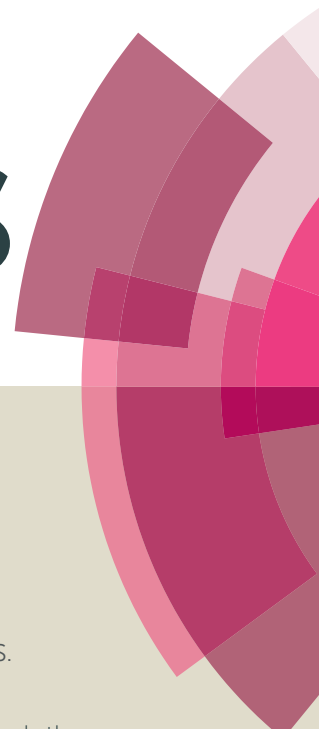


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Alkali Metal Complexes Having Sterically Bulky Bis-Iminopyrrolyl Ligands – Control of Dimeric to Monomeric Complex

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Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

We report the syntheses and structural diversity of three different bis-iminopyrrole ligands and their alkali metal (Li, Na, K) complexes featuring a shift from dimeric to monomeric nature by a simple tuning of the steric control of the imine nitrogen substituents. The bis-iminopyrrole ligands having molecular formula [(ArN=CH)₂C₄H₂NH] [Ar = CHPh₂ (**1-H**), Ad (**2-H**), Ad = adamantyl, and CPh₃ (**3-H**)], were prepared through the reaction of 2,5-pyrrole-dicarbaldehyde with corresponding amines (ArNH₂) in 1:2 molar ratio and under acidic conditions. Using ligand **1-H**, the lithium [[Li(Ph₂CHN=CH)₂C₄H₂N]₂] (**1-Li**), sodium [[Na(Ph₂CHN=CH)₂C₄H₂N]₂(THF)] (**1-Na**) and potassium [{κ²-(Ph₂CHN=CH)₂C₄H₂N}-K(THF)₂] (**1-K**) complexes were obtained through either alkane elimination (for Li) or amine elimination (for Na, K). The alkali metal complexes [{κ²-(Ph₃CHN=CH)₂C₄H₂N}M(THF)_n] [n = 2, M = Li (**3-Li**), Na (**3-Na**); n = 3, M = K (**3-K**)] were synthesized using the ligand **3-H**. Molecular structures of ligands **1-3-H**, and alkali metal complexes **1-Li**, **1-Na**, **1-K**, **3-Li**, **3-Na** and **3-K**, in solid state were established. The complexes **1-Li** and **1-Na** were found to be dimeric in the solid state whereas the complexes **1-K**, **3-Li**, **3-Na** and **3-K** were all monomeric – either due to a larger ionic radius (for **1-K**) or because of the presence of the bulky triphenylmethyl group in the imine nitrogen.

Introduction

The use of di- and tridentate nitrogen based ligands has received significant attention of many research groups due to their comprehensive application in coordination chemistry.¹ Among the multi-dentate nitrogen based ligands, bis-iminopyrrolyl ligands played a decisive role as unique monoanionic ligands to stabilize the various oxo-philic metal complexes. They also served as an excellent ancillary ligand which could be used to stabilize a wide range of metal ions across the periodic table. Bochmann *et al.* were the first to introduce the tridentate 2,5-bis(aryliminomethyl)pyrrolyl ligand into transition metal chemistry.² Subsequently, many research groups introduced this ligand into groups 1-4,³⁻⁶ aluminium,⁷ chromium,⁸ iron,² cobalt,² nickel² and copper⁹ in addition to actinide chemistry too.¹⁰ Many of these complexes were used as active pre-catalysts in various catalytic applications.²⁻⁹ Through an amine elimination method, Mashima *et al.* reported a series of homoleptic and heteroleptic yttrium complexes with different bis-iminopyrroles and varying substituents at the imine nitrogen atom.¹¹ Using this methodology, one could control the formation of mono-, bis-, and tris- pyrrolyl complexes. This can be done by

diversifying the steric control of the ligand. In some cases, the ligand is coordinated to the yttrium metal ion in tri- and di- dentate fashions. From these observations one can envisage that, depending upon the substituents present on the imine nitrogen atoms, bis-iminopyrrolyl ligands can act as both di- (mode A), and tridentate (mode B) coordination modes (Chart 1).¹²

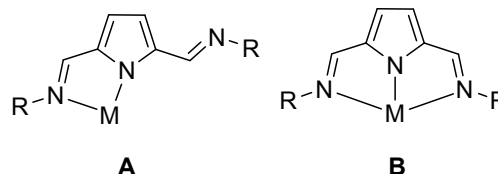


Chart 1. Coordination modes of bis-iminopyrrolyl ligand.

Roesky *et al.* recently reported about lithium and sodium complexes of the 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrole ligand. Both the complexes are dimeric in their solid state structures and are regarded as very rare structural motifs in alkali metal chemistry.³

In our ongoing research, we recently introduced the sterically bulky imino pyrrole ligand into alkali and alkaline earth metal chemistry.¹³ In continuation of our work, we extended our chemistry into two bulkier bis-iminopyrrolyl ligands. We did so in order to study their structural trends in terms of coordination modes. In addition, we also wanted to study the fate of nuclearity of the resulting metal complexes due to the impact of increasing bulk over the ligand backbone. We envisaged that, by adopting sterically demanding substituents on the imine nitrogen atoms of bis-iminopyrrolyl ligands, we would be able to isolate alkali metal complexes having

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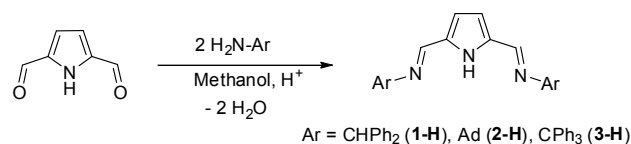
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unusual structural motifs and coordination modes from their observed ones.³⁻⁵

Here, we describe the detailed synthesis and structural properties of bulky bis-iminopyrrole ligands of molecular formula $[(ArN=CH)_2C_4H_2NH]$ [Ar = $CHPh_2$ (**1-H**), Ad (**2-H**), Ad = adamantyl and CPh_3 (**3-H**)], and their corresponding alkali metal complexes $[[Li(Ph_2CHN=CH)_2C_4H_2N]_2]$ (**1-Li**), $[[Na(Ph_2CH-N=CH)_2C_4H_2N]_2(THF)]$ (**1-Na**), $[[\kappa^3-(Ph_2CHN=CH)_2C_4H_2N]-K(THF)_2]$ (**1-K**), and $[[\kappa^2-(Ph_3CHN=CH)_2C_4H_2N]M(THF)_n]$ [$n=2$, M = Li (**3-Li**), Na (**3-Na**); $n=3$, M = K (**3-K**)].

