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Bulky guanidinate calcium and zinc complexes as catalysts for the intramolecular hydroamination

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ABSTRACT

Mixed guanidinato-amido supported complexes of calcium, $LCaN(SiMe_3)_2 \cdot 2THF$ (**1**) [L = {ArNC(N^{i}Pr$_2$)NAr} (Ar = 2,6-Me$_2$-C$_6$H$_3$)] and zinc, $LZnN(SiMe_3)_2$ (**2**) & $L^1ZnN(SiMe_3)_2$ (**3**) [L^1 = {Ar'NC(N^{i}Pr$_2$)NAr'} (Ar' = 2,6-^{i}Pr$_2$-C$_6$H$_3$)] have been synthesized by salt metathesis method. Reaction between LH or L^1H and two equivalents of $KN(SiMe_3)_2$ in THF and the resultant reaction mixture upon treatment with CaI_2 or $ZnCl_2$ led to the formation of heteroleptic calcium or zinc complexes. All three compounds (**1**–**3**) were characterized by multinuclear (^{1}H, ^{13}C, ^{29}Si) magnetic resonance spectroscopy, elemental analysis and single crystal X-ray diffraction methods. Solid state structures confirm that all are monomeric species. Furthermore, we have shown the catalytic application of these complexes for intramolecular hydroamination of amino alkenes. Interestingly, compound **1** exhibits as an excellent pre-catalyst for intramolecular hydroamination of various primary amino alkenes in the absence of any additional activator (co-catalyst). However, both compounds **1** and **2** show very good catalytic activity of hydroamination of various secondary amines in the presence of co-catalyst.

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1. Introduction

The hydroamination of alkenes or alkynes is an attractive atom-efficient synthetic method for the synthesis of nitrogen-containing molecules from cheaper precursors [1]. The hydroamination reaction can be defined as the formal addition of a N–H bond over C–C double or triple bond, which can either proceed through inter or intra molecular fashion [2]. However, to overcome the high barrier for this addition reaction, catalytic pathways are required.

The intramolecular hydroamination of amino alkenes has been rigorously described [3] with several main group, transition and lanthanide based catalysts. Marks et al. have developed some highly active lanthanide based catalysts for intramolecular hydroamination reactions [4]. Roesky and co-workers demonstrated the homoleptic lanthanide amide catalysed hydroamination/cyclization of aminoalkynes [5]. Livinghouse and co-workers have reported homoleptic yttrium and lanthanide bis(trimethysilyl) amides, $[Ln\{N(SiMe_3)_2\}_3]$ as catalysts for the intramolecular hydroamination of amino olefins [6]. As far as main group, in particular, calcium based catalysts are concerned, Hill and co-workers reported the heteroleptic β-diketiminate supported calcium amide catalysed intramolecular hydroamination of amino alkenes for the first time [7]. This well-defined calcium amide complex was originally reported by Chisholm in 2004 [8]. Intramolecular hydroamination of amino olefins is extended by the research groups of Hill [9], Harder [10], Roesky [11], Tamm [12] and many others [13]. Recently, Thiel and co-workers have isolated and structurally characterized the zinc metal alkyl complex, which is the intermediate in the β-diketiminate supported heteroleptic zinc amide catalysed intramolecular hydroamination reaction of an amino olefin in the absence of activator [14].

Traditionally, second- and third-row transition metals have been broadly exploited in catalytic applications [15]. The recent trend of homogeneous catalysis is the use of main group metal or elements [10a,16].

This is due to their low-cost, low toxicity and the large abundance of main group elements in comparison to transition or lanthanide metals. In addition, molecular compound catalysed organic transformations are in advantageous to understand the reaction mechanism by isolating reactive intermediates. This is possible because actual chemistry occurs at the coordination sphere of the metal centre.

In this regard, we have previously reported complexes of Mg, Ca and Zn bearing guanidinate ligand and their catalytic activity in the

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Tishchenko reaction [17] and heteroleptic magnesium complexes as pre-catalysts for the hydroboration of esters [18]. Although there are some reports on synthesis and characterization of guanidinate supported calcium [19] and zinc [20] complexes, which are utilized as catalysts for ring opening polymerization of lactide, styrene polymerization, cyclotrimerization of isocyanate, dimerization of aldehyde to corresponding ester *i.e.* Tishchenko reaction etc. However, to the best of our knowledge there have been no reports on heteroleptic guanidinate calcium and zinc amide catalysed hydroamination of amino alkenes till date.

