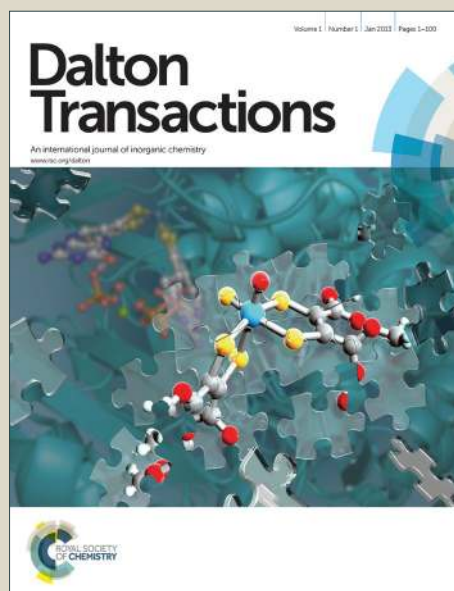


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ARTICLE TYPE

Imidazol-2-ylidene-N'-phenylureate Ligands in Alkali and Alkaline Earth Metal Coordination Sphere - Heterocubane Core to Polymeric Structural Motif Formation

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The synthesis and isolation of two potassium, one lithium and two calcium complexes of imidazol-2-ylidene-N'-phenylureate ligand [Im^RNCON(H)Ph] [(R = tBu (**1a**); Mes (**1b**) and Dipp (**1c**); Mes = mesityl, Dipp = 2,6-diisopropylphenyl] are described here. The potassium complexes, [κ^2 -(Im^{Mes}NCONPh)K]₄ (**2b**) and [κ^3 -(Im^{Dipp}NCONPh)K]₂{KN(SiMe₃)₂]₂ (**2c**), were prepared in good yield by the reactions of **1b** and **1c** respectively with potassium bis(trimethyl)silyl amide at an ambient temperature in toluene. The lithium complex [κ^2 -(2,6-tBu₃-4-Me-C₆H₂O)Li(Im^{tBu}NCON(H)Ph)]₂{Im^{tBu}NCON(H)Ph} (**3a**) was isolated by a one-pot reaction between **1a** and LiCH₂SiMe₃ followed by the addition of 2,6-tBu₃-4-Me-C₆H₂OH in toluene. The calcium complex [κ^2 -(Im^{tBu}NCONPh)Ca{N(SiMe₃)₂}-{KN(SiMe₃)₂}]_n (**4a**) was isolated by the one-pot reaction of **1a**, with [KN(SiMe₃)₂] and calcium diiodide in THF at an ambient temperature. The solid-state structures of ligand **1a** and complexes **2b**, **2c**, **3a** and **4a** were confirmed by single-crystal X-ray diffraction analysis. It was observed that, in the solid-state structure of **2b**, potassium was coordinated to the oxygen atom of the ureate group and the nitrogen atom from the imidazol-2-imine group. In the complex **4a** though, the calcium ion was ligated to the monoanionic imidazol-2-ylidene-N'-phenylureate ligand in bi-dentate (κ^2) fashion through the oxygen and nitrogen atoms of the isocyanate building block, leaving the imidazol-2-imine fragment uncoordinated. In the solid state of the potassium complex **2c**, tri-dentate (κ^3) coordination from imidazol-2-ylidene-N'-phenylureate ligand was observed through the oxygen and nitrogen atoms of the isocyanate building block and the imidazol-2-imine fragment. In contrast, in the dimeric lithium complex **3a**, the neutral imidazol-2-ylidene-N'-phenylureate ligand was bound to the lithium centre in a mono-dentate fashion (κ^1) through an oxygen atom of the isocyanate moiety. It is to be noted that in each complex thus observed, the elongated carbon–nitrogen bond distances indicate substantial electron delocalisation from the imidazole ring to the ureate group present in ligand **1**.

Introduction

From an early stage, ligands having amine or imine functionality have played an important role in the field of coordination chemistry.¹ 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 the development of diverse research areas such as homogeneous catalysis,² materials science³ and medicinal chemistry.⁴

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. The analogous principle can be applied to organic imidazolin derivatives containing an exo-cyclic atom or organic moiety X attached at the 2-position of the N-heterocycle such that, for species such as 2-methylen-, 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}

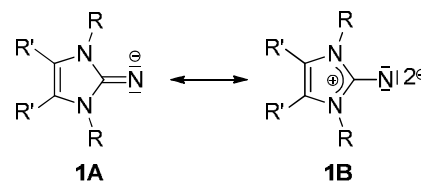


Chart 1. Mesomeric forms of imidazol-2-iminato ligand.

It was established that, the resulting build-up of negative charge at X atom due to mesomeric form **1B**, the atom X possesses enhanced basicity and nucleophilicity.⁷ In recent years, Tamm and co-workers have exploited this concept by providing access to a large variety of novel imidazol-2-imines (ImNH, X = NH) that can be used for the preparation of imidazol-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.⁸ The M–N bond possesses a multiple bonding character - its reactivity is described as being very similar to a M=N imido bond.⁹ It has been observed that various metal complexes supported by imidazolin-2-iminato ligands display high activity in ethylene (co)polymerisation and alkyne metathesis.¹⁰

Lavoie et al. recently reported the preparation of urea and thio-urea derivatives imidazol-2-ylidene-N'-p-tolylureate and imidazol-2-ylidene-N'-p-tolylthioureate from imidazolin-2-imines and *p*-tolyl isocyanate and isothiocyanate respectively.¹¹ This family of neutral polydentate ligands incorporates the imidazolin-2-imine fragment in its fold. Lavoie et al. also introduced these urea- and thio-urea functionalised ligands into groups 4 and 10 of transition metal chemistry in order to explore their coordination behaviours. It was observed that these bi-dentate urea- and thio-urea functionalised ligands bound the more electro positive titanium (Ti⁴⁺) ions through the nitrogen and oxygen atoms of the isocyanate building block, while leaving the imidazol-2-imine fragment uncoordinated. However, the lesser electropositive metal ions (Ni²⁺ and Pd²⁺) are ligated through both the nitrogen atoms of the ligand. Nevertheless their work was restricted to transition metal chemistry. The structural aspects of alkali metal and alkaline earth metal complexes with these ligands have not been reported till date.

We have earlier reported about phosphine functionalised imidazolin-2-imines, imidazolin-2-ylidene-1,1-diphenylphosphinamine and their chalcogenide derivatives (O, S, Se, and Te).¹² In our ongoing efforts to prepare functionalised imidazolin-2-imines, and with an interest to observe and record their coordination behaviour towards main group organometallics, we prepared various alkali metal and alkaline earth metal complexes with imidazolin-2-imine urea derivatives.

