratio in toluene with one equivalent of 2,6-di-tert-butyl-4-methyl phenol to afford a lithium derivative, complex 3a (Scheme 4). Complex 3a was characterised using $^1$H, $^{13}$C($^1$H) NMR and combustion analysis, while its solid-state structure was established using single-crystal X-ray crystallography.
neutral ligand 1a was trapped by and coordinated to the lithium ion, while another molecule of 1a remained uncoordinated in the asymmetric unit. Several hydrogen bonding interactions with the adjacent methyl protons from 'Bu groups with more electronegative oxygen atoms, important for the crystallisation of the compound (Fig. 5), were also observed in complex 3a.

Calcium complex

Alkaline earth metal compounds have been recently employed in various catalytic applications in order to achieve the ring-opening polymerisation of various cyclic esters,\textsuperscript{20} the polymerisation of styrene and dienes,\textsuperscript{21} and hydroamination and hydrophosphination reactions of alkenes and alkynes.\textsuperscript{22} Determining the structure and reactivity of alkaline earth metal species is an important step towards the design and development of efficient catalysts. However, a full realisation of the catalytic potential of these elements still requires substantial advances to be made in order to understand their basic coordination and organometallic chemistry. We recently studied various group 2 metal complexes with amido-phosphine and related ligands in order to explore their structure, coordination behaviour and catalytic efficiency.\textsuperscript{23} In our ongoing study of alkaline earth metal chemistry, we aim to introduce the mononuclear 1,3,4-urea ligand 1 into group 2 metal chemistry.

The calcium potassium mixed metal complex 4a was isolated as a major product from a one-pot reaction with 1a and potassium precursor [KN(SiMe$_3$)$_2$] in a 1 : 3 molar ratio in THF, followed by the addition of one equivalent calcium diiodide at ambient temperature (Scheme 5). However, initial attempts to isolate the potassium free calcium iodo complex [(1a)CaI(THF)$_3$] using the starting reagents in a 1 : 1 : 1 molar ratio did not meet success. The mixed Ca–K metal complex 4a was characterised using spectroscopic/analytic techniques and the molecular structure of 4a in its solid-state structure was established using single-crystal X-ray crystallography.

Complex 4a crystallised in the monoclinic space group $P2_1/c$, with four molecules in the unit cell. From the solid-state structure, it was evident that complex 4a was polymeric in nature. Details of the structural parameters are given in Table TS1 in the ESI;\textsuperscript{†} the asymmetric unit of complex 4a is shown in Fig. 6, and the polymeric unit is given in Fig. 7. It is clearly seen in the asymmetric unit that two metal ions of calcium and potassium are, respectively, connected via $\mu_2$ bridging of the oxygen atom of the ureate ligand and the nitrogen atom from the bis(trimethylsilyl)amido group. This results in the four-fold coordinated central metal calcium ion adopting a distorted tetrahedral geometry due to the $x^2$ coordination of nitrogen and oxygen atoms from the isocyanate building block of ligand 1a while leaving the imidazolin-2-imine fragment uncoordinated. Two amido ligands bond the calcium ion to

![Fig. 5 Solid-state structure of complex 3a. The hydrogen atoms are omitted for clarity except for those which have bonding interactions with oxygen atoms. Selected bond lengths [Å] and bond angles [°]: L1–O1 1.835(9), L1–O2 1.863(9), L1–O2' 1.911(8), O2–Li1' 1.911(8), O1–C12 1.270(6), N3–C12 1.310(6), C12–N4 1.394(6), C1–N1 1.363(6), L1–O2–Li1' 49.0(3), O2–Li1–O2' 95.9(4), O1–Li1–O2 140.9(5), O1–C12–N3 127.3(5), O1–C12–N4 115.8(5), N3–C12–N4 116.9(4).](image1)

![Scheme 5 Synthesis of the calcium complex 4a.](image2)

