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Hydroamination of isocyanates and isothiocyanates by alkaline earth metal initiators supported by bulky iminopyrrolyl ligand

Kulsum Bano,^a Srinivas Anga,^a Archana Jain,^b Hari Pada Nayek,^c and Tarun K. Panda*^a

Abstract: A series of new heteroleptic alkaline earth (Ae) metal complexes of general formula $[\{(Ph_2CHN=CH)_2C_4H_2N\}Ael(THF)_3]$ {Ae = Ca (2), Sr (3), and Ba (4)} were synthesized via salt metathesis by reacting potassium salt of ligand 1-K $[\{(Ph_2CHN=CH)_2C_4H_2N\}K(THF)_2]$ with anhydrous alkaline earth metal diiodides (Ael₂). The homoleptic calcium and barium complexes $[\{(Ph_2CHN=CH)_2C_4H_2N\}_2Ae]$ [Ae = Ca (5), Ba (6)] were prepared by treating metal bishexamethyldisilazide [Ae{N(SiMe_3)_2}_2(THF)_2] with the protic ligand 1-H $[(Ph_2CH-N=CH)_2C_4H_2NH]$ in 1:2 molar ratio. Calcium complex 5 was employed as an active pre-catalyst for the addition of N-H bond of arylamines across the heterocumulenes such as phenylisocyanate (PhNCO) and phenylisothiocyanate (PhNCS) under the neat condition and a yield of corresponding urea and thiourea derivatives up to 99% was obtained.

Introduction

Ureas and thioureas, also known as carbamides and thiocarbamides, respectively, have a wide range of applications in organic, medicinal, supramolecular, and materials chemistry.¹⁻⁷ Several methodologies including transition metalcatalyzed oxidative carbonylation of amines,⁸⁻¹³ a reductive coupling of nitro compounds with amines and CO,¹⁴⁻¹⁷ the ironmediated dehydrogenative coupling of methanol and amines,18,19 and coupling of silylamines and carbon dioxide using indium pre-catalyst²⁰ have been adopted for the preparation of urea derivatives. Most of these methods involve expensive metals, stoichiometric amounts of reagent and/or harsh reaction conditions. Therefore, the development of an atom-efficient and environmentally benign process for urea an d thiourea preparation remains an important target. Recently, catalytic hydroamination of isocyanates and isothiocyanates have provided a facile route to obtain urea and thiourea derivatives. Catalytic hydroamination of alkenes, allenes or alkyne has been widely exploited to prepare amines, enamines, and imines.²¹⁻³⁰ On the other hand, catalytic addition of N-H to isocyanates and isothiocyanates is limited to very few metal complexes including zinc,³¹ iron,³² titanium,³³⁻³⁵ actinides,^{36,37} and alkaline earth metals,^{38,39} etc.

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▶Department of Physics and Chemistry, Mahatma Gandhi Institute of Technology, Gandipet, Hyderabad 500075, Telangana, India. There is a growing interest in the syntheses and characterization of group II metal-based complexes due to their utility as versatile catalysts in various organic transformations and their nontoxicity, biocompatibility, easy availability and low cost are also attractive features.⁴⁰⁻⁵⁴ However, one major problem in studying the catalytic features of alkaline-earth (Ae) metalbased complexes is that they easily undergo Schlenk equilibrium and show different molecular compositions in the solution state. To overcome this problem, a wide variety of sterically bulky nitrogen-based ancillary ligands, such as tris(pyrazolyl)borates,⁵⁵⁻⁵⁸ aminotroponiminates, 59,60 βdiketiminates,⁶¹⁻⁶⁵ iminopyrroles,66-75 1,4-diaza-1,3butadiene,^{76,77} and mixed nitrogen–oxygen based phenolate and alkoxo ligands78-82 have been introduced which resulted in the formation of a variety of well-defined alkaline earth metal complexes with the controlled catalytic activity and selectivity. Among the multi-dentate nitrogen-based ligands, bisiminopyrrolyl ligands played an important role as unique monoanionic ligands to stabilize the various oxophilic Ae-metal complexes. Bochmann et al. were the first to introduce the 2,5-bis(aryliminomethyl)pyrrolyl ligand tridentate into transition metal chemistry.83 Mashima et al. also reported a series of homoleptic and heteroleptic yttrium complexes with different bis-iminopyrroles and varying substituents at the imine nitrogen atom.84,85 Roesky et al. reported the study of alkali metal, alkaline earth and divalent lanthanide complexes of the 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}-pyrrole ligand.⁸⁶⁻⁹³ Recently, our research group developed alkali metal complexes bearing bulky substituted bis-iminopyrrolyl ligands and explored their structural diversity in terms of their coordination modes and nuclearity.94 Upon varying the substituent bulkiness present on the imine nitrogen, these ligands κ^2 and κ^3 -coordination modes and produced interesting structural motifs. As a continuation of this investigation, we are prompted to learn about the effect of the introduction of the

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Electronic supporting information available: Crystallographic data of complexes **2-4** and **6**, and ¹H, ¹³C NMR spectra and characterization data of **7a-7i**, **8a-8i**, and **9a-9i** reported in this article is given.

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57 58 59 sterically demanding bulky bis-iminopyrrolyl ligands on the structure, stability, and reactivity of alkaline earth metal complexes. Determining the structure and reactivity of the alkaline earth metal species is an important step towards the design and development of efficient catalysts; however, a full realization of the catalytic potential of these elements still requires substantial advances in terms of understanding their basic coordination and organometallic chemistry.