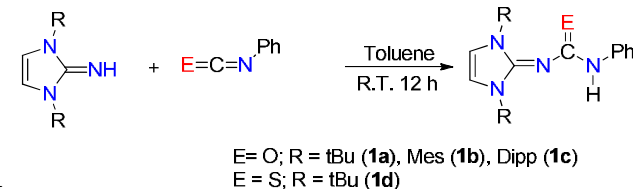
It is in this context that we present here the synthetic and structural details of two potassium complexes [$\{\kappa^2\text{-(Im}^{\text{Mes}}\text{NCONPh)K}\}_4$] (**2b**) and [$\{\kappa^3\text{-(Im}^{\text{Dipp}}\text{NCONPh)K}\}_2\{\text{KN}(\text{SiMe}_3)_2\}_2\}_n$] (**2c**), one lithium complex (**3a**) and one calcium complex [$\{\kappa^2\text{-(Im}^{\text{tBu}}\text{NCONPh)-Ca}\{\text{N}(\text{SiMe}_3)_2\}\{\text{KN}(\text{SiMe}_3)_2\}_n$] (**4a**) of imidazol-2-ylidene-N'-phenylureate ligand [$\text{Im}^{\text{R}}\text{NCON}(\text{H})\text{Ph}$] [$\text{R} = \text{tBu}$ (**1a**); Mes (**1b**) and Dipp (**1c**); Mes = mesityl, Dipp = 2,6-diisopropylphenyl]. We also report the molecular structures of imidazol-2-ylidene-N'-phenylureate ligand (**1d**) and a siloxane incorporated calcium complex [$\{\kappa^3\text{-(Im}^{\text{tBu}}\text{NCONPh)}\}_2\{\text{Ca}(\text{OSiMe}_2\text{OSiMe}_2\text{O})_2\}\{\kappa^3\text{-(Im}^{\text{tBu}}\text{NCONPh)CaK}\}_2\{\text{KN}(\text{SiMe}_3)_2\}_2\}\{\text{Ca}(\text{N}(\text{SiMe}_3)_2)_2\}_n$] (**5a**).

Results and discussion

Ligand synthesis:

The imidazol-2-ylidene-N'-phenylureate and -thioureate ligands were prepared by the analogous method reported by Lavoie et al.¹¹ Imidazolin-2-imines (Im^RNH) having 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^RNCON(H)Ph] (R = tBu (**1a**); Mes (**1b**) and Dipp (**1c**)) (Scheme 1). The analogous thioureate ligand [Im^{tBu}NCSN(H)Ph] (**1d**) was isolated by the reaction of [Im^{tBu}NH] 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.



Scheme 1. Synthesis of imidazol-2-ylidene-N'-phenylureate/thioureate ligands.

The ¹H NMR spectra measured in C₆D₆ for the compounds **1a–c** and CDCl₃ (**1d**) are similar and show a characteristic singlet resonance [d 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 respective imidazol-2-imines [d 5.96 (tBu); 5.71 (Mes); 5.87 (Dipp) ppm]. The resonances for 18 protons from 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 having 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 (**1c**) 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,¹³ a manifestation of the electron delocalisation from the imidazole ring to the acyl group, a further decreasing the C–O bond order can be realised. The resonance for 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 FT-IR spectrum of **1d** indicated the presence of C=S group. However the exact band was difficult to identify due to the mixing of other vibration modes.¹⁴

Single crystals of **1a** and **1d** were obtained from the concentrated toluene solution of respective compounds at ambient temperatures. Compound **1a** crystallised in the monoclinic space group *P*₂₁/*c* with four molecules in the unit cell. In contrast, the thiourea derivative **1d** crystallised in the trigonal space group *R*-3 with 18 molecules in the unit cell. The details of structural parameters are given in Table TS1 in the supporting information. The solid-state structure of complex **1a** is shown in Figure 1 whereas Figure S1 in the supporting information represents the solid-state structure of **1d**. The C1–N1 bond distance of 1.346(3) Å in **1a** is elongated as compared to Im^{tBu}NH [1.295(2) Å]¹⁵. This is 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 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] as compared to the N4–C12 bond [1.389(3) Å] is also supportive of the above delocalisation over N1–C12–O1 unit on ligand **1a**. Short hydrogen bonding between electronegative oxygen atom and hydrogen atoms from adjacent methyl groups, O1...H5a (2.706 Å) and O1...H9c (2.541 Å), are observed (Figure 1).

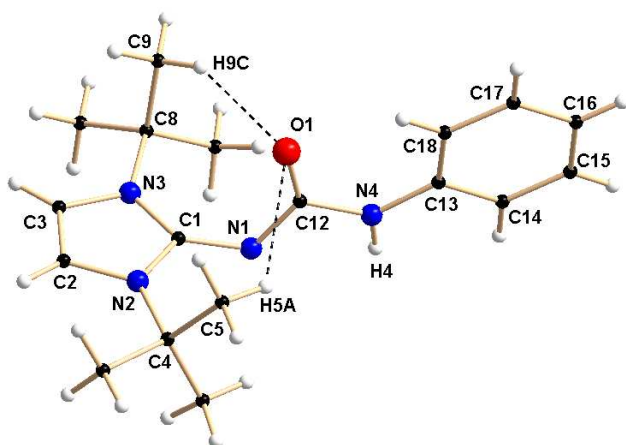
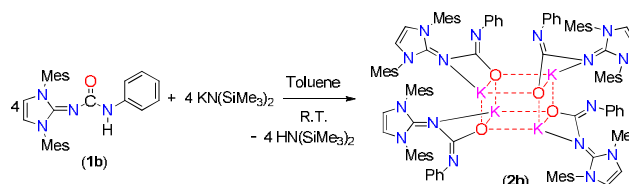


Figure 1. Solid-state structure of complex **1a**. Selected bond lengths [Å] and bond angles [°]: N1–C12 1.339(3), N4–C12 1.389(3), C12–O1 1.236(3), N1–C1 1.346(3), C1–N2 1.362(3), C1–N3 1.358(3), C2–C3 1.324(4), N1–C12–N4 111.1(2), N1–C12–O1 127.1(2), N4–C12–O1 121.8(2).

Potassium complexes:

In the recent past, we reported the syntheses and structural studies of highly reactive alkali metal complexes to apply them well-defined precursor for various salt metathesis reactions.¹⁶ To get additional insight into the structure–reactivity relationships of alkali metal complexes of imidazol-2-ylidene-*N'*-phenylureate ligand, 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 tetra-nuclear structure **2b** in good yield (Scheme 2). The ligand **1d** was reacted in similar fashion with alkali and alkaline earth metal precursors; however we could not isolate any of the corresponding alkali metal or alkaline earth metal complex probably due to soft nature of the sulfur atom which did not preferred hard metal ions. The polymeric potassium complex **2c** was isolated in 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 NMR spectroscopy and the solid-state structures of complexes **2b** and **2c** were established by single-crystal X-ray diffraction analysis.



Scheme 2. Synthesis of heterocubane potassium complex **2b**.

The ¹H NMR spectra of complexes **2b** and **2c**, measured in C₆D₆, 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 measures are in a similar range with 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 146.7 ppm for **1b**) and at 147.5 ppm for **2c** (versus 150.5 ppm 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.