Results and Discussion

Ligand Synthesis: The ligands $[(Ar-N=CH)_2C_4H_2NH]$ (**1-H**, **2-H**, **3-H**) were obtained in good yield and in high purity as a result of the standard condensation reaction of 2,5-pyrrole-dicarbaldehyde with suitable amine [benzhydryl amine for **1-H**, adamantyl amine for **2-H** and triphenylmethyl amine for **3-H**] in 1:2 molar ratio and under acidic conditions (Scheme 1). The ligands **1-H**, **2-H** and **3-H** were characterized by spectroscopic and analytical techniques.



Scheme 1. Syntheses of ligands **1-H**, **2-H** and **3-H**.

The 1H NMR spectrum showed a sharp singlet at δ 8.15 (for **1-H**), 8.05 (for **2-H**) and 7.71 (for **3-H**) ppm respectively. This can be assigned to the imine proton present on the ligand backbone $N=CH$. Sharp singlets appeared at δ 6.45 (**1-H**), 6.42 (**2-H**) and 6.41 (**3-H**) ppm due to the resonance of pyrrolyl ring protons. In ligand **1-H**, an additional singlet resonance at δ 5.54 ppm was observed – this can be assigned to the C-H proton of the $CHPh_2$ group. All aromatic protons were in the expected region and as per reported literature values.¹³ Strong resonance signals for the imine carbon atom $-C=N$ were observed at δ 151.2 ppm (for **1-H**), 145.4 (for **2-H**) and 150.4 ppm (for **3-H**) respectively in the $^{13}C\{^1H\}$ NMR spectra. This was well in agreement with the compounds reported in the literature.¹³ The resonance signals observed at δ 77.6 (**1-H**), 57.2 (**2-H**), and 78.4 ppm (**3-H**) corresponded to the secondary (**1-H**) and tertiary carbon atoms (**2-H** and **3-H**) respectively.

The molecular structures of three ligands (**1-H**, **2-H** and **3-H**) in solid state were established by single crystal X-ray diffraction analysis. The solid state structures of the ligands **1-H** and **3-H** are shown in the figure 1, and details of their structural parameters are given in table TS1. Ligand **1-H** crystallized in the monoclinic space group $P2_1/n$ with four independent molecules in the unit cell along with six THF molecules as solvents. Ligand **2-H** crystallized in monoclinic space group $C2/c$ with eight molecules in the unit cell. However, ligand **3-H** crystallized in the orthorhombic space group $Pbcm$ having four individual molecules in the unit cell. The C-N double

bond distances observed in ligands **1-H**, **2-H** and **3-H** were similar and in agreement with our previously reported bulky iminopyrrole ligand (1.261 Å).¹³

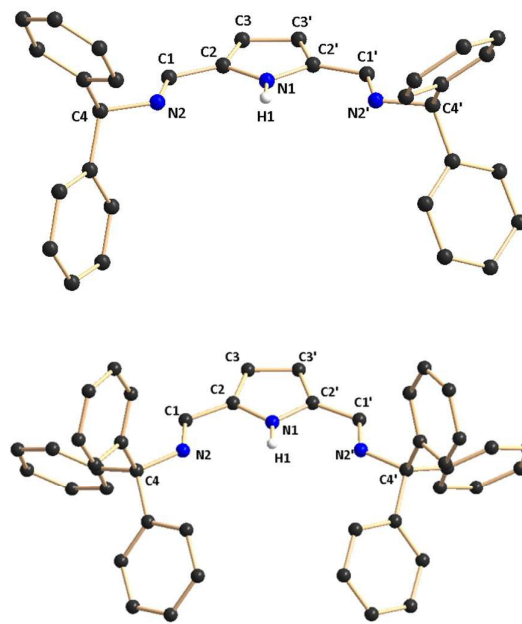
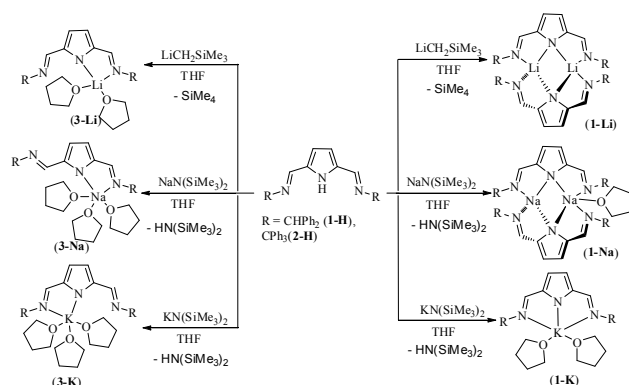


Figure 1. Molecular structure of complex **1-H** (top) and **3-H** (bottom) in their respective solid states. **1-H**: N2-C1 1.271(8), N2-C4 1.478(8), N1-C2 1.376(2), N2-C1-C2 118.2(2), C2-N1-C2¹ 110.5(2), C1-N2-C4 122.7(2); **3-H**: N2-C1 1.271(2), N2-C4 1.484(2), N1-C2 1.376(8), N2-C1-C2 117.1(5), C2-N1-C2¹ 109.7(5), C1-N2-C4 123.2(5).

Alkali metal complexes: As reported by Roesky *et al.*,³ bis-iminopyrrole ligands having 2,6-diisopropylphenyl (Dipp) substitution, $[(DippN=CH)_2C_4H_2NH]$, exhibited the formation of dimeric alkali metals (Li, Na) complexes. Thus, the three different bulky bis-iminopyrrolyl ligands **1-H**, **2-H** and **3-H** presented by us with an excellent opportunity to study the nuclearity of the above mentioned alkali metal complexes. The isolation of these alkali metal complexes demonstrated further the stability of the respective complexes either dimeric or monomeric form accounting the steric factors of the ligands. To study the comparative stability of dimeric and monomeric complexes, and in order to isolate the corresponding metal complexes, we chose the complexes **1-H** and **3-H** to react with three alkali metal precursors. Both the lithium complexes, $[[Li(Ph_2CHN=CH)_2C_4H_2N]_2]$ (**1-Li**) and $[Li\{(Ph_3CH-N=CH)_2C_4H_2N\}(THF)_2]$ (**3-Li**), were obtained by the reaction of $LiCH_2SiMe_3$ with **1-H** and **3-H** respectively *via* elimination of tetramethylsilane ($SiMe_4$). In a similar manner, the sodium, $[[Na(Ph_2CH-N=CH)_2C_4H_2N]_2(THF)]$ (**1-Na**) and $[Na\{(Ph_3CHN=CH)_2C_4H_2N\}(THF)_2]$ (**3-Na**), and potassium, $[K\{(Ph_2CHN=CH)_2C_4H_2N\}(THF)_2]$ (**1-K**) and $[K\{(Ph_3CHN=CH)_2C_4H_2N\}(THF)_2]$ (**3-K**), complexes were synthesized in good yield by the reaction of metal hexamethyldisilazides with respective proteo

ligands **1-H** and **3-H** through the elimination of volatile hexamethyldisilazane (Scheme 2).