Herein, we describe a full account of the synthesis and structural aspects of heteroleptic alkaline earth metal complexes of general formula $[{(Ph_2CHN=CH)_2C_4H_2N}Ael(THF)_3]$ [Ae = Ca (2), Sr (3) and Ba (4)] and homoleptic alkaline earth metal complexes $[{(Ph_2CHN=CH)_2C_4H_2N}_2Ae]$ [Ae = Ca (5), Ba (6)]. We also describe an efficient protocol for the catalytic addition of N–H bonds to isocyanates and isothiocyanates with a broader substrate scope using calcium complex 5 as an active pre-catalyst to yield urea and thiourea derivatives.

Results and Discussion

Synthesis and structure details of heteroleptic alkaline-earth metal complexes.

The mono-iodo Ae complexes $[{(Ph_2CHN=CH)_2C_4H_2N}Ael(THF)_3]$ (2–4) were prepared in good yields (ca. 75–82%) via salt metathesis reaction of the potassium salt of the ligand (1-K) with anhydrous Ael₂ in 1:1 equivalent ratio in THF at 60 °C for 12 hours (Scheme 1).



Scheme 1. Synthesis of heteroleptic alkaline earth metal complexes **2-4** from **1-K**.

The air and moisture sensitive complexes 2-4 were fully characterized by standard NMR spectroscopy and combustion analysis. In the ¹H NMR spectra, each complex displayed a sharp singlet at δ_{H} 8.03 ppm (for **2** and **4**) and 8.19 ppm (for **3**) for the resonance of corresponding imine (N=CH) proton, and a singlet at δ_H 5.53 (for 2), 5.27 (for 3), and 5.52 (for 4) ppm for the resonance of the corresponding N–CHPh₂ proton of the ligand. The resonance signal of imine proton of complex **3** is slightly deshielded presumably due to the adjacent pyrrole ring and exhibits modest low field shift compared to those of complexes 2 and 4. In the ¹³C{¹H} NMR spectra, resonance signals for the corresponding imine carbon (N=CH) were observed at δ_{C} 160.6 (for 2), 160.4 (for 3), and 160.6 ppm (for 4), which are significantly shifted to the low-field region when compared to the free ligand 1-H (151.2 ppm).⁹⁴ The corresponding resonance signal for the CH carbon appeared at δ_c 79.0 (for **2**), 77.8 (for **3**), and 79.2 ppm (for 4).



Figure 1. The solid-state structure of calcium complex **2**, with all hydrogen atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ca1–N1 2.407(4), Ca1–N3 2.638(4), Ca1–I1 3.186(1), Ca1–O1 2.380(4), Ca1–O2 2.459(4), Ca1–O3 2.367(3), O3–Ca1–O1 165.83(1), O3–Ca1–N1 83.59(1), O1–Ca1–N1 87.46(1), O3–Ca1–O2 84.13(2), O1–Ca1–O2 93.681(2), N1–Ca1–O2 131.43(1), O3–Ca1–N3 89.36(1), O1–Ca1–N3 97.24(1), N1–Ca1–N3 66.97(1), N1-Ca1-N2 [37.89(1)°], O2–Ca1–N3 159.17(1), O3–Ca1–I1 98.35(9), O1–Ca1–I1 94.87(9), N1–Ca1–I1 150.42(1), O2–Ca1–I1 77.94(9), N3–Ca1–I1 83.50(9).



Figure 2. The solid-state structure of strontium complex **3**, with all hydrogen atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°): Sr1–N1 2.506(2), Sr1–N2 3.106(3), Sr1–N3 2.846(3), Sr1–O1 2.543(2), Sr1–O2 2.601(2), Sr1–O3 2.529(2), Sr1–I1 3.291(4), N1–Sr1–O3 81.39(8), N1–Sr1–O1 88.21(8), O3–Sr1–O1 166.97(8), N1–Sr1–O2 139.16(8), O3–Sr1–O2 86.58(8), O1–Sr1–O2 96.33(8), N1–Sr1–N3 61.94(8), O3–Sr1–N3 87.70(8), O1–Sr1–N3 94.35(8), O2–Sr1–N3 156.49(8), N1–Sr1–N2 59.01(8), O3–Sr1–N2 80.19(7), O1–Sr1–N2 87.73(8), O2–Sr1–N2 80.57(7), N3–Sr1–N2 120.81(7), N1–Sr1–I1 143.31(6), O3–Sr1–I1 97.19(6), O1–Sr1–I1 95.84(6), O2–Sr1–I1 76.75(6), N3–Sr1–I1 81.38(5), N2–Sr1–I1 157.29(5).

The solid-state molecular structures of complexes **2–4** were determined by single-crystal X-ray diffraction analysis. The mono-iodo calcium complex **2** crystallizes in the triclinic space group *P*-1, with two independent molecules in the unit cell. The molecular structure of compound **2** is shown in Figure 1 and details of the structural and refinement parameters are given in Table TS1 in supporting information. As shown in Figure 1, the