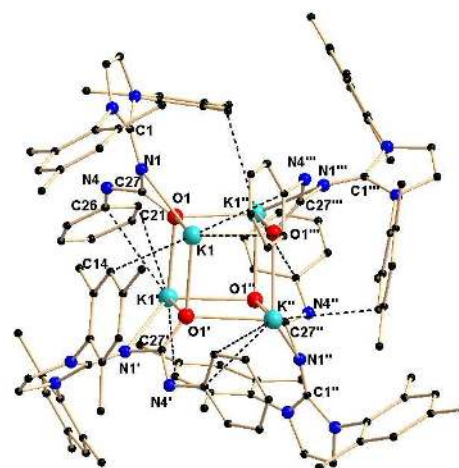


Figure 2. Solid-state structure of complex **2b**. Hydrogen atoms are omitted for clarity. Secondary interaction of potassium atoms and carbon atoms are shown. Selected bond lengths [Å] and bond angles [°] K1–O1 2.709(2), K1–O1' 2.659(3), K1–O1'' 2.662(3), K1–N1 2.803(3), N1–C27 1.411(5), N4–C27 1.309(5), C27–O1 1.279(4), N1–C1 1.285(5), K1–C14 3.499(4), K1'–C21 3.423(7), O1–K1–N1 49.01(8), K1–N1–C27 90.0(2), N1–C27–O1 116.4(3), O1–K1–O1' 80.42(8), O1–K1–O1'' 80.37(8), O1'–K1–O1'' 87.87(8), K1–O1–K1' 99.56(8), K1–O1–K1'' 99.64(9), K1'–O1–K1'' 89.15(8), N1–C27–N4 115.5(3).



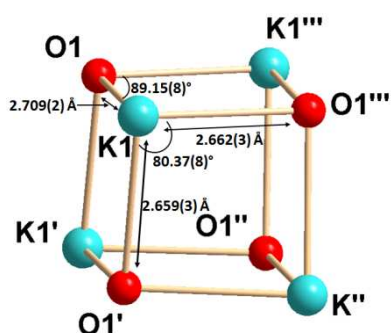
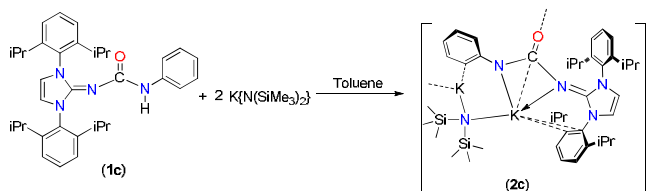


Figure 3. The heterocubane core in **2b** formed by potassium and oxygen atoms.

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 $P-4_2/c$, 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 $P2_1/c$ 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 supporting information. The solid-state structure of complex **2b** is shown in Figure 2. This solid-state structure of the tetra-nuclear potassium complex **2b** has 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 isocyanate 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 the K–O–K angle being between 80.37(8) and 89.15(8) $^{\circ}$, thus confirming a 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 (Figure 3). Significant electron donation from the imidazolium ring to the ureate group is evident from the unusual elongation of 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 bond and double bond respectively, thus indicating extensive electron delocalisation over N1–C27–O1. A similar observation has been reported in [CpTiCl₂(Im^{Mes}NCONTo)](Tol = *p*-tolyl) by Lavoie et al.¹¹ They have however reported a bi-dentate mode of coordination of the ureate ligand through the oxygen and nitrogen atoms of the isocyanate 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. Even similar pattern of bonding was discussed by Snaith et al, it must also be noted that such a heterocubane structural motif, derived using an ureate ligand in alkali metal chemistry, has not been reported so far.¹⁷



Scheme 3. Synthesis of polymeric potassium complex **2c**.

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 potassium precursor for its preparation compared to one equivalent used for synthesis of **2b**. The asymmetric unit of complex **2c** is shown in Figure 4. The molecular structure of **2c** confirms the κ^3 coordination of the ureate ligand towards potassium. It further reveals that two molecules [K(N(SiMe₃)₂)] are also present in the asymmetric unit in order to stabilise 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 which 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 ligand with the potassium ion. The phenyl ring of the isocyanate building block plays a key role in holding two [(Im^{Dipp}NCONPh)K] units through the bridging of two phenyl–carbon atoms. Thus, an additional two six-membered metallacycles, K1–N4–C29–C34–K2–N5 and K3–N6–K4–N10–C72–C73, are observed as a result of the coordination of phenyl carbon and nitrogen from bis(trimethyl)silyl amide fragment. Further units of the molecule grow from the ends of potassium ions K3 and K4 to lead to complex **2c** as a polymer. The bond distances in complex **2c** (C1–N1 1.289 Å, C44–N7 1.283(6) Å, N1–C28 1.418(5) Å, N7–C71 1.418(5) Å, N4–C28 1.327(6) Å, C71–N10 1.324(6) Å, C28–O1 1.248(5) Å, C71–O2 1.255(6) Å) are in a range similar to those in complex **2b** and indicate significant electron delocalisation over N1–C28–N4 and N7–C71–N10. To the best of our knowledge, complex **2c** is the first example where the monoanionic ureate ligand acts as the κ^3 coordination mode using its three donor atoms. A similar polymeric potassium complex $\{[(K(\mu_4\text{-oMP})(\text{THF}))][K(\mu_3\text{-oMP})]\}_n$ (oMP = *o*-methyl phenol) has been reported by Boyle and his co-workers.¹⁸ Due to the fluxional nature of the complex **2c**, only one set of NMR signals was observed.



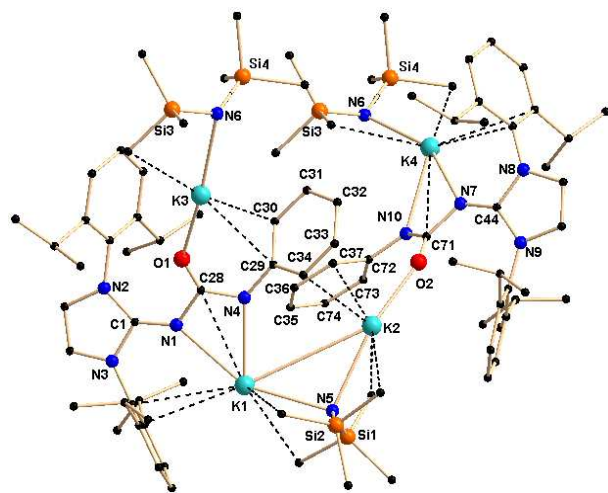
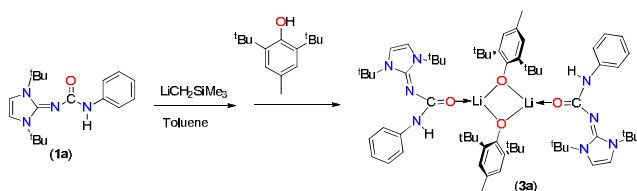


Figure 4. Solid-state structure of complex **2c**. Hydrogen atoms are omitted for clarity. Secondary interaction of potassium atoms and methyl carbon atoms are shown. Selected bond lengths [Å] and bond angles [°]: K1–N1 2.734(4), K1–N4 2.726(4), K1–N5 2.769(4), N1–C28 1.417(5), N4–C28 1.327(6), N4–C29 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–C29 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).

15 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 two oxygen atoms. We were interested in exploring the coordination behaviour of monoanionic ureate ligand 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 $\text{LiCH}_2\text{SiMe}_3$ in 1:1 molar ratio in toluene with one equivalent of 2,6-tert-butyl-3-methyl phenol to afford a lithium derivative, complex **3a** (Scheme 4). Complex **3a** was characterised using ^1H , ^{13}C NMR and combustion analysis, while its solid-state structure was established using single-crystal X-ray crystallography.