Scheme 2. Syntheses of alkali metal complexes using ligand **1-H** and **3-H**.

All the complexes were fully characterized by standard spectroscopic techniques and combustion analysis. The molecular structures of these complexes in the solid state were established by single crystal x-ray analysis. The ^1H NMR spectra measured in C_6D_6 of the alkali metal complexes **1-Li/Na/K** and **3-Li/Na/K** were similar. Further, each showed a sharp singlet resonance signal at δ 7.87 (for **1-Li**), 8.14 (for **1-Na**), 8.19 (for **1-K**), 8.10 (for **3-Li**), 8.08 (for **3-Na**) and 8.25 (for **3-K**) ppm respectively. This can be assigned to the imine proton ($\text{N}=\text{CH}$) of the ligand moiety. In addition, the resonance of methine protons of $-\text{CHPh}_2$ fragments present in ligand **1** was observed at δ 5.13 (for **1-Li**), 5.16 (for **1-Na**) and 5.27 (for **1-K**) ppm respectively. The resonance signals for pyrrolyl protons of all the above mentioned alkali metal complexes appeared within the expected region.^{3,13} The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra further indicated the presence of the imine carbon atom in each complex which exhibited resonance signals at δ 157.3 (for **1-Li**), 160.9 (for **1-Na**), and 160.0 (for **1-K**), 165.2 (for **3-Li**), 163.7 (for **3-Na**), 160.7 (for **3-K**) ppm and the values were slightly shifted to a lower field region with respect to that of free ligands (151.2 ppm for **1-H** and 150.4 ppm for **3-H**). It is to be noted that only one set of ^1H and ^{13}C signals were observed for all the complexes.

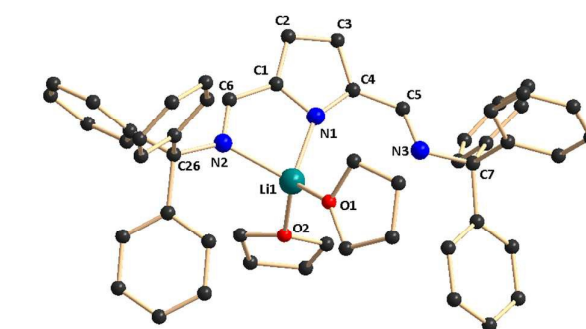
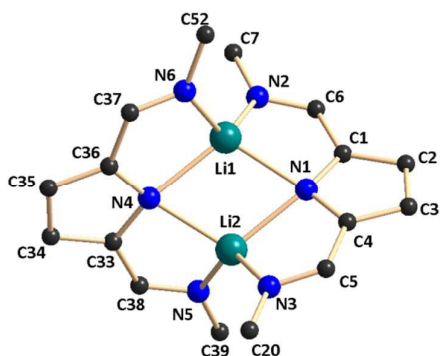


Figure 2. Solid-state structures of lithium complex **1-Li** (top) and **3-Li** (down). All hydrogen atoms have been omitted for clarity. In case of **1-Li**, phenyl groups are omitted for clarity. Selected bond lengths (Å) and bond angles (°): **1-Li**: Li1-N1 2.082(3), Li1-N2 2.010(3), Li1-N4 2.117(3), Li1-N6 1.999(3), Li2-N1 2.074(3), Li2-N3 2.016(3), Li2-N4 2.091(3), Li2-N5 2.027(3), Li1-Li2 2.439(4), N6-Li1-N2 123.60(16), N6-Li1-N1 129.49(17), N2-Li1-N1 87.51(13), N6-Li1-N4 86.14(13), N2-Li1-N4 125.72(16), N1-Li1-N4 107.98(15), N6-Li1-Li2 120.10(16), N2-Li1-Li2 116.14(15), N1-Li1-Li2 53.91(11), N4-Li1-Li2 54.08(11); **3-Li**: Li1-N1 1.992(3), Li1-N2 2.143(3), Li1-O1 1.931(3), Li1-O2 1.938(3), N1-Li1-N2 86.48(3), O1-Li1-O2 112.63(6), O1-Li1-N1 113.01(6), O2-Li1-N1 115.21(6), O1-Li1-N2 114.62(6), O2-Li1-N2 112.51(5).

The single crystals of complexes **1-Li/Na/K** and **3-Li/Na/K** were readily obtained from THF/pentane (1:3). The molecular structures of all the metal complexes in solid state were established by single crystal x-ray diffraction analysis. The details of structural and refinement parameters are given in TS1 in the supporting information. Solid state structures of the alkali metal complexes confirmed attachments of ligands **1** or **3** onto the metal ion. However, when considered within the same ligand moiety **1**, the trend observed between lithium and potassium ions was movement from dimeric nature to monomeric. In contrast, while changing the ligand moiety from **1** to a bulkier **3**, all the metal complexes **3-Li/Na/K** were observed to be monomeric (Table 1).

Both the lithium complexes **1-Li** and **3-Li** crystallized in the triclinic space group $P-1$ which had, two THF molecules per molecular formula of **1-Li**, and two molecules of **3-Li** in latter's unit cell. The sodium complexes **1-Na** and **3-Na** having two molecules each in their respective unit cells crystallized in the triclinic space group $P-1$. The molecular structures of complexes **1-Li** and **1-Na** were found to be quite similar and dimeric in nature as compared to the solid state structure of **3-Li** and **3-Na** which are both monomeric. The solid state structures of complexes **1-Li** and **3-Li** are shown in fig. 2 whereas fig. 3 represents the molecular structures of **1-Na** and **3-Na**. Thus, the difference in nuclearity between the lithium and sodium complexes clearly indicates that steric factor is the primary reason as the introduction of triphenylmethyl (Ph_3C) group in place of diphenylmethyl (Ph_2CH) moiety forced to shrink the N2-N1-N3 cavity of the ligands which could no longer accommodate two metal ions. In both the dimeric complexes **1-Li** and **1-Na**, the coordination

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polyhedron was formed by the ligation of pyrrolylide and imine nitrogen atoms of mono anionic bis-iminopyrrolyl ligand **1** to two alkali metal ions.