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The strontium and barium complexes 3 and 4 are isostructural. Both the complexes crystallized in the triclinic space group P-1. The solid-state structures of complex 3 and 4 are shown in Figures 2 and 3, respectively, and details of the structural parameters are given in Table TS 1 in supporting information. Similar to complex 2, the monoanionic ligand 1 is chelated to the central metal ion (Sr and Ba) in a κ^3 fashion through one pyrrolide nitrogen and two imine nitrogen atoms. Both complexes 3 and 4 displayed two sets of long-short bond distances, indicating coordination of amido and imine nitrogen atoms to the metal ion. The metal-nitrogen bond lengths, Sr1-N1 (2.506(2) Å), Sr1–N2 (3.106(3) Å), and Sr1–N3 (2.846(3) Å) and Ba1–N1 (2.665(3) Å), Ba1–N2 (2.978(3) Å), and Ba1–N3 (3.119(3) Å) are good in agreement with reported literature values and similar to [(Dipp₂Pyr)MI(THF)_n (M = Sr and Ba).⁸⁶ Based on long-short bond lengths within the imine nitrogen atoms, imine nitrogen atom which is trans to iodine exhibited a weak σ donor character (long bond); however, imine nitrogen atom *cis* to iodine showed a strong σ donor character (short bond). The Sr1–I1 bond (3.291(4) Å) is quite longer than the Ca1-I1 (3.078(1) Å) bond in complex 2, and shorter than the Ba1-I1 (3.514(4) Å) due to increase in the metal ionic radius from Ca²⁺ (1.00 Å), Sr²⁺ (1.18 Å) to Ba²⁺ (1.35 Å). The sevenfold coordination number of both strontium and barium is observed by the κ^3 -coordination of the ligand, one iodine atom, and three THF molecules adopting distorted pentagonal bipyramidal geometry around the central metal ion. In the distorted pentagonal bipyramidal arrangement, pyrrolide nitrogen, imine nitrogen atoms, an iodine atom, and one oxygen atom from THF [N1, N2, N3, I1, and O2 (for Sr) or O3 (for Ba)] occupy equatorial positions and the remaining two oxygen atoms from two THF molecules (O1 and O3 (for Sr) or O1 and O2 (for Ba) are in an apical position. The bite angles, N1-Sr1-N2 [59.01(8)°], N1-Sr1–N3 [61.94(8)°], N3–Sr1–O2 [156.49(8)°], O2–Sr1–I1 N2–Sr1–I1 [157.29(5)°], and 01–Sr1–O3 [76.75(6)°]. [166.97(8)°] are in the expected range.⁸⁶ The bite angles for the complex 4 N1-Ba1-N2 [58.96(8)°], N1-Ba1-N3 [57.09(9)°], N2-Ba1-I1 [82.96(6)°], N3-Ba1-O3 [84.81(8)°], O3-Ba1-I1 [76.70(6)°], and O1-Ba1-O2 [171.48(1)°] are greater than the complex 3. It is noted that analogous strontium and samarium derivatives tend to form isostructural complexes due to their similar ionic radii, and in the present case, the complex 3 is isostructural to the analogous samarium and europium complexes [(Dipp₂Pyr)LnI(THF)₃] (Ln = Sm, Eu).⁸⁸

Table 1. Comparison of the bond lengths of complexes 2-4.

Bond length (Å)	Ca (2)	Sr (3)	Ba (4)
M–N1 _{pyrrolyl}	2.407(4)	2.506(2)	2.665(3)
M–N2 _{imine}	3.320(4)	3.106(3)	2.978(3)
M–N3 _{imine}	2.638(4)	2.846(3)	3.119(3)
M–I1	3.186(1)	3.291(4)	3.514(4)



Figure 3. Solid-state structure of barium complex **4**, with all hydrogen atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ba1–N1 2.665(3), Ba1–N2 2.978(3), Ba1–N3 3.119(3), Ba1–O1 2.686(3), Ba1–O2 2.779(3), Ba1–O3 2.767(3), Ba1–I1 3.514(4), N1–Ba1–O1 83.30(9), N1–Ba1–O3 141.39(8), O1–Ba1–O3 101.32(10), N1–Ba1–O2 94.92(9), O1–Ba1–O2 171.48(10), O3–Ba1–O2 85.29(8), N1–Ba1–N2 58.96(8), O1–Ba1–N2 82.45(10), O3–Ba1–N2 159.32(8), O2–Ba1–N2 89.48(8), N1–Ba1–N3 57.09(9), O1–Ba1–N3 85.73(9), O3–Ba1–N3 84.81(8), O2–Ba1–N3 100.34(8), N2–Ba1–N3 115.84(8), N1–Ba1–I1 141.89(6), O1–Ba1–I1 90.71(7), O3–Ba1–I1 76.70(6), O2–Ba1–I1 85.55(7), N2–Ba1–I1 82.96(6), N3–Ba1–I1 160.11(6).

monoanionic ligand is coordinated to the central calcium ion in a κ^3 fashion through two imine nitrogen and one pyrrolyl nitrogen atoms. The calcium-nitrogen bond length of N1-Ca1 2.407(4) Å indicates the formation of amido bond with calcium ion through pyrrolyl nitrogen. The bond distance of N3-Ca1 2.638(4) Å represents the coordination of imine nitrogen N3 of ligand 1 to the calcium ion to form a Ca1-N3 dative bond. However, the second imine nitrogen (N2) atom is very weakly coordinated to the calcium ion, as reflected by the longer distance [3.320(4) Å] between Ca1 and N2 atoms. The bite angle N1-Ca1-O2 of 131.43(1)° is also larger than that of N1-Ca1-N2 [37.89(1)°] indicating the nitrogen atom N2 as a neighbouring atom to calcium ion rather than oxygen atom O2. It is also observed that the Ca1–I1 bond distance of 3.186(1) Å is slightly found longer than that in a similar complex [(Dipp₂Pyr)Cal(THF)₃],⁸⁶ 3.078(1) Å reported by Roesky et al. (where $Dipp_2Pyr = bis-2,6-diisopropylphenyl pyrrolyl$). It may be due to the presence of bulky CHPh₂ groups in the ligand moiety 1 instead of 2,6-diisopropylphenyl groups. The Ca-O bond distances are also well in agreement with the values reported in the literature.⁸⁶ The seven-fold coordination number of the calcium ion is observed by the κ^3 -coordination of the ligand **1**, one iodine atom and three THF molecules adopting a distorted pentagonal bipyramidal geometry around the central calcium ion. The iodine, imine nitrogen atoms and one oxygen atom (O2) are in the equatorial position and two oxygen atoms from two other THF molecules are in the apical position. The bite angle of imine nitrogen N1 and iodine atom is 83.504° (N1-Ca1-11). The other bite angles, N3-Ca1-N1 [66.97(1)°], N3-Ca1-O2