Scheme 4. Synthesis of lithium complex **3a**.

In the ^1H NMR spectra of complex **3a** measured in C_6D_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-butyl methyl protons of the imidazol scaffold resonated at 1.46 ppm whereas

the ^1Bu 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 phenoxy moiety. In ^{13}C spectra, resonance 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**.

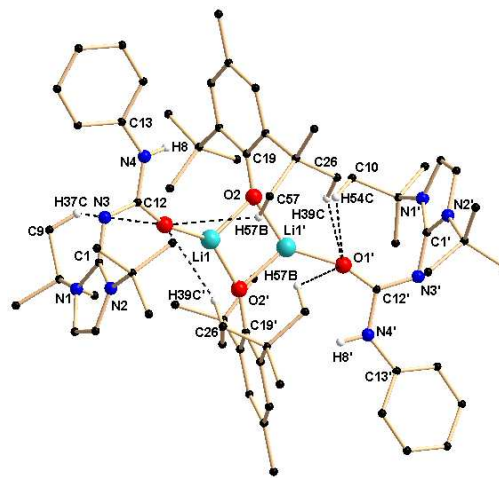


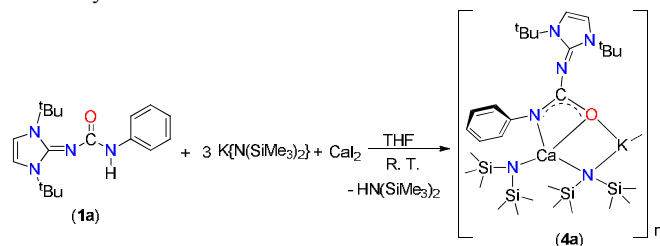
Figure 5. Solid-state structure of complex **3a**. Hydrogen atoms are omitted for clarity except for those which have bonding interactions with oxygen atoms. Selected bond lengths [Å] and bond angles [°]: Li1–O1 1.835(9), Li1–O2 1.863(9), Li1–O2' 1.911(8), O2–Li1' 1.911(8), O1–C12 1.270(6), N3–C12 1.310(6), C12–N4 1.394(6), C1–N1 1.363(6), Li1–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).

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 $P2_1/c$ along with a molecule of **1a**. The details of structural parameters are given in Table TS1 in the supporting information. The solid-state structure of the lithium fragment of complex **3a** is shown in Figure 5. The molecular structure clearly indicates that neutral urea ligand **1a** coordinated to the lithium ion in a κ^1 mode through the oxygen atom of the isocyanate building block of the ligand. A four-membered Li_2O_2 diamond core is 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 Li–O2 bond (1.863(9) Å) where the oxygen atom is anionic. Dimeric lithium phenoxy complexes $[(2,6\text{-tBu}_3\text{-4-Me-C}_6\text{H}_2\text{O})\text{Li}(\text{THF})]_2$ and $[(2,6\text{-tBu}_3\text{-C}_6\text{H}_2\text{O})\text{-Li}(\text{DMSO})]_2$, where one solvent (THF or DMSO) molecule is attached with each lithium centre to stabilise the respective complex, are reported in literature.¹⁹ Thus, delocalisation of electrons over N3–C12–O1 centres are observed in complex **3a**. Furthermore, elongation of the C1–N3 bond [1.360(6) Å versus 1.346(3) Å for **1a**] and O1–C12 bond [1.270(6) Å versus 1.236(3) Å for **1a**] also supports the above fact. It is assumed that the more nucleophilic lithium complex $[\text{Im}^{\text{tBu}}\text{NCONPhLi}]$ generated from **1a** and $\text{LiCH}_2\text{SiMe}_3$ undergoes protonolysis reaction with 2,6-tert-butyl-3-methyl phenol to form the neutral urea ligand and the lithium bis-phenoxy complex **3a**. Thus, the 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 ^tBu groups with more electronegative oxygen atoms, important for the crystallisation of the compound (Figure 5), were also observed in complex **3a**.

Calcium complex:

The alkaline earth metal compounds have been recently employed in various catalytic applications in order to achieve ring-opening polymerisation of various cyclic esters,²⁰ polymerisation of styrene and dienes,²¹ and hydroamination and hydrophosphination reactions of alkenes and alkynes.²² Determining the structure and reactivity of alkaline earth metal species is an important step towards the design and development of efficient catalysts. However, full realisation of the catalytic potential of these elements still requires substantial advances 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.²³ In our ongoing study of alkaline earth metal chemistry, we wish to introduce mono-anionic ureate ligand **1** into group 2 metal chemistry.



Scheme 5. Synthesis of calcium complex **4a**.

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 1:3 molar ratio in THF followed by the addition of one equivalent calcium diiodide at ambient temperature (Scheme 5). However initial attempt to isolate the potassium free calcium iodo complex $(1a)CaI(THF)_n$ using the starting reagents in 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 solid-state structure was established using single-crystal X-ray crystallography.

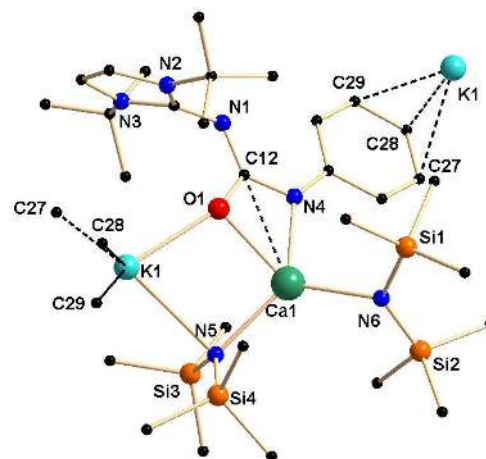


Figure 6. Solid-state structure of asymmetric unit of complex **4a**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Ca1–O1 2.3558(17), Ca1–N4 2.367(2), Ca1–N6 2.317(2), Ca1–N5 2.348(2), K1–O1 2.6199(18), K1–N5 2.989(2), O1–C12 1.308(3), N4–C12 1.357(3), C12–N1 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).

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. The details of structural parameters are given in Table TS1 in the supporting information, the asymmetric unit of complex **4a** is shown in Figure 6, and the polymeric unit is given in Figure 7. It is clearly seen in the asymmetric unit that two metal ions of calcium and potassium are respectively connected via μ_2 bridging of the oxygen atom of the ureate ligand and the nitrogen atom from the bis(trimethylsilyl)amido group. This resulted in the four-fold coordinated central metal calcium ion adopting a distorted tetrahedral geometry due to the κ^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 bound the calcium ion to give two additional bonds. Thus, a four-membered metallacycle C1–O2–Ca1–N6 was formed to demonstrate the κ^2 coordination of ligand **1a** towards the calcium ion. The slight elongation of the C12–O1 bond [1.308(3) versus 1.236(3) Å for **1a**] and the slight shortening of the C12–N4 bond [1.357(3) versus 1.389(3) Å] indicated an electron delocalisation over the O1–C12–N4 skeleton. The unperturbed bond distances of N1–C1 [1.338(3) versus 1.346(3) Å] and N1–C12 [1.342(3) versus 1.339(3) Å] are supportive of the non-interacting nature of the imidazolin-2-imine fragment towards ligation with either metal ions. In addition, a four-membered metallacycle O1–K1–N5–Ca1 was also formed. The bond distances Ca1–N4 [2.367(2) Å] and Ca1–O1 [2.355(2) Å] were similar to those [(2.4356(2) and 2.2805(1) Å respectively] in the monomeric calcium ureate complex $[(\text{NacNac})Ca(\eta^2\text{-AdN}=\text{C}(\text{NPh}_2)\text{O})]$ (Ad = adamantyl) reported by Hill and co-workers.²⁴ Similar mixed metal complexes having potassium-calcium, potassium zinc, lithium-calcium and lithium-magnesium are reported in literature.²⁵ The potassium ion K1 led the



formation of the polymeric network by growing repetitive asymmetric units via η^3 interaction with the phenyl ring of the adjacent ureate ligand fragment from another unit (Figure 7). Such a polymeric network structure was realised due to the existence of multiple donor atoms in the ligand. In the NMR spectra of **4a**, the presence of only one set of signals confirmed the fluxional nature of the complex.