![Fig. 6 Solid-state structure of the asymmetric unit of complex 4a. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Ca1–O1 2.3558(17), Ca1–N4 2.367(2), Ca1–N6 2.317(2), Ca1–N5 2.348(2), K1–O1 2.619(18), K1–N5 2.989(2), O1–C12 1.308(3), N4–C12 1.357(3), C12–N1 1.342(3), N1–C1 1.338(3), N4–C13 1.389(3), O1–Ca1–N4 56.51(6), N4–Ca1–N6 104.47(8), N5–Ca1–N6 123.39(8), O1–K1–N5 73.68(5), K1–N5–Ca1 91.05(6), O1–C12–N4 114.0(2).](image3)
give two additional bonds. Thus, a four-membered metallocycle C1–O2–Ca1–N6 was formed to demonstrate the κ² coordination of ligand 1a towards the calcium ion. The slight elongation of the C12–O1 bond [1.308(3) Å versus 1.236(3) Å for 1a] and the slight shortening of the C12–N4 bond [1.357(3) Å versus 1.389(3) Å] indicate an electron delocalisation over the O1–C12–N4 skeleton. The unperturbed bond distances of N1–C1 [1.338(3) Å] and N1–C12 [1.342(3) Å] for the trimethylsilyl groups in the complex. The 1^1C{1^1H} NMR spectra of 4a was hexa-coordinated through the four oxygen atoms from the trimethylsilyl groups was also observed at δ 0.43 ppm, thus confirming the presence of SiMe₃ groups in the complex. The 1^1C{1^1H} NMR spectra of 4a was also within the expected range and very similar to that of complex 4a.

Complex 5a crystallised in the triclinic space group P1, with one molecule in the unit cell. Details of the structural parameters are given in Table TS1 in the ESI,† and the asymmetric unit of complex 5a in its solid-state structure is shown in Fig. 8. The molecular structure is evidence of the incorporation of two fragments of dianionic disiloxane units [(Me₂SiO₂)O]²⁻, which bound three calcium ions in a bridging fashion. Three different chemical environments were observed for four calcium ions present in the molecule. The central calcium ion Ca1 was hexa-coordinated through the four oxygen atoms of two siloxane [(Me₂SiO₂)O]²⁻ units and two oxygen atoms from two ureate ligands, resulting in the adoption of a distorted octahedral geometry around it. One of the remaining two calcium ions had similar coordination spheres formed by the chelation of two μ₁ oxygen atoms O1 and O2 of two siloxane [(Me₂SiO₂)O]²⁻ units, and two nitrogen and two oxygen atoms of two monoanionic ureate ligands, resulting in the adoption of a distorted tetrahedral geometry around the calcium ion. Interestingly, for two ureate ligands, the nitrogen atoms from the isocyanate building block and the imidazolin-2-imine fragment alternatively bound either a calcium ion (Ca2) or a potassium ion (K2), thus making the ureate ligand a tridentate; the coordination mode can be best described as κ³ towards a metal ion. Apart from these calcium ions, the fourth calcium ion Ca3 exists as a [CaN(SiMe₃)₂]²⁻ fragment in the molecule. Two kinds of potassium ions were also observed. The potassium ion K1 bound with two μ₁ oxygen atoms (O1 and O2) from the two siloxane [(Me₂SiO₂)O]²⁻ units and with two oxygen atoms (O3 and O4) from two isocyanate building blocks of the ureate ligand. Furthermore, a κ⁰ attachment with an adjacent phenyl ring with a distance of (2.992–3.317 Å), which is quite common in potassium organometallic complexes, was also obtained. The second potassium atom K2, having one [N(SiMe₃)₂]⁻ group attached, was coordinated by one
imidazolin-2-imine nitrogen N3 along with a η⁶ arene interaction with the adjacent phenyl ring with a distance of (3.165–3.452 Å). Even the imidazol-2-iminato exocyclic C–N bond distances [N3–C14 1.342(6) Å and N6–C13 1.349(6) Å versus 1.346(3) Å for 1a] remained unchanged. The bond elongation of the ureate fragments [N3–C12 1.362(6) and N6–C11 1.391(6) Å versus 1.339(3) Å for 1a; C12–O4 1.299(6) and C11–O3 1.301(6) Å versus 1.236(3) Å for 1a] indicated a localised carbon–nitrogen double bond rather than any involvement of electron delocalisation with the C=O group. Thus, it can be assumed that compound 4a partly underwent decomposition with silicon grease under the reaction conditions so as to a separate reaction, using a silicon-free grease, complex 5a was prepared without contamination from complex 5a. In complex 5a, the calcium ion Ca3 led to the repetition of the asymmetric unit, resulting in the growth of the polymeric chain.