Table 1. Structural comparison among the alkali metal complexes using various bis-iminopyrrolyl ligands.

Ligands	Metal ions	Structure
[(Ph ₂ CH) ₂ Pyr] (1-H)	Li	Dimeric
[(Ph ₂ CH) ₂ Pyr] (1-H)	Na	Dimeric
[(Ph ₂ CH) ₂ Pyr] (1-H)	K	Monomeric
[(Ph ₃ C) ₂ Pyr] (3-H)	Li	Monomeric
[(Ph ₃ C) ₂ Pyr] (3-H)	Na	Monomeric
[(Ph ₃ C) ₂ Pyr] (3-H)	K	Monomeric
[(Dipp) ₂ Pyr]	Li	Dimeric ³
[(Dipp) ₂ Pyr]	Na	Dimeric ³
[(Dipp) ₂ Pyr]	K	Not reported ^{5,14}

In each case, it was found that ligand **1** was forming a diamond-shaped M₂N₂ core in which each pyrrolylide nitrogen atom was chelated to the two metal ions through μ² coordination mode. Two imine nitrogen atoms from each ligand **1** coordinated to two metal ions. In the lithium complex, each lithium ion was four-fold coordinated. The geometry around each lithium ion could best be described as distorted tetrahedral. In sodium complex **1-Na**, one of the sodium ions coordinated additionally with the THF molecule to make the two sodium ions non-equivalent. A distorted tetrahedral geometry was observed around one sodium ion which was four-fold coordinated, whereas distorted bipyramidal geometry could be obtained around the second sodium ion which was five-fold coordinated. The Li-N bond distances around the two lithium centers Li1-N1 2.082(3), Li1-N2 2.010(3), Li1-N4 2.117(3), Li1-N6 1.999(3), Li2-N1 2.074(3), Li2-N3 2.016(3), Li2-N4 2.091(3) and Li2-N5 2.027(3) Å were within a similar range thereby indicating that both amido nitrogen's N1 and N4 were chelated to two lithium ions thus forming the dimeric form. The distance between two lithium ions was 2.439(4) Å for molecule 1 (and 2.445(4) Å for molecule 2) which is considerably shorter than the distance between metallic lithium atoms (3.04 Å). The Na-N bond lengths N1-Na1 2.438(1), N1-Na2 2.460(1), N2-Na1 2.423(1), N3-Na2 2.400(1), N4-Na1 2.676(1), N4-Na2 2.402(1), N5-Na1 2.382(1) and N6-Na2 2.362(1) Å were same as the previously reported sodium complex.³ The

distance between two sodium ions in **1-Na** 2.982(1) Å was found to be significantly larger than that of complex **1-Li**, but significantly smaller than the sodium metal atoms (3.720 Å). In complex **1-Li**, two bis-iminopyrrolyl ligands deviated from the orthogonal position that they were in initially. A dihedral angle of 74.31° was observed between the bis-iminopyrrolyl planes. This deviation can be due to the presence of bulky substituent in the bis-iminopyrrolyl nitrogen atoms. However, in complex **1-Na**, two bis-iminopyrrolyl ligands were in a near orthogonal position to each other. A dihedral angle of 82.92° was observed between the bisiminopyrrolyl planes. The overall structural unit in each case consisted of four five-membered rings fused together to form a tetrametallacyclobuta[1,2:1,4:2,3:3,4]-tetracyclopentane structure. A similar structural motif was recently reported by Roesky *et al.* in similar complexes [(DIP₂-pyr)₂M] (M = Li and Na).³ However the M...M distances [2.439(4) Å for **1-Li** and 2.983(1) Å for **1-Na**] in the M₂N₂ cores were slightly smaller as compared to those in [(DIP₂-pyr)₂M] (2.565(5) Å for Li and 3.045(2) Å for Na) due to the presence of a bulky substituent in the bis-iminopyrrolyl nitrogen atoms.

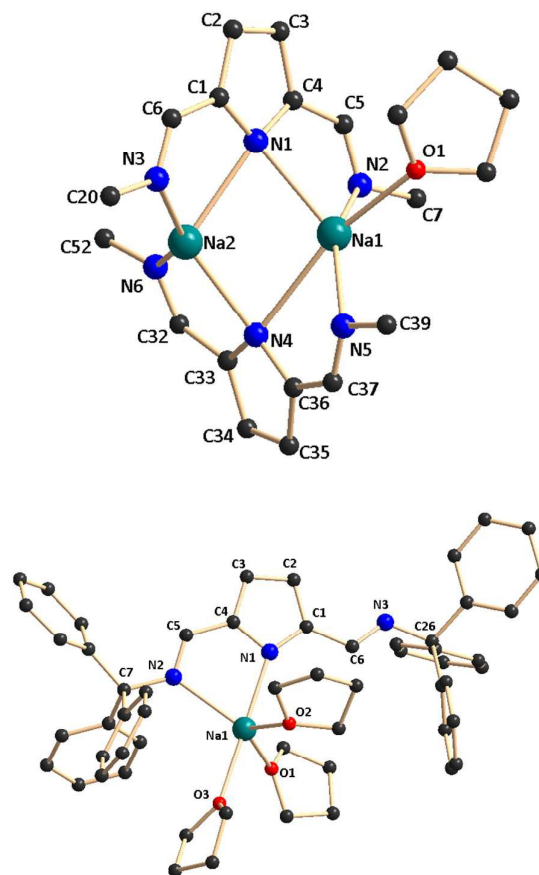


Figure 3. Solid-state structures of lithium complex **1-Li** (top) and **1-Na** (down). All hydrogen atoms have been omitted for clarity. In case of **1-Na**, phenyl groups are omitted for clarity. Selected bond lengths (Å) and bond angles (°): **1-Na**: Na1-N1 2.438(1), Na1-N2 2.423(1), Na1-N4 2.676(1), Na1-N5 2.382(1), Na1-O1 2.327(1), Na2-

N6 2.362(1), Na2-N3 2.400(1), Na2-N4 2.402(1), Na2-N1 2.460(1), Na2-Na1 2.982(1), N6-Na2-N3 145.45(6), N6-Na2-N4 75.78(6), N3-Na2-N4 137.94(6), N6-Na2-N1 107.55(6), N3-Na2-N1 73.94(6), N4-Na2-N1 107.06(6), N6-Na2-Na1 109.46(5), N3-Na2-Na1 98.53(5), N4-Na2-Na1 58.41(4), N1-Na2-Na1 52.17(4). **3-Na**: Na1-N1 2.425(1), Na1-N2 2.520(1), Na1-O1 2.331(1), Na1-O2 2.342(1), Na1-O3 2.410(1), O1-Na1-O2 121.07(6), O1-Na1-O3 85.10(5), O2-Na1-O3 86.80(5), O1-Na1-N1 97.05(5), O2-Na1-N1 91.25(5), O3-Na1-N1 177.65(5), O1-Na1-N2 122.13(5), O2-Na1-N2 115.96(5), O3-Na1-N2 107.56(5), N1-Na1-N2 72.13(4).