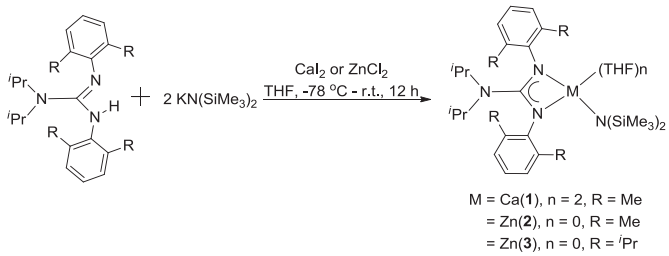
Therefore, herein, we report three new examples of structurally characterized heteroleptic calcium and zinc amide complexes (**1**–**3**). Furthermore, we have investigated the catalytic application of these complexes for the intramolecular hydroamination reaction of both primary and secondary amino olefins.

2. Result and discussion

Two bulky tetra-substituted guanidines such as LH [L = {ArNC(N^{i}Pr$_2$)NAr}; (Ar = 2,6-Me$_2$-C$_6$H$_3$)] and L^{1}H [L^1 = {Ar'NC(N^{i}Pr$_2$)NAr'}; (Ar' = 2,6- ^{i}Pr$_2$-C$_6$H$_3$)] have been utilized to synthesize heteroleptic calcium and zinc amide complexes. The synthesis of heteroleptic bulky guanidinate supported calcium and zinc amide complexes **1**–**3**, LCaN(SiMe$_3$)$_2$·2THF (**1**), LZnN(SiMe$_3$)$_2$ (**2**) and L^{1}ZnN(SiMe$_3$)$_2$ (**3**) was achieved by the salt metathesis method. Reaction of a bulky guanidine ligand, LH with two equivalents of potassium bis(trimethylsilyl) amide, KN(SiMe$_3$)$_2$ in tetrahydrofuran (THF) and subsequent treatment with one equivalent of CaI$_2$ in THF afforded the expected product LCaN(SiMe$_3$)$_2$·2THF (**1**) (Scheme 1). Similarly, the reaction of a bulky guanidine ligand, either LH or L^{1}H with two equivalents of KN(SiMe$_3$)$_2$ in THF and subsequent treatment with one equivalent of ZnCl$_2$ led to the formation of LZnN(SiMe$_3$)$_2$ (**2**) and L^{1}ZnN(SiMe$_3$)$_2$ (**3**), respectively (Scheme 1).

Recently, Westerhausen and co-workers reported the structurally characterized heteroleptic guanidinate stabilized calcium amide, L^{1}CaN(SiMe$_3$)$_2$·THF·(hexane); [L^1 = {Ar'NC(N^{i}Pr$_2$)NAr'}; (Ar' = 2,6- ^{i}Pr$_2$-C$_6$H$_3$)] (**4**) by deprotonation method [19c]. The compound **4** was synthesized by the reaction of Ca{N(SiMe$_3$)$_2$}$_2$·2THF with L^{1}H in hexane at reflux temperature for 18 h.

The mixed guanidinato-amido calcium and zinc complexes (**1**–**3**) are freely soluble in organic solvents such as *n*-hexane, benzene, toluene, tetrahydrofuran and diethylether. These compounds are moderately air and moisture sensitive. All three compounds were characterized by multinuclear (^{1}H, ^{13}C, and ^{29}Si) magnetic resonance spectroscopy and elemental analysis. Furthermore, the molecular structures of **1**, **2** and **3** were confirmed by X-ray single crystal structural analysis. All three compounds **1**–**3** exhibit the expected number of signals in the ^{1}H and ^{13}C NMR spectra and are consistent with their composition. The ^{1}H NMR spectrum of compound **1** exhibits singlet resonance for the amide moiety, N(SiMe$_3$)$_2$ at 0.1 ppm in C$_6$D$_6$, while both compounds **2** and **3** exhibit singlet resonances for amide moiety, N(SiMe$_3$)$_2$ at 0.2 ppm in C$_6$D$_6$. The ^{13}C NMR spectra for compounds **1**–**3** show a characteristic peak for the N3*C* resonances at 172.5, 169.9 and 170.4 ppm respectively. The ^{29}Si NMR spectra show signals at −1.98, −0.51 and −0.80 ppm for compound **1**, **2** and **3**, respectively, and are attributed to the amido, N(*Si*Me$_3$)$_2$ moiety.