(Figure 7 here)

Figure 7. Polymeric network of complex **4a** in the solid state.

The synthesis of complex **4a** was performed as a one-pot reaction followed by the crystallisation process. An undesired minor product **5a** was also isolated from the re-crystallisation of the second crop solution after complex **4a** had been separated. Complex **5a** was characterised using NMR spectroscopy and the solid-state structure of **5a** was established by single-crystal X-ray diffraction analysis.

Complex **5a** showed one set of signals in the ^1H NMR spectra measured in C_6D_6 . The resonances for the olefinic protons were obtained at δ 6.12 ppm as singlet whereas the sharp singlet at δ 1.42 ppm could be assigned to the *tert*-butyl group in the imidazol fragment. In addition, sharp singlet for the trimethylsilyl groups were also observed at δ 0.43 ppm confirming the presence of SiMe_3 groups in the complex. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra was also within the expected range and very similar to that of complex **4a**.

(Figure 8 here)

Figure 8. Solid-state structure of asymmetric unit of complex **5a**. Hydrogen atoms are omitted for clarity. Selected bond lengths [\AA] and bond angles [$^\circ$]: Ca1–O1 2.329(3), Ca1–O1' 2.329(3), Ca1–O2 2.339(3), Ca1–O3 2.370(3), Ca2–O1 2.332(3), Ca2–O2 2.290(3), Ca2–O4 2.389(3), Ca2–N7 2.390(4), Ca2–N6 2.372(4), Ca2–C11 2.965(5), Ca2–C12 2.804(5), K1–O3' 3.314(4), K1–O1 2.768(3), K1–O2 2.694(4), K2–N8 2.734(4), K2–N3 2.907(4), O3–C11 1.301(6), N6–C11 1.390(6), N10–C11 1.316(6), Si1–O5 1.634(4), Si1–O1 1.606(3), O1–Ca1–O2 79.75(11), O1–Ca1–O2' 80.71(12), O1–Ca1–O2' 100.25(11), O1–Ca1–O1' 180.000(1), O1–Ca1–O3 83.22(12), O1–Ca2–O3 77.57(11), O1–Si1–O5 112.20(19), O5'–Si2–O2 110.86(19).

Complex **5a** crystallised in the triclinic space group *P*-1 with one molecule in the unit cell. The details of structural parameters are given in Table TS1 in the supporting information, and the asymmetric unit of complex **5a** in solid-state structure is shown in Figure 8. The molecular structure is evidence of incorporation of two fragments of dianionic disiloxane units $[(\text{Me}_2\text{SiO})_2\text{O}]^{2-}$ 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 from two siloxane $[(\text{Me}_2\text{SiO})_2\text{O}]^{2-}$ units and two oxygen atoms from two ureate ligands resulting in the adoption of a distorted octahedral geometry around it. Each of the remaining two calcium ions had similar coordination spheres formed by the chelation of two μ_3

oxygen atoms O1 and O2 of two siloxane $[(\text{Me}_2\text{SiO})_2\text{O}]^{2-}$ 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) making the ureate ligand a tridentate; the coordination mode can be best described as κ^3 towards a metal ion. Apart from these calcium ions, the fourth calcium ion Ca3 exists as a $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]$ fragment in the molecule. Two kinds of potassium ions were also observed. The potassium ion K1 bound with two μ_3 oxygen atoms (O1 and O2) from the two siloxane $[(\text{Me}_2\text{SiO})_2\text{O}]^{2-}$ units and with two oxygen atoms (O3 and O4) from two isocyanate building blocks of ureate ligand. Furthermore, a η^6 attachment with adjacent phenyl ring with a distance of (2.992–3.317 \AA), which is quite common in potassium organometallic complexes, was also obtained.²⁶ The second potassium atom K2, having one $[\text{N}(\text{SiMe}_3)_2]^-$ group attached, was coordinated by one imidazolin-2-imine nitrogen N3 along with η^6 arene interaction with the adjacent phenyl ring with a distance of (3.165–3.452 \AA). Even the imidazol-2-iminato exocyclic C–N bond distances [N3–C24 1.342(6) \AA and N6–C13 1.349(6) \AA versus 1.346(3) \AA for **1a**] remained unchanged. The bond elongation of urate fragments [N3–C12 1.362(6) and N6–C11 1.391(6) \AA versus 1.339(3) \AA for **1a**; C12–O4 1.299(6) and C11–O3 1.301(6) \AA versus 1.236(3) \AA for **1a**] led to the conclusion that electron delocalisation occurs mainly on N3–C12–O4 and N6–C11–O3 skeletons. The shortening of bonds C12–N7 1.341(6) and C11–N10 1.316(6) [versus 1.389(3) \AA 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 reaction conditions so as to afford complex **5a**. However, in a separate reaction, using silicon-free grease, complex **4a** was prepared without contamination from complex **5a**. In complex **5a**, calcium ion Ca3 led to the repetition of 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 LiAlH_4 and stored in the glove box. ^1H NMR (400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a BRUKER AVANCE III-400 spectrometer. BRUKER ALPHA FT-IR was used for FT-IR measurement. Elemental analyses were performed on a BRUKER EURO EA at the Indian Institute of Technology Hyderabad (IITH). Imidazolin-2-imines $[(\text{Im}^R\text{NH})]$ (R = *t*Bu, Mes, Dipp) and trimethylsilylmethyl lithium $[\text{LiCH}_2\text{SiMe}_3]$ were prepared according to procedures specified in literature.¹⁵ Phenyl isocyanate, phenyl isothiocyanate, 2,6-di-*tert*-butyl-4-methyl phenol, $[\text{K}\{\text{N}(\text{SiMe}_3)_2\}]$ and Ca_2 were purchased from Alfa Aesar and used in their original forms.



The NMR solvents CDCl₃ and C₆D₆ were purchased from Sigma Aldrich and dried under Na/K alloy prior to use (for C₆D₆).