In monomeric complexes **3-Li** and **3-Na**, the metal ions were attached to the bis(imino)pyrrolide moiety **3** through the chelation of pyrrolide nitrogen and one imine nitrogen atom N1. The other imine nitrogen atom N3 was dangling away from the metal ion (*Cis* in **3-Li** and *Trans* in **3-Na**) – this was indicated by their relatively longer distances (Li1-N2 2.143(3) vs. Li1-N3 3.726(3) Å for **3-Li**, and Na1-N2 2.520(1) vs. Na1-N3 5.400(1) Å for **3-Na**). Thus bisiminopyrrolide moiety **3** acted as a bidentate ligand to both the complexes. In addition, two and three THF molecules were coordinated to the lithium and sodium ions respectively. Thus, in the complex **3-Li**, lithium ion adopted a distorted tetrahedral geometry while in the complex **3-Na**, the geometry of sodium ion could best be described as a distorted trigonal bipyramidal with pyrrolide nitrogen N1 and imine nitrogen N2 atoms, and O3; oxygen atom of one of the coordinated THF molecules was in the equatorial plane while two oxygen atoms O1 and O2 from the remaining THF molecules were located in the apical position. The Li-N bond distances observed in complex **3-Li**, 1.992(3) and 2.143(3) Å, were similar to those observed in complex **1-Li**, and indicated the presence of amido (Li-N1 1.991(3) Å) and imine (Li-N2 2.14 Å) linkages. The amido Na1-N1 and imino Na1-N2 bond distances of 2.425(1) and 2.520(1) Å respectively present in complex **3-Na** were similar to those in complex **1-Na**. In the dimeric complexes **1-Li** and **1-Na**, both the metal coordination spheres were very crowded - no void spaces were available for solvent coordination. However, in monomeric complexes **3-Li** and **3-Na**, due to the presence of sufficient void space in the coordination sphere, solvent THFs preferred coordination to the alkali metal ions, thus leaving the imino nitrogen uncoordinated. The Li-O and Na-O distances were well in agreement with those in the reported complexes.¹³ Thus, to the best of our knowledge, complexes **3-Li** and **3-Na** represented the first structurally characterized monomeric lithium and sodium complexes of bis-iminopyrrolyl ligand in comparison with all dimeric structures given in earlier reports.³

The potassium complex **1-K** crystallized in the monoclinic space group *C2/c* having four molecules in the unit cell. However, the complex **3-K** was observed to show triclinic space group *P-1* with two molecules in the unit cell. Molecular structures of **1-K** and **3-K** are given in fig 4. Both the potassium complexes **1-K** and **3-K** are monomeric in nature. The monomeric structure of **1-K** with respect to dimeric structures of **1-Li** and **1-Na** having the same ligand **1** can be explained by considering the larger ionic radius of K⁺ (1.38 Å) as

against that of Li⁺ (0.76 Å) and Na⁺ (1.02 Å). Thus, the observation indicated that the larger potassium ion preferred to form a monomeric complex rather than a dimeric one. It is to be noted that the complex **3-K** was monomerically similar to the congeneric lithium and sodium complexes **3-Li** and **3-Na** due to the use of the bulkier ligand **3**.

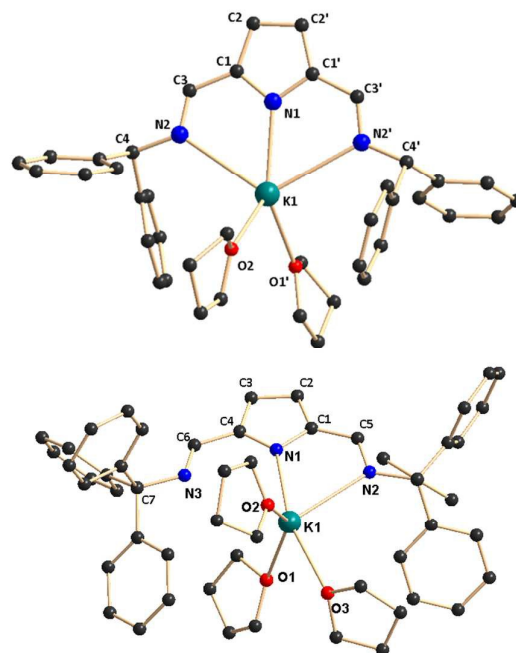


Figure 4. Solid-state structures of potassium complexes **1-K** (top) and **3-K** (bottom). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): **1-K**: K1-N1 2.638(2), K1-O1 2.682(1), K1-O1i 2.682(1), K1-N2 3.035(1), K1-N2i 3.035(1), N1-K1-O1 131.97(3), N1-K1-O1i 131.97(3), O1-K1-O1i 96.07(7), N1-K1-N2i 58.24(2), O1-K1-N2i 123.34(4), O1-K1-N2i 98.88(4), N1-K1-N2 58.24(2), O1-K1-N2 98.88(4), O1-K1-N2 123.34(4), N2-K1-N2 116.48(5). **3-K**: N1-K1 2.671(2), N2-K1 3.026(2), O1-K1 2.746(3), O2-K1 2.649(3), O3-K1 2.708(2), O2-K1-N1 109.51(8), O2-K1-O3 138.20(9), N1-K1-O3 94.94(7), O2-K1-O1 79.39(1), N1-K1-O1 163.60(8), O3-K1-O1 86.30(8), O2-K1-N2 115.52(8), N1-K1-N2 60.94(6), O3-K1-N2 105.89(7), O1-K1-N2 102.96(8).