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The complexes **2-4** were also found to be isostructural with the Ae metal complexes bearing [(Dipp₂Pyr)]-ligand moiety (where Dipp₂Pyr = bis-2,6-diisopropyl phenyl pyrrolyl) reported by Roesky *et al.*⁸⁶ It was noted that all the complexes **2-4** are monomeric and this is quite unusual since strontium and barium ions tend to form dimeric complexes, bridging through iodine atoms.⁸⁶⁻⁹³ There is a limited number of monomeric heteroleptic mono-iodo complexes bearing very bulky ligands reported in the literature.⁹⁴ Furthermore, the solid-state structures of complexes **2-4** reveal that there is a trend of increase in metal–nitrogen and metal–iodine bond lengths from calcium to barium (Table 1), due to increase in the ionic radius of metal ions from calcium to barium: Ca²⁺ (1.00 Å), Sr²⁺ (1.18 Å), and Ba²⁺ (1.35 Å).

Synthesis and structure details of homoleptic alkaline earth amido complexes.

The treatment of the protic ligand 1-H with [Ae{N(SiMe₃)₂}₂(THF)₂] in a 1:2 ratio at ambient temperature affords the homoleptic alkaline earth metal complexes of molecular formula $[{(Ph_2CHN=CH)_2C_4H_2N}_2C_a]$ (5) and $[\{(\mathsf{Ph}_2\mathsf{CHN}{=}\mathsf{CH})_2{-}\mathsf{C}_4\mathsf{H}_2\mathsf{N}\}_2\mathsf{Ba}]$ (6) in 72% and 80% yield respectively (Scheme 2). We attempted to introduce the [N(SiMe₃)₂] moiety as the leaving group into the metal coordination sphere by treating the protic ligand 1-H with $[Ca{N(SiMe_3)_2}_2(THF)_2]$ in a 1:1 ratio at ambient temperature, however, complex 5 was isolated as the stable major product in this case too. This is due to the high reactivity of the calcium bis-hexamethyldisilazide and the dynamic Schlenk equilibrium of alkaline earth metal ions.



Scheme 2. Synthesis of alkaline earth metal complexes 5 and 6.

Both air and moisture sensitive complexes **5** and **6** were fully characterized using standard NMR spectroscopy and analytical techniques. The ¹H NMR spectra of complex **5** and **6** were measured in C₆D₆, displayed a sharp singlet at δ_H 7.85 ppm for **5** and 7.92 ppm for **6**, which can be best assigned to the imine CH proton (N=CH), slightly shifted to the high-field region, when compared to the neutral ligand **1**-H (δ_H 8.15 ppm).⁷⁸⁻⁸² Also, the resonance of the methine proton of the -CHPh₂ group present in ligand **1** appeared at δ_H 5.15 ppm for **5** and 5.20 ppm for **6**.

The solid-state structure of complex **5** could not be established due to the poor data set of the crystals. However, we have established the molecular structure of complex **6** using singlecrystal X-ray diffraction analysis. The homoleptic barium complex **6** crystallizes in the monoclinic space group $P2_1/c$, with four independent molecules in the unit cell. The solid-state

structure of complex 6 is shown in Figure 4 and the details of the structural parameters are given in Table TS1.039/DONJ01509A



Figure 4. The solid-state structure of barium complex 6. All hydrogen atoms and selected phenyl groups are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ba1–N1 2.641(2), Ba1–N2 3.057(2), Ba1–N3 3.017(2), Ba1–N4 2.664(2), Ba1–N5 2.837(6), Ba1–N6 3.057(2), N1–Ba1–N5 126.06(13), N2–Ba1–N5 109.2(3), N2–Ba1–N1 58.50(7), N4–Ba1–N5 58.50(14), N4–Ba1–N1 168.36(8), N4–Ba1–N2 110.35(7), N3–Ba1–N5 106.3(3), N3–Ba1–N1 58.17(7), N3–Ba1–N2 116.66(6), N3–Ba1–N4 132.90(7), N6–Ba1–N5 113.34(12), N6–Ba1–N1 120.56(7), N6–Ba1–N2 106.19(7), N6–Ba1–N4 56.81(7), N6–Ba1–N3 105.38(7).