Preparation of [Im^RNCON(H)Ph] (R = tBu) (**1a**); Mes (**1b**) and Dipp (**1c**)

To a toluene solution (10 ml) of imidazole-2-imine (Im^RNH) (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 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, C₆D₆): δ 7.9 (br, 1H, HN), 7.81 (d, ³J_{H-H} = 7.75 Hz, 2H, Ph), 7.18 (m, 2H, Ph), 6.83 (t, ³J_{H-H} = 7.32 Hz, 1H, Ph), 6.18 (s, 2H, HC=CH), 1.43 (s, 18 H, C(CH₃)₃) ppm. ¹³C {¹H} NMR (100 MHz, C₆D₆): δ 158.8 (C=O), 150.4 (NCN), 143.4 (Ar), 128.9 (Ar), 120.2 (Ar), 117.8 (Ar), 112.0 (HC=CH), 58.4 (NC(Me)₂), 29.1 (C(CH₃)₃) ppm. FTIR selected peaks (cm⁻¹): 1627 (C=O), 1574 (C=N), 2979 (CH), 3155, 3287 (N-H). (C₁₈H₂₆N₄O) (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, ³J_{H-H} = 7.88 Hz, 2H, Ph), 6.89 (m, 2H, Ph), 6.72 (s, 4H, *m*-CH(mesityl)), 6.62 (t, ³J_{H-H} = 7.48 Hz, 1H, Ph), 6.44 (br s, 1H, NH), 5.81 (s, 2H, HC=CH), 2.26 (s, 12H, *o*-CH₃(mesityl)), 2.05 (s, 6H, *p*-CH₃(mesityl)) ppm. ¹³C {¹H} NMR (100 MHz, C₆D₆): 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 (HC=CH), 21.0 (CH₃), 18.2 (CH₃) ppm. FTIR selected peaks (cm⁻¹): 1580 (C=N), 1647 (C=O), 2916, 3211 (N-H). (C₂₈H₃₀N₄O) (438.56) Calc. C 76.68, H 6.89, N 12.78; found C 76.31 H 6.39, N 12.29.

1c: Yield 506 mg, 78%. ¹H NMR (400 MHz, C₆D₆): δ 7.22-7.20 (m, 4H, Ar), 7.12-7.10 (m, 2H, Ar), 6.98 (d, ³J_{H-H} = 8.72 Hz, 2H, Ph), 6.92-6.88 (m, 2H, Ph), 6.63 (t, ³J_{H-H} = 7.20 Hz, 1H, Ph), 6.10 (s, 2H, HC=CH), 3.12 (sept, ³J_{H-H} = 6.80 Hz, 4H, CH(CH₃)₂), 1.45 (d, ³J_{H-H} = 6.80 Hz, 12H, CH(CH₃)₂), 1.16 (d, ³J_{H-H} = 6.80 Hz, 12H, CH(CH₃)₂) ppm. ¹³C {¹H} NMR (100 MHz, C₆D₆): δ 157.1 (C=O), 151.2 (NCN), 146.6 (*ipso*-Ar), 141.5 (*ipso*-Ph), 133.9 (*o*-Ar), 124.2 (*o*-Ph), 120.8 (*p*-Ph), 118.1 (*m*-Ph), 116.6 (HC=CH), 29.2 (CH(CH₃)₂), 24.4 (CH(CH₃)₂), 23.7 (CH(CH₃)₂) ppm. FTIR selected peaks (cm⁻¹): 1580 (C=N), 1650 (C=O), 2962, 3053, 3419 (N-H). (C₃₄H₄₂N₄O) (522.72) Calc. C 78.12, H 8.10, N 10.72; found C 77.86, H 7.91, N 10.51.

Preparation of [Im^{tBu}NCSN(H)Ph] (**1d**)

To a toluene solution (10 ml) of 1,3-di-*tert*-butylimidazole-2-imine (300 mg, 1.536 mmol), 5% 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 spectroscopically pure off-white solid. The title compound **1d** was re-crystallised from concentrated solution of toluene.

Yield: 436 mg 86%. ¹H NMR (400 MHz, C₆D₆): δ 7.80 (s, 1H, HN), 7.62 (d, ³J_{H-H} = 7.84 Hz, 2H, Ph), 7.20 (m, 2H, Ph), 6.89 (t, ³J_{H-H} = 7.32 Hz, 1H, Ph), 6.77 (s, 2H, HC=CH), 1.63 (s, 18 H, C(CH₃)₃) ppm. ¹³C {¹H} NMR (100 MHz, C₆D₆): δ 178.2 (C=O), 151.4 (*ipso*-Ph), 140.9 (NCN), 128.7 (Ph), 121.6 (Ph), 119.6 (Ph), 113.6 (HC=CH), 58.5 (NC(CH₃)₃), 29.7 (C(CH₃)₃) ppm. FTIR selected peaks (cm⁻¹): 1654 (C=S), 1567 (C=N), 2967, 3126, 3235 (N-H). (C₁₈H₂₆N₄S) (330.49) Calc. C 65.42, H 7.93, N 16.95; found C 65.19 H 7.62, N 16.77.

Preparation of [{κ²-(Im^{Mes}NCONPh)K]₂] (**2b**)

In an argon-filled glovebox, toluene (10 ml) solution of compound **1b** (200 mg, 0.456 mmol) was added dropwise to the 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 x 3 ml) and dried in 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, C₆D₆): 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, HC=CH), 3.57 (thf), 2.26 (s, 12H, CH₃), 2.06 (s, 6H, CH₃), 1.40 (thf) ppm. ¹³C {¹H} NMR (100 MHz, C₆D₆): δ 158.2 (C=O), 149.6 (NCN), 146.4 (*ipso*-Ar), 138.4 (*ipso*-Ph), 135.9 (*o*-Ar), 133.9 (Ph), 129.4 (Ph), 128.3 (Ar), 120.1 (Ph), 115.3 (HC=CH), 20.9 (CH₃), 18.2 (CH₃) ppm. FTIR selected peaks (cm⁻¹): 1623 (C=O), 2956, 3078. (C₁₂₈H₁₄₈K₂N₁₆O₈) (2077.75) Calc. C 73.99, H 7.18, N 10.79; found C 73.54 H 6.94, N 10.32.

Preparation of [{κ³-(Im^{Dipp}NCONPh)K]₂{KN(SiMe₃)₂}]_n (**2c**)

Compound **1c** (200 mg, 0.038 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 get a red-coloured residue. The red solid was washed with *n*-hexane (3 x 5 ml) to get a red powder. The title compound **2c** was re-crystallised from concentrated toluene at -35 °C.

Yield 395 mg, 52%. ¹H NMR (400 MHz, C₆D₆): δ 7.53 (m, 2H, Ar), 7.34 (m, 4H, Ar), 7.11 (m, 3H, Ph), 7.00 (m, 2H, Ph), 5.95 (s, 2H, HC=CH), 3.16 (m, 4H, CH(CH₃)₂), 1.29 (d, ³J_{H-H} = 8.43 Hz, 12H, CH(CH₃)₂), 1.12 (d, ³J_{H-H} = 8.43 Hz, 12H, CH(CH₃)₂), 0.09 (s, 18H, Si(CH₃)₃) ppm. ¹³C {¹H} NMR (100 MHz, C₆D₆): δ 165.2 (C=O), 147.5 (NCN), 135.8 (*ipso*-Ar), 135.3 (*ipso*-Ph), 129.3 (Ar), 127.8 (Ph), 120.6 (Ph), 125.7 (Ar), 123.8 (Ar), 115.4 (HC=CH), 29.0 (CH(CH₃)₂), 24.7 (CH(CH₃)₂), 23.5 (CH(CH₃)₂) 2.65 (Si(CH₃)₃) ppm. FTIR selected peaks (cm⁻¹): 1620 (C=O), 2962, 3053. (C₈₀H₁₁₈K₄N₁₀O₂Si₄) (1520.61) Calc. C 63.19, H 7.82, N 9.21; found C 62.72 H 7.41, N 9.01.