**Experimental**

### General Consideration

All manipulations of air-sensitive materials were performed by rigorously excluding oxygen and moisture in flame-dried Schlenk-type glassware, either on a dual manifold Schlenk line interfaced to a high vacuum (10⁻⁴ torr) line, or in an argon-filled M-BRAUN glovebox. Toluene was distilled under nitrogen from LiAlH₄ and stored in the glove box. ¹H NMR (400 MHz) and ¹³C{¹H} NMR spectra were recorded on a BRUKER AVANCE III-400 spectrometer. BRUKER ALPHA FT-IR was used for the FT-IR measurements. Elemental analyses were performed on a BRUKER EURO EA at the Indian Institute of Technology Hyderabad (IITH). Imidazolin-2-imines [(Im²NHNH); (R = tBu, Mes, Dipp)] and trimethylsilylmethyl lithium [LiCH₂SiMe₃] were prepared according to procedures specified in literature.³ Phenyl isocyanate, phenyl isothiocyanate, 2,6-di-tert-butyl-4-methyl phenol, [K(N(SiMe₃)₂)] and CaI₂ were purchased from Alfa Aesar and used in their original forms. The NMR solvents CDC₁₃ and CD₂CD₂ were purchased from Sigma Aldrich and dried under Na/K alloy prior to use (for CD₂CD₂).

#### Preparation of [Im²NCON(H)Ph] (R = tBu) (1a); Mes (1b) and Dipp (1c)

To a toluene solution (10 mL) of imidazole-2-imine (Im²NHNH) (1.56 mmol), 5% molar excess of phenyl-isocyanate (192 mg, 1.612 mmol) was added, and the reaction mixture was stirred for two hours. The solvent was evaporated in vacuo leaving behind a solid residue. This colourless solid was washed with n-pentane (5 mL) to afford a spectroscopically pure off-white solid. The title compounds were crystallised from concentrated toluene solution at 15°C.

**1a:** Yield 420 mg, 86%. ¹H NMR (400 MHz, CD₂CD₂): δ 7.9 (br, 1H, JHH = 7.75 Hz, 2H, Ph), 7.18 (m, 2H, Ph), 6.83 (t, JHH = 7.32 Hz, 1H, Ph), 6.18 (s, 2H, HCC=CH), 1.43 (s, 18H, C(CH₃)₃) ppm. ¹³C{¹H} NMR (100 MHz, CD₂CD₂): δ 138.8 (C=O), 150.4 (NCN), 143.4 (Ar), 128.9 (Ar), 120.2 (Ar), 117.8 (Ar), 112.0 (HCC=CH), 58.4 (NC(CH₃)₃), 29.1 (C(CH₃)₃) ppm. FTIR selected peaks (cm⁻¹): 1627 (C=O), 1574 (C≡N), 2979 (CH), 3155, 3287 (N–H). (C₁₈H₂₂N₄O) (314.43) Calc. C 68.76, H 8.33, N 17.82; found C 68.23 H 8.11, N 17.59.