The six-fold coordination number is observed by the κ^3 -chelation mode of two ligands to the central barium ion adopting a distorted octahedral. Ba-N bond lengths, Ba1-N1 [2.643(3) Å], Ba1-N2 [3.061(3) Å], Ba1–N3 [3.018(3) Å], Ba1–N4 [2.663(4) Å], Ba1–N5 [3.063(3) Å], and Ba1-N6 [2.860(5) Å] are similar to those we previously reported for the barium complex [Ba(2-(Ph₃CN=CH)C₄H₃N)₂(THF)₃]⁷⁰ where Ba–N bond distances were Ba– N1 [2.731(5) Å], Ba1–N2 [2.762(5) Å], Ba1–N3 [2.946(5) Å] and Ba1– N4 [2.933(5) Å], and for [(ImpDipp)₂Ba(THF)₂] (ImpDipp = [(2,6– ⁱPr₂C₆H₃–CN=CH)₂–C₄H₃N]) where Ba–N bond distances were [Ba–N1 2.821(5) Å and Ba–N2 2.823(4) Å].⁶⁹ The bite angle between N1–Ba1– N4 is nearly linear and measures 168.28(1)°. A dihedral angle of 86.04° between two planes containing N1, N2, N3, and Ba1 atoms and N4, N5, N6, and Ba1 atoms, indicates an orthogonal arrangement of the two ligands with the central barium metal ion to avoid steric crowding with each other.

Catalytic hydroamination of isocyanates or iso-thiocyanates

In the beginning, all Ae-metal complexes **2-6** synthesized were screened as catalysts to meditate the hydroamination reaction of isocyanate and isothiocyanates with aniline. Catalytic experiments were performed using 5 mol % of the complex (i.e. **2-6**) along with equimolar amounts of phenylisothiocyanate and aniline under the neat condition at 60 °C for 12 h. It was observed that only homoleptic complexes **5** and **6** exhibited catalytic activity for the same reaction and resulted in the formation of the corresponding thiourea derivative in an excellent yield ~98 % (Table 2, Entries 2 & 3). As a control experiment, when the hydroamination reaction of isothiocyanate with aniline was performed in the absence of the catalyst, it did not yield any product at room temperature as well as

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at elevated temperature (Table 2, Entries 10 & 11). Table 2 also shows that temperature has a considerable effect on the reaction. No formation of thiourea was observed even in the presence of catalyst 5 when the hydroamination reaction of isothiocyanate with aniline was carried out at room temperature for a prolonged time (Table 2, Entry 1). It presumably due to the activation of catalysts 5 and **6** at an elevated temperature only and exhibited comparable activity for the given reaction under a similar reaction condition (Table 2, Entries 2 & 3). Besides, when the hydroamination of isothiocyanate and aniline was performed using 3 mol % of the complex 5 or 6, almost the similar yield of thiourea was obtained as that with 5 mol% of catalyst (Table 2, Entries 4 & 5). We also studied the effect of various solvents such as THF, toluene, benzene, and hexane, etc. on the product yield when the hydroamination of isothiocyanate with aniline was performed using 3 mol % of the complex 5 at 60 °C for 12 h (Table 2, Entries 6-9). It was observed that the least yield ~70% of the thiourea product obtained when THF was used as a solvent.

Table 2. Screening results for hydroamination of phenylisothiocyanate with aniline

Entry	Catalyst	mol	Solvent	Temp.,	Isolated
		%		Time	Yield
1	5	5	Neat	RT, 12 h	-
2	5	5	Neat	60°C, 12 h	98
3	6	5	Neat	60°C, 12 h	98
4	5	3	Neat	60°C, 12 h	98
5	6	3	Neat	60°C, 12 h	98
6	5	3	Toluene	60°C, 12 h	98
7	5	3	THF	60°C, 12 h	70
8	5	3	Benzene	60°C, 12 h	95
9	5	3	Hexane	60°C, 12 h	86
10	5	0	Neat	RT, 12 h	-
11	5	0	Neat	60°C, 12 h	-

In a further study to analyze the substrate scope, the hydroamination reactions of several aryl amines with isocyanate and isothiocyanate catalyzed by homoleptic calcium complex $[{(Ph_2CHN=CH)_2-C_4H_2N}_2Ca]$ (5) were investigated under mild conditions. Catalytic experiments were performed using 3 mol % of calcium complex (5) and equimolar amounts of either isocyanate or isothiocyanate and arylamines, which were stirred and heated at 60 °C temperature for 12 h under a neat condition in an inert atmosphere. The respective urea or thiourea derivatives were isolated in each case and analyzed through ¹H and ¹³C NMR spectroscopy (see ESI). The yields were calculated after the isolation of pure products. The reactions displayed a broad substrate scope. The results of the catalytic hydroamination to isocyanates and phenyl isothiocyanate are presented in Table 3 and 4, respectively. In most of the cases, complete substrate conversion resulting in the corresponding urea/thiourea with excellent chemoselectivity was achieved. It was observed that the reaction of 4-methyl-phenyl isocyanate with aniline and the substituted arylamines such as 4-OMePhNH₂, PhCH₂NH₂, 2-MePhNH₂, and 2,6-(Me)₂PhNH₂, bearing electron-donating group, proceeded smoothly at 60°C temperature under neat conditions and afforded the respective urea derivatives

Table 3. Hydroamination of isocyanates and arylamines catalyzed by calcium complex **5** as pre-catalyst.^a



^oAll reactions were performed under neat conditions; Yields are calculated from isolated pure products.

The catalytic hydroamination of arylamines was further extended to 4-chlorophenylisocyanate (CIPhNCO), and similar types of results were obtained as with phenyl isocyanate (Table 2, **8a-8i**).