Preparation of [(2,6-*t*Bu-4-Me-C₆H₂O)Li(Im^{tBu}NCON(H)Ph)]₂{Im^{tBu}NCON(H)Ph} (**3a**)

To a stirred solution of toluene (5 ml) and compound **1a** (200 mg, 0.636 mmol), a toluene (3 ml) solution of trimethylsilyl methyl lithium (60 mg, 0.636 mmol) was added dropwise in 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, C₆D₆): δ 7.57 (d, ³J_{H-H} = 8.0 Hz, 2H, Ar), 7.22 (t, ³J_{H-H} = 8.0 Hz, 2H, Ar), 7.02 (s, 2H, Ar), 6.85 (t, ³J_{H-H} = 8.0 Hz, 1H, Ar), 6.28 (s, 2H, HC=CH), 2.10 (6H, CH₃), 1.46 (s, 18 H, C(CH₃)₃), 1.30 (18H, C(CH₃)₃) ppm. ¹³C {¹H} NMR (100 MHz, C₆D₆): 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 (HC=CH), 58.6 (NC(Me)₂), 33.8 (C(CH₃)₃), 32.6 (C(CH₃)₃), 32.3 (CH₃), 29.1 (C(CH₃)₃) ppm. FTIR selected peaks (cm⁻¹): 1627 (C=O), 2980, 3155, 3297 (N-H). (C₁₀₂H₁₅₀Li₂N₁₆O₆) (1710.27) Calc. C 71.63, H 8.84, N 13.10; found C 71.33 H 8.37, N 12.87.

Preparation of [{κ²-(Im^{tBu}NCONPh)Ca}{N(SiMe₃)₂}{KN-(SiMe₃)₂}]_n (**4a**)

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 mg, 0.636) and potassium bis(trimethylsilyl)amide (380.6 mg, 1.90 mmol) was added dropwise at ambient temperature. The resulting reaction mixture was further stirred at room temperature for 12 hours. The white precipitate obtained from the reaction mixture was separated by filtration through a G4 frit. The solvent was evaporated under reduced



pressure to obtain an off-white residue which was washed with *n*-hexane (3 x 10 ml) and dried *in vacuo*. The title compound **4a** was re-crystallised from a mixture of THF and toluene (1:3) at -35 °C.

5 Yield 426 mg, 57%. ¹H NMR (400 MHz, C₆D₆): δ 7.80 (m, 2H, Ar), 7.29 (m, ³J_{H-H} = 8.0 Hz, 2H, Ar), 7.06 (m, 1H, Ar), 6.16 (s, 2H, HC=CH), 3.42 (thf), 1.40 (thf), 1.49 (s, 18 H, C(CH₃)₃), 0.43 (s, 18H, Si(CH₃)₃), 0.21 (s, 18H, Si(CH₃)₃) ppm. ¹³C {¹H} NMR (100 MHz, C₆D₆): δ 164.1 (C=O), 152.7 (NCN), 129.5 (Ar), 129.1 (Ar), 128.1 (Ar), 127.2 (Ar), 123.9 (Ar), 119.2 (Ar), 111.6 (HC=CH), 68.5 (NC(CH₃)₃), 57.8 (thf), 29.4 (C(CH₃)₃) 25.2 (thf), 6.16 (Si(CH₃)₃), 2.90 (Si(CH₃)₃) ppm. FTIR selected peaks (cm⁻¹): 1619 (C=O), 2954. (C₃₃H₆₄CaKN₆OSi₄) (752.42) Calc. C 52.68, H 8.57, N 11.17; found C 52.22 H 8.13, N 10.88.

15 **5a**: Compound **5a** was obtained as a minor product from the second crop solution after the crystals of **4a** were isolated. Yield 195 mg, 8%. ¹H NMR (400 MHz, C₆D₆): δ 7.81-7.68 (m, 2H, Ar), 7.31-7.27 (m, 2H, Ar), 7.14-7.08 (m, 1H, Ar), 6.12 (s, 2H, HC=CH), 3.57 (thf), 1.45 (thf), 1.42 (s, 18 H, C(CH₃)₃), 0.43 (s, 18H, Si(CH₃)₃), 0.21 (s, 18H, Si(CH₃)₃) 0.09 (s, 24H, OSi(CH₃)₂) ppm. ¹³C {¹H} NMR (100 MHz, C₆D₆): δ 168.1 (C=O), 156.3 (NCN), 129.8 (Ar), 129.3 (Ar), 128.0 (Ar), 127.6 (Ar), 125.1 (Ar), 120.2 (Ar), 115.4 (HC=CH), 66.5 (NC(CH₃)₃), 57.8 (thf), 28.4 (C(CH₃)₃) 25.2 (thf), 7.15 (Si(CH₃)₃), 3.76 (Si(CH₃)₃), 1.02 (OSi(CH₃)₂) ppm. FTIR selected peaks (cm⁻¹): 1672 (C=O), 2956. (C₁₁₈H₂₁₂Ca₅K₄N₂₀O₁₀Si₁₂) (2764.96) Calc. C 51.26, H 7.73, N 10.13; found C 50.94 H 7.34, N 9.79.

X-Ray crystallographic studies of complexes **1a**, **1d**, **2b**, **2c**, **3a**, **4a**, **5a**.

30 Single crystals of compounds **1a** and **1d** were grown from concentrated toluene under inert atmosphere at 15 °C. Crystals of **2c** were grown from concentrated solution of toluene at -35 °C, whereas single crystals of **2b**, **4a** and **5a** were grown from a mixture of THF and toluene (1:3) at -35 °C. For all complexes, a crystal of suitable dimensions was mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed either at room temperature (for **1a**) or in a nitrogen stream at 150(2) K. All measurements were made on an Agilent Supernova X-calibur Eos CCD detector with graphite-monochromatic Cu-Kα (1.54184 Å) radiation. Crystal data and structure refinement parameters are 40 summarised in Table TS1 in the supporting information. The structures were solved by direct methods (SIR92)²⁷ and refined on *F*² by full-matrix least-squares methods using SHELXL-97.²⁸ Non-hydrogen atoms were anisotropically refined. H atoms were included in the refinement in calculated positions riding on their carrier atoms. No restraint was made 45 for any of the complexes. The function minimised was $[\sum w(F_o^2 - F_c^2)^2]$ ($w = 1 / [s^2 (F_o^2) + (aP)^2 + bP]$), where $P = (\text{Max}(F_o^2, 0) + 2F_c^2) / 3$ with $s^2(F_o^2)$ from counting statistics. The function R1 and wR2 were $(\sum |F_o| - |F_c|) / \sum |F_o|$ and $[\sum w(F_o^2 - F_c^2)^2 / \sum (wF_o^4)]^{1/2}$ respectively. Diamond-3.0 program was used to draw the molecule. Crystallographic data (excluding 50 structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1046050-1046056. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: + (44)1223-336-033; email: 55 deposit@ccdc.cam.ac.uk).