**1b:** Yield 515 mg, 75%. δ 7.09 (d, JHH = 7.88 Hz, 2H, Ph), 6.89 (m, 2H, Ph), 6.72 (s, 4H, m-CH(mesityl)), 6.62 (t, JHH = 7.48 Hz, 1H, Ph), 6.44 (br s, 1H, NH), 5.81 (s, 2H, HCC=CH), 2.26 (s, 12H, o-CH₂(mesityl)), 2.05 (s, 6H, p-CH₂(mesityl)) ppm. ¹³C{¹H} NMR (100 MHz, CD₂CD₂): δ 158.0 (C=O), 149.8 (ipso-Ar), 141.7 (NCN), 138.4 (ipso-Ph), 135.8 (o-Ar), 133.8 (p-Ar), 129.4 (m-Ar), 128.3 (o-Ph), 120.8 (p-Ph), 118.2 (m-Ph), 115.5 (HCC=CH), 21.0 (CH₃), 18.2 (CH₃) ppm. FTIR selected...
Preparation of [k^3-(Im^BuNCONPh)]_2{KN(SiMe_3)_2}_2 (2c)

To a toluene solution (10 mL) of 1,3-di-tert-butylimidazole-2-imine a (300 mg, 1.536 mmol) excess of phenyl-isothiocyanate (218 mg, 1.612 mmol) was added, and the reaction mixture was stirred for two hours. The solvent was evaporated in vacuo leaving behind a solid residue, which was washed with n-pentane (5 mL) to afford a spectroscopically pure off-white solid. The title compound 1d was re-crystallised from a concentrated solution of toluene.

Yield: 436 mg 86%. ^1H NMR (400 MHz, C_6D_6): δ 7.80 (s, 1H, HN), 7.62 (d, J_H-H = 7.84 Hz, 2H, Ph), 7.20 (m, 2H, Ph), 6.89 (t, J_H-H = 7.32 Hz, 1H, Ph), 6.77 (s, 2H, HCC=CH), 1.63 (s, 18 H, C(CH_3)_3) ppm. ^13C{1H} NMR (100 MHz, C_6D_6): δ 178.2 (C-O), 151.4 (ipso-Ph), 140.9 (NCN), 128.7 (Ph), 121.6 (Ph), 119.6 (Ph), 113.6 (HCC=CH), 58.5 (NC(CH_3)_3), 29.7 (C(CH_3)_3) ppm. FTIR selected peaks (cm\(^{-1}\)): 1654 (C≡S), 1567 (C≡N), 2967, 3126, 3235 (N-H). (C_30H_36N_2O_2) (330.49) Calc. C 65.42, H 7.93, N 16.95; found C 65.19 H 7.62, N 16.77.

Preparation of [k^3-(Im^MesNCONPh)]_2 (2b)

In an argon-filled glovebox, toluene (10 mL) solution of compound 1b (200 mg, 0.456 mmol) was added dropwise to a 25 mL Schlenk tube containing potassium bis(trimethylsilyl)amide (91 mg, 0.456 mmol) and 5 mL of toluene. The reaction mixture was kept for further stirring at room temperature for 12 hours. The solvent was evaporated in vacuo leaving behind a red-coloured residue, which was washed with n-hexane (10 × 3 mL) and dried under reduced pressure. The title compound 2b was crystallised from a mixture of THF and toluene (1:3) at −35 °C.

Yield 141 mg, 65%. ^1H NMR (400 MHz, C_6D_6): δ 7.12–7.08 (m, 2H, Ph), 6.94–6.84 (m, 3H, Ph), 6.73 (s, 4H, m-CH (mesityl)), 5.80 (s, 2H, HCC=CH), 3.57 (thf), 2.26 (s, 12H, CH_2), 2.06 (s, 6H, CH_3), 1.40 (thf) ppm. ^13C{1H} NMR (100 MHz, C_6D_6): δ 158.2 (C≡O), 149.6 (NCN), 146.4 (ipso-Ph), 135.9 (o-Ph), 133.9 (Ph), 129.4 (Ph), 128.3 (Ar), 120.1 (Ph), 115.3 (HCC=CH), 20.9 (CH_3), 18.2 (CH_3) ppm. FTIR selected peaks (cm\(^{-1}\)): 1623 (C≡O), 2956, 3078. (C_{12}H_{14}K N_{18}O_{3}) (2077.75) Calc. C 73.99, H 7.18, N 10.79; found C 73.54 H 6.94, N 10.32.