The substrate scope was further expanded to phenyl isothiocyanate (PhNCS). The reaction of phenyl isothiocyanate with unsubstituted aniline and substituted arylamines, having o-/p-OMe, alkyl groups, halides proceeded conveniently at 60°C temperature and resulted in the selective production of the corresponding thiourea with ~82-96% yield (Table 4, **9a-9i**). The molecular structure of **9f** is shown in Figure 5. From this survey, we see that complex **5** displayed broad substrate scope and showed comparable activity with previously reported precatalysts such as zinc (II) complex [κ^{2} -{(Ph₂P-(=Se)}₂NCH₂(C₅H₄N)ZnCl₂],³¹ low coordinate Fe (II) complex (2,6-Mes₂C₆H₃)₂Fe (Mes = 2,4,6-Me₃C₆H₂),³² and thorium (IV) complex [Th(Im^{Dipp}N){N(SiMe₃)₂}].^{36,37}

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59 60 The most plausible mechanistic pathway for the insertion reaction between heterocumulenes and arylamines mediated by homoleptic calcium complex, [$(Ph_2CHN=CH)_2-C_4H_2N$ Ca] (5) as a pre-catalyst is depicted in Scheme 3. Similar mechanistic cycles were also recently proposed by Tamm and Eisen for the actinide complex and titanium complexes by us.^{34,37,95-98} In the initial step of this stepwise process, the calcium precatalyst 5 reacted with one

Table 4. Substrate scope for hydroamination of isothiocyanate andarylamines using complex **5** as pre-catalyst.^a



^aAll reactions were performed under neat conditions; Yields are calculated from isolated pure products.

equivalent of arylamine. The nucleophilic attack of the nitrogen atom from the incoming arylamine onto the electrophilic calcium center resulted in the formation of the intermediate complex (I) upon the elimination of protic ligand 1-H. Complex (I), the active catalyst, further reacted with two equivalents of isocyanate/isothiocynate to give ureate/thioureate complex (II). In the final step to propagate the catalytic cycle (Scheme 3), complex (II) reacted with one more equivalent of arylamine to yield the corresponding urea/thiourea product and the active catalyst (I).



Scheme 3: A most plausible mechanism for the catalytic addition of the N–H bond to isocyanate/isothiocyanate by homoleptic calcium(II) precatalyst $\mathbf{5}$.



Figure 5. The solid-state structure of 1-(2,6-dimethylphenyl)-3-phenylthiourea **9f**. Some hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): S(1)-C(1) 1.681(2), N(1)-C(1) 1.340(3), N(1)-C(10) 1.425(3), N(1)-H(2) 0.8600, N(2)-C(1) 1.344(3), N(2)-C(2) 1.437(3), N(2)-H(1) 0.8600, C(1)-N(1)-C(10) 127.11(18), C(10)-N(1)-H(2) 116.4, C(1)-N(2)-C(2) 123.04(17), C(1)-N(2)-H(1) 118.5, C(2)-N(2)-H(1) 118.5, N(1)-C(1)-N(2) 117.54(18), N(1)-C(1)-S(1) 120.86(16), N(2)-C(1)-S(1) 121.58(16). CCDC No. 1993225.

Experimental Section

General Information

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenktype 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 and diethyl ether were pre-dried over Na wire and distilled under nitrogen from sodium and benzophenone ketyl before use and n-pentane were distilled under nitrogen from LiAlH₄ and stored in the glove box. ¹H NMR (400 MHz) and ¹³C{1H} NMR spectra were recorded on a Bruker Avance III-400 spectrometer. Elemental analyses were performed on a Bruker Euro EA at the Indian Institute of Technology Hyderabad (IITH). Ligand 1-H, 1-K, [Ca{N(SiMe₃)₂}₂(THF)₂], and [Ba{N(SiMe₃)₂}₂(THF)₂] were prepared according to the procedure described in the literature.94,99,100 The anhydrous Cal₂, Srl₂, Bal₂ (99.999%), and NMR solvent C₆D₆ were purchased from Sigma-Aldrich, and C₆D₆ was dried under Na/K alloy before use.

Preparation of [{(Ph₂CHN=CH)₂C₄H₂N}Cal(THF)₃] (2)

In a 50 mL dry Schlenk flask, the potassium salt of the ligand **1-K** (200 mg, 0.31 mmol) and Cal₂ (92 mg, 0.31 mmol) were mixed in 15 mL THF at ambient temperature and the reaction mixture was stirred for 16 hours at 60 °C. The precipitate of KI was filtered through a glass fiber filter paper and the filtrate was dried in vacuo. The resulting white compound was further purified by washing with pentane and crystals suitable for X-ray analysis were grown from THF/pentane at -20 °C. Yield 201 mg (76%). ¹H NMR (400 MHz C₆D₆, 25 °C): $\delta_{\rm H}$ = 8.03 (s, 2H, CH=N), 7.50 (d, 8H, ArH), 7.23 (m, 8H, ArH), 7.04 (t, 4H, ArH), 6.73 (s, 2H, PyH), 5.53 (s, 2H, CH), 3.45 (br s, 12H, O–CH2–CH2), 1.17 (br s, 12H, O–CH₂–CH₂) ppm; ¹³C¹H} NMR (100 MHz, C₆D₆, 25 °C): $\delta_{\rm C}$ = 160.5 (N=C), 143.7 (Ar–C) 141.1 (Ar-C), 129.3 (Ar–C), 129.0 (Ar–C), 127.7 (py–C), 116.5 (Py–C), 79.0 (CH), 69.2 (O–CH2–CH2), 25.7 (O–

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63.22, H 6.03, N 5.03. Found C 62.91, H 5.84, N 4.88.