Conclusion

We have demonstrated the synthetic and structural details of potassium, lithium and calcium complexes of imidazol-2-ylidene-N'-phenylureate ligand which display various coordination modes 60 such as κ^1 , κ^2 and κ^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 imidazol-2-imine nitrogen atom takes part in coordination with potassium and calcium ions. Due to the larger size of the potassium and calcium 65 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 imidazol ring, a heterocubane core K₄O₄ was isolated in potassium complex **2b**.

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Notes and references

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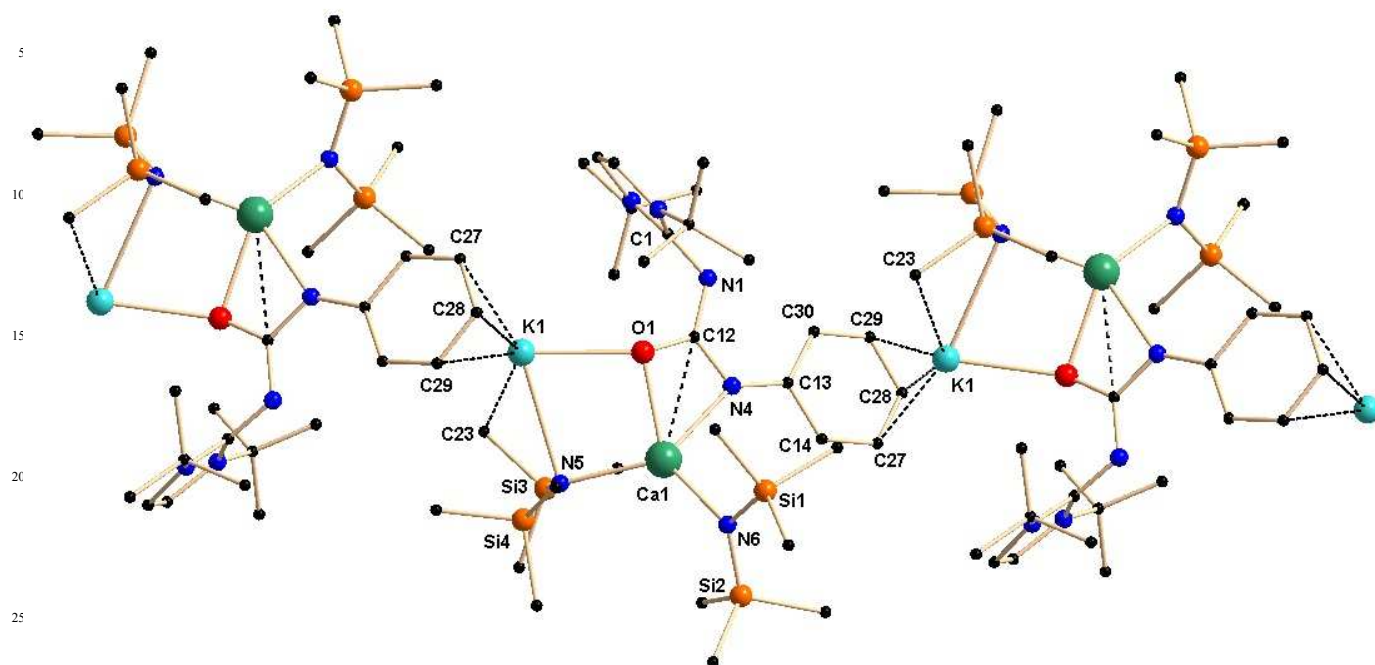
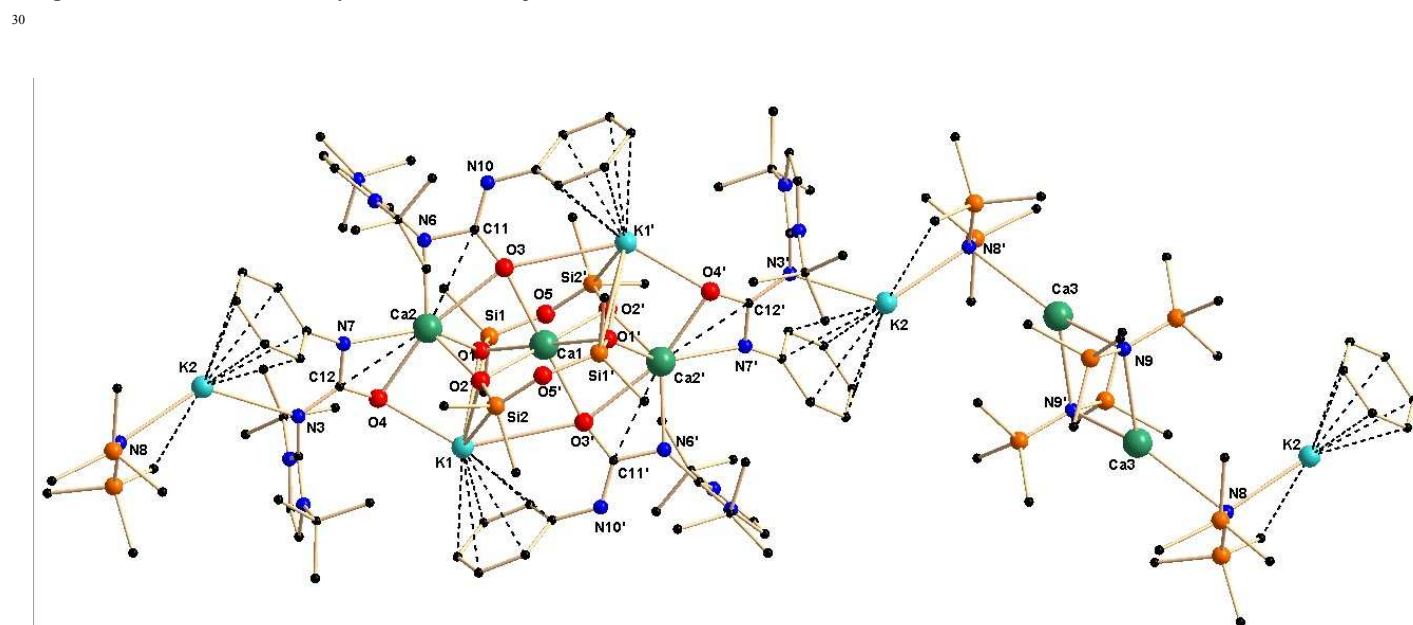


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Figure 7. Polymeric network of complex **4a** in the solid state.**Figure 8.** Solid-state structure of asymmetric unit of complex **5a**.

Imidazol-2-ylidene-N'-phenylureate Ligands in Alkali and Alkaline Earth Metal Coordination Sphere - Heterocubane Core to Polymeric Structural Motif Formation

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Synthetic and structural details of imidazol-2-ylidene-N'-phenylureate ligand supported two potassium complexes having a hetero-cubane K₄O₄ core, and a polymeric structure along with a mixed metal Ca-K complex have been presented.