Preparation of [k^3-(Im^BuNCONPh)]_2{KN(SiMe_3)_2}_2 (2c)

Compound 1c (200 mg, 0.38 mmol) and potassium bis(trimethylsilyl)amide (153 mg, 0.765 mmol) were placed in a 25 mL Schlenk flask in an inert atmosphere. Toluene (8 mL) was added to the flask at room temperature. The resultant reaction mixture was stirred for another 12 hours. The solvent was evaporated under reduced pressure to obtain a red-coloured residue. The red solid was washed with n-hexane (3 × 5 mL) to obtain a red powder. The title compound 2c was re-crystallised from concentrated toluene at −35 °C.

Yield 395 mg, 52%. ^1H NMR (400 MHz, C_6D_6): δ 7.53 (m, 2H, Ph), 7.34 (m, 4H, Ar), 7.11 (m, 3H, Ph), 7.00 (m, 2H, Ph), 5.95 (d, J_H-H = 8.43 Hz, 2H, CH(CH_3)_2), 1.29 (d, J_H-H = 7.20 Hz, 12H, CH(CH_3)_2), 1.12 (d, J_H-H = 6.80 Hz, 4H, CH(CH_3)_2), 1.45 (d, J_H-H = 6.80 Hz, 12H, CH(CH_3)_2), 1.16 (d, J_H-H = 6.80 Hz, 12H, CH(CH_3)_2) ppm. ^13C{1H} NMR (100 MHz, C_6D_6): δ 157.1 (C≡O), 151.2 (NCN), 146.6 (ipso-Ph), 141.5 (ipso-Ph), 133.9 (o-Ph), 124.2 (o-Ph), 120.8 (p-Ph), 118.1 (p-Ph), 116.6 (HCC=CH), 29.2 (CH(CH_3)_3), 24.4 (CH(CH_3)_3), 23.7 (CH(CH_3)_3) ppm. FTIR selected peaks (cm\(^{-1}\)): 1580 (C≡N), 1650 (C≡O), 2962, 3053, 3419 (N-H). (C_32H_42N_4O_2) (522.72) Calc. C 78.12, H 8.10, N 10.72; found C 77.86, H 7.91, N 10.51.

Preparation of [k^3-(Im^BuNCONPh)]_2{KN(SiMe_3)_2}_2 (3a)

To a stirred solution of toluene (5 mL) and compound 1a (200 mg, 0.636 mmol), a toluene (3 mL) solution of trimethylsilylmethyl lithium (60 mg, 0.636 mmol) was added dropwise at ambient temperature. The resulting reaction mixture was stirred for another 12 hours. 2,6-di-tert-butyl-4-methyl phenol (140 mg, 0.636 mmol) was added to this solution, and the reaction mixture was stirred for a further 2 hours. The solvent was evaporated and the solution mixture was reduced to 1/3 of the original volume. It was thereafter placed for crystallisation at −35 °C. Colourless crystals were obtained two days later.