Preparation of [{(Ph₂CHN=CH)₂C₄H₂N}SrI(THF)₃] (3)

Following a procedure similar to that described for complex 2, using 1-K (200 mg, 0.31 mmol) and Srl₂ (108 mg, 0.31 mmol). Yield 227 mg (82%). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ_{H} = 8.19 (s, 2H, CH=N), 7.12 (d, 8H, ArH), 7.03 (t, 8H, ArH), 6.98 (d, 4H, ArH), 6.90 (s, 2H, PyH), 5.27 (s, 2H, CH), 3.51 (m, 12H, O-CH2-CH2), 1.39 (m, 12H, O-CH2-CH2) ppm; ${}^{13}C{}^{1}H$ NMR (100 MHz, C_6D_6 , 25 °C): δ_C = 160.4 (N=C), 145.1 (Ar-C), 129.1 (Ar-C), 127.3 (py-C), 119.9 (Py-C), 77.8 (CH), 68.1 $(O-CH_2-CH_2)$, 26.1 $(O-CH_2-CH_2)$ ppm. Elemental analysis: C₄₄H₅₀IN₃O₃Sr (883.39): Calcd. C 59.82, H 5.70, N 4.76. Found C 59.39, H 5.43, N 4.45.

Preparation of [{(Ph₂CHN=CH)₂C₄H₂N}Bal(THF)₃] (4)

Following a procedure similar to that described for complex 2, using 1-K (200 mg, 0.31 mmol) and Bal₂ (123 mg, 0.31 mmol). Yield 220 mg (75%). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ_H = 8.03 (s, 2H, CH=N), 7.50 (d, 8H, ArH), 7.23 (t, 8H, ArH), 7.04 (t, 4H, ArH), 6.73 (s, 2H, PyH), 5.52 (s, 2H, CH), 3.45 (m, 12H, O-CH2-CH2), 1.20 (m, 12H, O-CH2-CH2) ppm; ¹³C{¹H} NMR (100 MHz, C₆D₆, 25 °C): δ_C = 160.5 (N=C), 143.7 (Ar-C), 141.1 (Ar-C), 129.4 (Ar-C), 129.0 (Ar-C), 127.7 (py-C), 116.5 (Py-C), 79.2 (CH), 69.0 (O-CH₂-CH₂), 25.8 (O-CH₂-CH₂) ppm. Elemental analysis: C44H50IN3O3Ba (933.11): Calcd. C 56.63, H 5.40, N 4.50. Found C 56.34, H 5.19, N 4.17.

Preparation of [{(Ph₂CHN=CH)₂C₄H₂N}₂Ca] (5)

In a 50 mL dry Schlenk flask, ligand 1-H (200 mg, 0.44 mmol) and [Ca{N(SiMe₃)₂}₂(THF)₂] (110 mg, 0.22 mmol) were mixed together in 20 mL of toluene at an ambient temperature and the reaction mixture was stirred for 6 hours. After evaporation of the toluene in vacuo, the white residue yielded was recrystallized from hexane at -20 °C and gave colorless crystals. Yield 150 mg (72%). ¹H NMR (400 MHz, C₆D₆. 25 °C) δ_H ppm 7.85 (s, 2H, CH=N) 6.93 - 7.01 (m, 20H, ArH), 6.59 (s, 2H, PyH), 5.15 (s, 2H, CH) ppm. ¹³C{¹H} NMR (100 MHz, C₆D₆,25 °C): δ_C = 156.0 (N=C), 141.2 (Ar–C), 138.2 (Ar C), 129.3 (Ar– C), 129.1 (Ar-C), 129.0 (Ar-C), 128.2 (Py-C), 119.2 (Py-C), 73.7 (CH) ppm. Elemental analysis: C₆₄H₅₂CaN₆ (944.39): Calcd. C 73.74, H 5.03, N 8.06. Found C 73.51, H 4.79, N 7.81.

Preparation of [(Ph₂CHN=CH)₂C₄H₂N)₂Ba] (6)

In a 50 mL dry Schlenk flask, ligand 1-H (200 mg, 0.44 mmol) and [Ba{N(SiMe₃)₂}₂(THF)₂] (132 mg, 0.22 mmol) were mixed together in 20 mL of toluene at an ambient temperature and the reaction mixture was stirred for 6 hours. After evaporation of the toluene in vacuo, the white residue yielded was recrystallized from diethyl ether/hexane at -20 °C and gave colorless crystals. Yield 126 mg (55%). ¹H NMR (400 MHz, C₆D₆ 25 °C): $\delta_{\rm H}$ = 7.92 (s, 2x2H, CH=N)), 6.93-7.02 (d, 2x20H, ArH), 6.69 (s, 2x2H, PyH), 5.20 (s, 2x2H, CH) ppm. ¹³C{¹H} NMR (100 MHz, C₆D₆,25 °C): δ_{C} = 156.0 (N=C), 141.2 (Ar–C), 138.2 (Ar C), 129.3 (Ar-C), 129.1 (Ar-C), 129.0 (Ar-C), 128.2 (Py-C),