A crystallographic *C*₂ axis was observed in complex **1-K** along the N1-K1 bond, and perpendicular to the pyrrolyl plane. The coordination polyhedron of complex **1-K** was formed by the chelation of pyrrolyl and the Schiff-base nitrogen atoms to the potassium ion that exhibited two-fused five-membered metallacycle K1-N1-C1-C3-N2 and K1-N1-C1ⁱ-C3ⁱ-N2ⁱ. Further, two THF molecules coordinated with the metal ion resulting in a distorted trigonal bipyramidal geometry around the potassium ion with pyrrolyl and the imine nitrogen atoms at the equatorial position, and two oxygen atoms at the apical position. In complex **3-K**, the potassium ion bonded with pyrrolyl nitrogen and an imine nitrogen from ligand **3** to form five-

membered metallacycle [K1-N1-C1-C5-N2 (molecule 1) and K2-N4-C60-C81-N6 (molecule 2)]. Three THF molecules were also attached to the potassium metal ion thus adopting distorted trigonal bipyramidal geometry around the potassium ion. The second imine nitrogen from ligand **3** remained non-bonded (*Cis* in molecule 1 and *Trans* in molecule 2) – this was indicated by the large distances between the metal ion and the nitrogen atom [K1-N2 3.026(2) vs. K1-N3 3.564 Å (molecule 1) and K2-N6 2.921(2) vs. K2-N5 5.257 Å (molecule 2)]. Thus, the iminopyrrolyl ligand **1** showed a tridentate chelation mode (κ^3) in complex **1-K**, whereas ligand **3** exhibited a bidentate coordination (κ^2) mode in complex **3-K**. The K-N distances in complex **1-K** [K1-N1 2.638(2) and K1-N2 3.035(2) Å] were found to be similar to those in complex **3-K** [K1-N1 2.671 and K1-N2 3.026 Å (molecule 1), and K2-N4 2.710 and K2-N6 2.921 Å (molecule 2)]. To the best of our knowledge, the complexes **1-K** and **3-K** represent the first structurally characterized potassium complexes using bis iminopyrrolyl ligands.^{5,14}

Conclusions

To sum up, we have successfully prepared three distinct bis(iminopyrrolyl) ligands (**1-H**, **2-H** and **3-H**) using diphenylmethyl, adamantyl and triphenylmethyl substitutions respectively at the imine nitrogen atoms. As a result of the use of bisiminopyrrolyl ligand **1-H**, the solid state structures of lithium and sodium complexes reveal the formation of dimeric complexes, each having an M2N2 diamond core. In contrast, on using the bulkier ligand **3-H**, monomeric complexes were observed in the lithium and sodium complexes. Thus, the substitution of the ligands **1-H** and **3-H** over the imine nitrogen atoms determined the nuclearity of the lithium and sodium complexes. However, owing to the larger cationic size, and as a consequence of the use of either of **1-H** or **3-H** ligands, potassium complexes were isolated as monomeric in their solid state. Additionally, as a result of using two different iminopyrrolyl ligands, switching of tridentate to bidentate coordination modes were also observed.

Experimental Section

All manipulations of air-sensitive materials were performed with the rigorous exclusion of 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 glove box. Tetrahydrofuran was pre-dried over Na wire and distilled under nitrogen from sodium and benzophenone ketyl prior to use. Hydrocarbon solvents (hexane and *n*-pentane) were distilled under nitrogen from LiAlH₄ and stored in the glovebox. ¹H NMR (400 MHz) and ¹³C{¹H} (100 MHz) NMR spectra were recorded on a Bruker Avance III-400 spectrometer. Elemental analyses were performed on a Bruker Euro EA at the Indian Institute of Technology Hyderabad (IITH). Pyrrole-2,5-dicarbaldehyde¹⁵, LiCH₂SiMe₃¹⁶ were prepared according to the literature procedure. [NaN(SiMe₃)₂], [KN(SiMe₃)₂] and NMR solvent C₆D₆ were purchased from Sigma Aldrich and dried under Na/K alloy (C₆D₆) prior to use.

Preparation of [Ph₂CHN=CH]₂C₆H₂NH] (1-H): To a stirred solution of pyrrole-2,5-dicarbaldehyde (1.23 g, 10 mmol) in methanol (100 mL) at ambient temperature, benzhydrylamine (H₂NCHPh₂) (3.66 g, 20 mmol) was added dropwise onto it. The resulting solution was stirred for overnight at ambient temperature. After being stirred for overnight, the white solid precipitate generated and was collected by filtration. The white solid was washed with *n*-hexane (5 mL x 2) and dried under *vacuo* to give a white solid. The compound **1-H** was crystallized from a mixture of CH₂Cl₂/pentane (1:3). Yield 4.1 g (90%). ¹H NMR (400 MHz, C₆D₆, 298 K): δ = 10.05 (br, 1H, NH), 8.15 (s, 2H, CH=N), 7.35-7.29 (m, 16H, ArH), 7.24-7.20 (m, 4H, ArH), 6.45 (s, 2H, PyH), 5.54 (s, 2H, CH) ppm; ¹³C{¹H} NMR (100 MHz, C₆D₆, 298 K): δ = 151.2 (N=C), 143.5 (Ar-C) 132.9 (Ar C), 128.5 (Ar-C), 127.9 (Ar-C), 127.1 (py-C), 115.3 (Py-C), 77.6 (CHPh₂) ppm. Elemental analysis: C₃₇H₃₇Cl₂N₃O (1-H·THF+CH₂Cl₂; 610.60): Calcd. C 72.78, H 6.11, N 6.88. Found C 72.53, H 5.98, N 6.59.

Preparation of [AdN=CH]₂C₆H₂NH] (2-H): To a stirred solution of pyrrole-2,5-dicarbaldehyde (1.23 g, 10 mmol) in methanol (100 mL) at ambient temperature, adamantylamine (H₂NAd) (3.02 g, 20 mmol) was added dropwise onto it. The resulting solution was stirred for overnight at ambient temperature. After being stirred for overnight, the white solid precipitate generated and was collected by filtration. The white solid was washed with *n*-hexane (5 mL x 2) and dried under *vacuo* to give a white solid. The compound **2-H** was recrystallized from a mixture of CH₂Cl₂/pentane (1:3). Yield 3.9 g (90%). ¹H NMR (400 MHz, C₆D₆, 298 K): δ = 8.05 (s, 2H, CH=N), 6.42 (s, 2H, PyH), 2.15 (d, 6H, ad-CH), 1.74 (t, 24H ad-CH₂) ppm; ¹³C{¹H} NMR (100 MHz, C₆D₆, 298 K): δ = 145.4 (N=C), 133.4 (Py-C), 113.9 (Py-C), 57.2 (C=N-C-Ad), 43.2 (Ad-CH), 36.6 (Ad-CH₂), 29.6 (Ad-CH₂) ppm. -NH resonance signal was not observed. Elemental analysis: C₂₆H₃₅N₃ (389.58): Calcd. C 80.16, H 9.06, N 10.79. Found C 79.97, H 8.89, N 10.65.