Yield 335 mg, 62%. ^1H NMR (400 MHz, C_6D_6): δ 7.57 (d, J_H-H = 8.0 Hz, 2H, Ar), 7.22 (t, J_H-H = 8.0 Hz, 2H, Ar), 7.02 (s, 2H, Ar), 6.85 (t, J_H-H = 8.0 Hz, 1H, Ar), 6.28 (s, 2H, HCC=CH), 2.10 (6H, CH_3), 1.46 (s, 18 H, C(CH_3)_3), 1.30 (18H, C(CH_3)_3) ppm. ^13C{1H} NMR (100 MHz, C_6D_6): δ 165.5 (ipso –Ar), 157.0 (C≡O), 149.9 (NCN), 141.1 (Ar), 133.1 (Ar), 129.3 (Ar), 128.5 (Ar), 128.3 (Ar), 125.8 (Ar), 120.4 (Ar), 119.3 (Ar), 112.1 (HCC=CH), 58.6 (NC(Me)_3), 33.8 (C(CH_3)_3), 32.6 (C(CH_3)_3), 32.3 (CH_3), 29.1 (C(CH_3)_3) ppm. FTIR selected peaks (cm\(^{-1}\)): 1627 (C≡O), 2980, 3155, 3297 (N-H). (C_{105}H_{150}LiN_13O_12) (1710.27) Calc. C 71.63, H 8.84, N 13.10; found C 71.33 H 8.37, N 12.87.

Preparation of [k^3-(Im^BuNCONPh)]_2{KN(SiMe_3)_2}_2 (2a)

In an argon-filled glovebox, to the toluene (5 mL) solution of calcium diiodide (186.9 mg, 0.636 mmol), a toluene (5 mL) solution of compound 1a (200 gm, 0.636) and potassium bis(trimethylsilyl)amide (380.6 mg, 1.90 mmol) was added
CryoLoop (Hampton Research Corp.) with a layer of light complexes, a crystal of suitable dimensions was mounted on a − with graphite-monochromatic Cu-Kα made on an Agilent Supernova X-calibur Eos CCD detector of concentrated toluene under an inert atmosphere at 15 °C. Crystals were grown by direct methods (SIR92)27 and refined on marised in Table TS1 in the ESI.

The crystal data and structure refinement parameters are summarised in Table TS1 in the ESI. The function minimised was $\sum \{F_A^2 - F_C^2\}$ with $F_A = 1/[S^2(F_A^2) + (a/b)]$, where $P = \{max(F_A^2, 0) + 2F_C^2\}/3$ with $S^2(F_A^2)$ from counting statistics. The function $R_1$ and $wR_2$ were $\sum [F_A - F_C]/\sum F_A$ and $[\sum w(F_A^2 - F_C^2)]^{1/2}$, respectively. The Diamond-3.0 program was used to draw the molecule. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary no CCDC 1046050–1046056.

Conclusion

We have demonstrated the synthetic and structural details of potassium, lithium and calcium complexes of the imidazol-2-ylidene-N-phenylurea ligand, which display various coordination modes such as $k^1$, $k^2$ and $k^3$. From the solid-state structures it is evident that not only are the nitrogen and oxygen atoms of the isocyanate building block coordinating, but also that the imidazolin-2-imine nitrogen atom takes part in a coordination with the potassium and calcium ions. Due to the larger size of the potassium and calcium ions and the multi-dentate nature of the ureate ligand, polymeric structures were obtained in most cases. However, by controlling the substituent as mesityl groups over the imidazol ring, a heterocubane core K$_3$O$_4$ was isolated in potassium complex 2b.

Acknowledgements

This work is supported by the Science and Engineering Research Board (SERB), Department of Science and Technology (DST), India, under project no. (SB/S1/IC/045/2013). The instrumental facilities were provided by the Indian Institute of Technology Hyderabad (IITH). K.N. and J.B. thank the University Grants Commission (UGC), India, for their PhD fellowships. We sincerely thank Prof. Kazushi Mashima and Dr Hayato Tsurugi, Osaka University for their generous support. We sincerely thank Prof. Kazushi Mashima and Dr Hayato Tsurugi, Osaka University for their generous support. We sincerely thank Prof. Kazushi Mashima and Dr Hayato Tsurugi, Osaka University for their generous support. We sincerely thank Prof. Kazushi Mashima and Dr Hayato Tsurugi, Osaka University for their generous support. We sincerely thank Prof. Kazushi Mashima and Dr Hayato Tsurugi, Osaka University for their generous support. We sincerely thank Prof. Kazushi Mashima and Dr Hayato Tsurugi, Osaka University for their generous support.

Notes and references