CH2–CH2) ppm. Elemental analysis: C₄₄H₅₀CalN₃O₃ (835.85): Calcd. C 119.2 (Py–C), 73.7 (CH) ppm. Elemental analysis: C₆₄H₅₀CalN₃O₃ (835.85): Calcd. C 119.2 (Py–C), 73.7 (CH) ppm. Elemental analysis: C₆₄H₅₀CalN₃O₃ (835.85): Calcd. C 119.2 (Py–C), 73.7 (CH) ppm. Elemental analysis: C₆₄H₅₀CalN₃O₃ (835.85): Calcd. C 119.2 (Py–C), 73.7 (CH) ppm. Elemental analysis: C₆₄H₅₀CalN₃O₃ (835.85): Calcd. C 119.2 (Py–C), 73.7 (CH) ppm. Elemental analysis: C₆₄H₅₀CalN₃O₃ (835.85): Calcd. C 119.2 (Py–C), 73.7 (CH) ppm. Elemental analysis: C₆₄H₅₀CalN₃O₃ (835.85): Calcd. C 119.2 (Py–C), 73.7 (CH) ppm. Elemental analysis: C₆₄H₅₀CalN₃O₃ (835.85): Calcd. C 119.2 (Py–C), 73.7 (CH) ppm. Elemental analysis: C₆₄H₅₀CalN₃O₃ (835.85): Calcd. C 119.2 (Py–C), 73.7 (CH) ppm. Elemental analysis: C₆₄H₅₀CalN₃O₃ (835.85): Calcd. C 119.2 (Py–C), 73.7 (CH) ppm. Elemental analysis: C₆₄H₅₀CalN₃O₃ (835.85): Calcd. C 119.2 (Py–C), 73.7 (CH) ppm. Elemental analysis: C₆₄H₅₀CalN₃O₃ (835.85): Calcd. C 119.2 (Py–C), 73.7 (CH) ppm. Elemental analysis: C₆₄H₅₀CalN₃O₃ (835.85): Calcd. C 119.2 (Py–C), 73.7 (CH) ppm. Elemental analysis: C₆₄H₅₀CalN₃O₃ (835.85): Calcd. C 119.2 (Py–C), 73.7 (CH) ppm. Elemental analysis: C₆₄H₅₀CalN₃O₃ (835.85): Calcd. C 119.2 (Py–C), 73.7 (CH) ppm. Elemental analysis: C₆₄H₅₀CalN₃O₃ (835.85): Calcd. C 119.2 (Py–C), 73.7 (CH) ppm. Elemental analysis: C₆₄H₅₀CalN₃O₃ (835.85): Calcd. C 119.2 (Py–C), 73.7 (CH) ppm. Elemental analysis: C₆₄H₅₀CalN₃O₃ (835.85): Calcd. C 119.2 (Py–C), 73.7 (CH) ppm. Elemental analysis: C₆₄H₅₀CalN₃O₃ (Py–C) (1042.33): Calcd. C 73.74, H 5.03, N 8.06. For du C 功多为2,04140,59,9N 7.81.

Typical Procedure for Hydroamination of isocyanates and isothiocyanates with arylamines

Arylamine (0.352 mmol) was added under neat condition into the reaction mixture of isocyanate or isothiocyanate (0.352 mmol) and calcium complex (5) (0.010 mmol). This was done in a 25 mL dry Schlenk flask inside the glovebox. The dark red reaction mixture was stirred for 12 h at 60°C temperature. The solvent was thereafter evaporated in vacuo. A white solid compound was obtained in each case which was purified by washing several times with n-hexane. The conversion of amines was calculated from isolated pure products.

X-Ray Crystallographic Studies of Complexes 2, 3, 4, 6 and 9f

Single crystals of compounds 2-4 were grown from a mixture of THF and n-pentane, and complexes 6 was grown either from hexane or diethyl ether/hexane at -20 °C in an inert atmosphere. For compounds, 2-6, 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 and all measurements were made on an Agilent Supernova X-Calibur Eos CCD detector with graphite monochromatic Cu-K α (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 (SIR92)^{101,102} and refined on F2 by full-matrix least-squares methods; using SHELXL-97.¹⁰³ Non-hydrogen atoms were anisotropically refined. H atoms were included in the refinement in calculated positions riding on their carrier atoms. The ORTEP-3 program was used to draw the molecules. 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 1518707 (2), 1518710 (3), 1518708 (4), 1518711(6), 1993225 (9f). 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).

Conclusions

In summary, we successfully prepared a series of new alkaline earth metal complexes 2-6 supported by the bulky bis-iminopyrrolyl ligand, and the solid-state structures of heteroleptic complexes $[{(Ph_2CHN=CH)_2C_4H_2N}AeI(THF)_3]$ Ae : Ca (2); Sr (3); Ba (4) and homoleptic barium complex [{($Ph_2CHN=CH$)₂C₄H₂N}₂Ba] (6) were established using X-ray crystallography. The solid-state structures of 2-4 and 6 reveal the flexibility and multidentate behavior of the bisiminopyrrolyl ligand **1-H**. In the solid-state, the monoanionic ligand **1** exhibited κ^3 -chelation mode in complex **2** to adopt a distorted octahedral geometry around the calcium ion, whereas κ^3 -chelation mode of the ligand 1 was observed in complexes 3 and 4 to adopt a pentagonal bipyramidal arrangement around the strontium and

barium ions. The homoleptic calcium and barium complexes **5** and **6** were synthesized through the silylamine elimination route. The solidstate structure of barium complex (**6**) adopts a distorted octahedral geometry *via* the κ^3 -chelation mode of two ligands to the central barium ion. The calcium complex **5** was used as an active pre-catalyst for the hydroamination of isocyanates and isothiocyanates with various arylamines and demonstrated excellent activity and chemoselectivity to the desired urea and thiourea products with a wide substrate scope.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

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Keywords: alkaline earth metals • bis-iminopyrrole • catalysis hydroamination • isocyanates

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Graphical Abstract Entry

Hydroamination of isocyanates and isothiocyanates by Alkaline Earth Metal Initiators supported by Bulky Iminopyrrolyl Ligand

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Synthesis and structural features of heteroleptic and homoleptic alkaline earth metal complexes supported by bulky bis-iminopyrrolyl ligands are reported. The catalytic hydroamination of isocyanates and isothiocyanates with aryl amines using calcium complex is presented.