Preparation of [Ph₃CN=CH]₂C₆H₂NH] (3-H): To a stirred solution of pyrrole-2,5-dicarbaldehyde (500 mg, 4 mmol) in methanol (100 mL), triphenylmethylamine (H₂NCPPh₃) (2.1 g, 8 mmol) was added at ambient temperature. The resulting solution was stirred for overnight at ambient temperature. After being stirred for overnight, the white solid precipitate generated and was collected by filtration. The white solid was washed with *n*-hexane (5 mL x 2) and dried under *vacuo* to give a white solid. The compound **3-H** was crystallized from a mixture of CH₂Cl₂/pentane (1:3). Yield 1.5 g (60%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 10.18 (br, 1H, NH), 7.71 (s, 2H, CH=N), 7.31-7.24 (m, 30H, ArH), 6.41 (s, 2H, PyH) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃, 298 K): δ = 150.4 (N=C), 145.6 (Ar-C) 133.4 (Ar C), 129.9 (Ar-C), 127.8 (Ar-C), 126.9 (py-C), 115.3 (Py-C), 78.4 (CPh₃) ppm. Elemental analysis: C₄₄H₃₅N₃ (605.77): Calcd. C 87.24, H 5.82, N 6.94. Found C 86.92, H 5.73, N 7.02.

Preparation of [(Li(Ph₂CHN=CH)₂C₆H₂NH]₂] (1-Li): In a 10 mL sample vial, ligand **1-H** (50 mg, 0.11 mmol) and neosilyllithium (LiCH₂SiMe₃) (10.5 mg, 0.11 mmol) were mixed together under inert atmosphere followed by addition of 2 mL of THF onto it. The mixture was stirred for 6 hours at ambient temperature. After that, 2 mL *n*-pentane was slowly added onto it and kept at -40°C. After 24 hours colorless crystals of **1-Li** were obtained. Yield 42 mg (83%). ¹H NMR (400 MHz, C₆D₆, 298 K): δ = 7.87 (s, 4H, CH=N), 7.05-7.03 (m, 16H, ArH), 6.95-6.93 (m, 24H, ArH), 6.59 (s, 4H, PyH), 5.13 (s, 4H, CH) ppm. ¹³C{¹H} NMR (100 MHz, C₆D₆, 298 K): δ = 157.3 (N=C), 143.7 (Ar-C) 140.7 (Ar C), 128.5 (Ar-C), 128.0 (Ar-C), 126.9 (py-C), 117.8 (Py-C), 76.1(CH) ppm. Elemental analysis: C₇₂H₆₈Li₂N₆O₂ (**1-Li**·**2 THF**; 1063.23): Calcd. C 81.33, H 6.45, N 7.90. Found C 81.03, H 6.21, N 7.64.

Preparation of [(Na(Ph₂CHN=CH)₂C₆H₂NH]₂(THF)] (1-Na): Similar procedure as described for the preparation of **1-Li** was followed by using **1-H** (50 mg, 0.11

mmol) and $[\text{NaN}(\text{SiMe}_3)_2]$ (20 mg, 0.11 mmol). Yield 40 mg (71%). ^1H NMR (400 MHz, C_6D_6 , 298 K): δ = 8.14 (s, 4H, $\text{CH}=\text{N}$), 6.98–6.91 (m, 40H, ArH), 6.84 (s, 4H, PyH), 5.16 (s, 4H, CH), 3.50 (m, 4H, $\text{O}-\text{CH}_2-\text{CH}_2$), 1.39 (m, 4H, $\text{O}-\text{CH}_2-\text{CH}_2$) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , 298 K): δ = 160.9 (N=C), 144.6 (Ar-C) 143.9 (Ar C), 128.8 (Ar-C), 128.3 (Ar-C), 126.9 (py-C), 119.9 (Py-C), 76.1 (CH), 67.7 (O- CH_2-CH_2), 25.7 (O- CH_2-CH_2) ppm. Elemental analysis: $\text{C}_{68}\text{H}_{59}\text{N}_6\text{Na}_2\text{O}$ (1022.19): Calcd. C 79.90, H 5.82, N 8.22. Found C 79.74, H 5.49, N 7.96.

Preparation of $[\{\kappa^3\text{-(Ph}_2\text{CHN=CH)}_2\text{C}_4\text{H}_2\text{N}\}(\text{THF})_2]$ (1-K): Similar procedure as described for the preparation of 1-Li was followed by using 1-H (50 mg, 0.11 mmol) and $[\text{KN}(\text{SiMe}_3)_2]$ (22 mg, 0.11 mmol). Yield 56 mg (80%). ^1H NMR (400 MHz, C_6D_6 , 298 K): δ = 8.19 (s, 2H, $\text{CH}=\text{N}$), 7.12–7.11 (d, 8H, ArH), 7.05–7.01 (t, 8H, ArH), 6.99–6.95 (m, 4H, ArH), 6.92 (s, 2H, PyH), 5.27 (s, 2H, CH), 3.50 (m, 8H, $\text{O}-\text{CH}_2-\text{CH}_2$), 1.38 (m, 8H, $\text{O}-\text{CH}_2-\text{CH}_2$) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , 298 K): δ = 160.0 (N=C), 144.6 (Ar-C) 143.7 (Ar C), 128.6 (Ar-C), 126.8 (Py-C), 119.5 (Py-C), 77.3 (CH), 67.6 (O- CH_2-CH_2), 25.6 (O- CH_2-CH_2) ppm. Elemental analysis: $\text{C}_{40}\text{H}_{42}\text{KN}_3\text{O}_2$ (635.88): Calcd. C 75.55, H 6.66, N 6.61. Found C 75.19, H 6.43, N 6.69.

Preparation of $[\{\kappa^2\text{-(Ph}_3\text{CN=CH)}_2\text{C}_4\text{H}_2\text{N}\}\text{Li}(\text{THF})_2]$ (3-Li): Similar procedure as described for the preparation of 1-Li was followed by using 3-H (60 mg, 0.10 mmol) and neosilyllithium ($\text{LiCH}_2\text{SiMe}_3$) (9.5 mg, 0.10 mmol). Yield 61 mg (81%). ^1H NMR (400 MHz, C_6D_6 , 298 K): δ = 8.10 (s, 2H, $\text{CH}=\text{N}$), 6.94–6.83 (m, 30H, CPh_3), 6.52 (s, 2H, PyH), 3.57 (m, 8H, $\text{O}-\text{CH}_2-\text{CH}_2$), 1.41 (m, 8H, $\text{O}-\text{CH}_2-\text{CH}_2$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , 298 K): δ = 165.2 ($\text{CH}=\text{N}$), 147.2 (ArC), 144.5 (ArC), 130.0 (ArC), 128.3 (ArC), 128.1 (ArC), 127.7 (ArC), 126.5 (Py-C), 122.0 (Py-C), 79.3 (CPh_3), 67.7 (O- CH_2-CH_2), 25.7 (O- CH_2-CH_2) ppm. Elemental analysis: $\text{C}_{52}\text{H}_{50}\text{LiN}_3\text{O}_2$ (755.89): Calcd. C 82.62, H 6.67, N 5.56. Found C 82.39, H 6.41, N 5.27.

Preparation of $[\{\kappa^2\text{-(Ph}_3\text{CN=CH)}_2\text{C}_4\text{H}_2\text{N}\}\text{Na}(\text{THF})_2]$ (3-Na): Similar procedure as described for the preparation of 1-Li was followed by using 3-H (60 mg, 0.10 mmol) and $[\text{NaN}(\text{SiMe}_3)_2]$ (18.3 mg, 0.10 mmol). Yield 63 mg (75%). ^1H NMR (400 MHz, C_6D_6 , 298 K): δ = 8.08 (s, 2H, $\text{CH}=\text{N}$), 7.02–6.83 (m, 30H, CPh_3), 6.56 (s, 2H, PyH), 3.57 (THF), 1.41 (THF) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , 298 K): δ = 163.7 ($\text{CH}=\text{N}$), 147.2 (ArC), 144.5 (ArC), 129.7 (ArC), 128.1 (ArC), 127.9 (ArC), 126.7 (PyC), 121.8 (PyC), 78.2 (CPh_3), 67.6 (O- CH_2-CH_2), 25.6 (O- CH_2-CH_2) ppm. Elemental analysis: $\text{C}_{56}\text{H}_{58}\text{N}_3\text{NaO}_3$ (844.04): Calcd. C 79.69, H 6.93, N 4.98. Found C 79.51, H 6.65, N 5.04.

Preparation of $[\{\kappa^2\text{-(Ph}_3\text{CN=CH)}_2\text{C}_4\text{H}_2\text{N}\}\text{K}(\text{THF})_3]$ (3-K): Similar procedure as described for the preparation of 1-Li was followed by using 3-H (60 mg, 0.10 mmol) and $[\text{KN}(\text{SiMe}_3)_2]$ (22 mg, 0.10 mmol). Yield 76 mg (88%). ^1H NMR (400 MHz, C_6D_6 , 298 K): δ = 8.25 (s, 2H, $\text{CH}=\text{N}$), 7.06 (br s, 15H, CPh_3), 6.83 (br s, 15H, CPh_3), 6.67 (s, 2H, PyH), 3.44 (THF), 1.30 (THF) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , 298 K): δ = 160.7 ($\text{CH}=\text{N}$), 146.6 (ArC), 144.9 (ArC), 130.1 (ArC), 128.0 (ArC), 126.0 (PyC), 122.0 (PyC), 78.9 (CPh_3), 67.6 (O- CH_2-CH_2), 25.6 (O- CH_2-CH_2) ppm. Elemental analysis: $\text{C}_{56}\text{H}_{58}\text{KN}_3\text{O}_3$ (860.15): Calcd. C 78.19, H 6.80, N 4.89. Found C 77.87, H 6.51, N 4.72.

X-ray crystallographic studies of complexes 1-H, 2-H, 3-H, 1-Li, 1-Na, 1-K, 3-Li, 3-Na and 3-K.

Single crystals of complex 1-H, 2-H and 3-H were obtained from a mixture of CH_2Cl_2 /pentane (1:3) at room temperature. However, complexes 1-Li/Na/K and 3-Li/Na/K were crystallized from a mixture of THF/pentane (2:3) at -35°C under argon atmosphere. In each case, a crystal of suitable dimensions was mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 150(2) K. All measurements were made on an Agilent Supernova X-calibur Eos CCD detector with graphite-monochromatic $\text{Cu}-\text{K}\alpha$ (1.54184 Å) radiation. Crystal data and

structure refinement parameters are summarized in Table TS1 in supporting information. The structures were solved by direct methods (SIR2004)¹⁷ and refined on F^2 using the full-matrix least-squares method, using SHELXL-2014/7¹⁸. Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimised was $[\sum w(\text{Fo}^2 - \text{Fc}^2)^2]$ ($w = 1 / [\sigma^2(\text{Fo}^2) + (aP)^2 + bP]$), where $P = (\text{Max}(\text{Fo}^2, 0) + 2\text{Fc}^2) / 3$ with $\sigma^2(\text{Fo}^2)$ from counting statistics. The function $R1$ and $wR2$ were $(\sum ||\text{Fo}| - |\text{Fc}||) / \sum |\text{Fo}|$ and $[\sum w(\text{Fo}^2 - \text{Fc}^2)^2 / \sum (w\text{Fo}^4)]^{1/2}$ respectively. The ORTEP-3 program was used to draw the molecule. Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1476165-1476173. 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: deposit@ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the Council of Scientific and Industrial Research (CSIR) scheme (No.01(2530)/11/EMRI), and 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). S. A. thanks CSIR for his PhD fellowship. We thank reviewers for their valuable comments to improve the manuscript.

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Alkali Metal Complexes Having Sterically Bulky Bis-Iminopyrrolyl Ligands – Control of Dimeric to Monomeric Complex

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Treatment of lithium alkyl and sodium hexamethyldisilazide with $\{(CHPh_2)_2\text{-pyr}\}(1\text{-H})$ and $\{(CPh_3)_2\text{-pyr}\}(3\text{-H})$ afforded corresponding alkali metal salts 1-Li, 1-Na, 3-Li and 3-Na. The solid state structures of the complexes displayed a shift from the formation of dimeric to monomeric alkali metal complexes due to the tuning of the steric control of the imine substitutions ($CHPh_2$ and CPh_3) of the ligands. However, potassium salts remained monomeric with both the ligands.