Scheme 1. Synthesis of compounds **1**–**3**.

2.1. Molecular structures of 1-3

Single crystals LCaN(SiMe$_3$)$_2$·2THF (**1**) were obtained from *n*-hexane solution upon cooling at 0 °C. Compound **1** crystallizes in the orthorhombic system with *Pca*2$_1$ space group. The molecular structure, selected bond distances and bond angles are depicted in Fig. 1.

The molecular structure of **1** reveals that the Ca centre is bonded to the guanidinate ligand in [*N,N'*] chelate fashion, and other three sites are occupied by a N atom of the amido ligand and two oxygen atoms of the THF molecules, resulting in a distorted square pyramidal geometry.

The Ca1–N4 bond distance 2.322(3) Å in **1** is slightly longer than the reported the Ca-N$_{amido}$ bond distance in compound **4** (2.284(3) Å). The Ca1–N4 bond distance 2.322(3) Å in **1** is shorter than the Ca1–N1 and Ca1–N2 bond lengths of 2.411(3) Å and 2.403(3) Å, respectively. The N2–Ca1–N1 bite angle 56.08(9)^o is significantly more acute than compound **4** (N2–Ca1–N1 57.05(8)^o). The Ca1–O1 and Ca1–O2 bond distances, 2.427(2) Å and 2.421(2) Å, respectively are longer than Ca1–O1 bond distance of compound **4** (2.350(2) Å). The molecular structures of **2** and **3**, selected bond distances and bond angles are depicted in Fig. 2.

Compounds **2** and **3** were crystallized in the triclinic $P\bar{1}$ and monoclinic $P2_1/c$ space groups, respectively. Both compounds **2** and **3** are isostructural. The solid state structures for **2** and **3** display three-coordinate metal centers with distorted trigonal-planar geometries. The molecular structures reveal that both compounds **2** and **3** exist as monomeric species. The Zn–N(amido) bond distances in compounds **2** and **3** 1.858(2) Å and 1.8689(15) Å, respectively, are shorter than those of [Bu^{t}Zn{μ-N(SiMe$_3$)$_2$}]$_2$ (2.084(2) Å), [C$_6$F$_5$ Zn{μ-N(SiMe$_3$)$_2$}]$_2$ (2.048(2) Å) [21] and these distances are longer than that of *β*-diketiminato zinc amide complex, ^{Dipp}NacnacZnNMe$_2$ [^{Dipp} Nacanac = CH

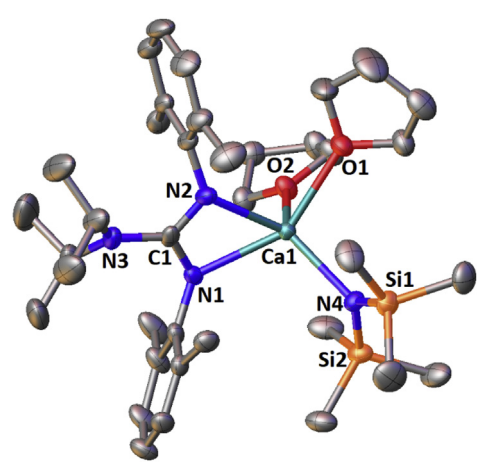


Fig. 1. Molecular structure of compound 1. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (^{o}): Ca1–N1 2.411(3), Ca1–N2 2.403(3), Ca1–N4 2.322(3), C1–N3 1.411(4), Ca1–O1 2.427(2), Ca1–O(2) 2.421(2), Si1–N4 1.690(3); N1–Ca1–N2 56.08(9), N2–C1–N1 115.22(3), N4–Ca1–N1 108.40(9), N4–Ca1–N2 131.82(10), N1–Ca1–O1 146.67(9), N1–Ca1–O2 99.52(8), N2–Ca1–O1 92.35(9), N2–Ca1–O2 108.80(10), Si2–N4–Si1 123.30(15).

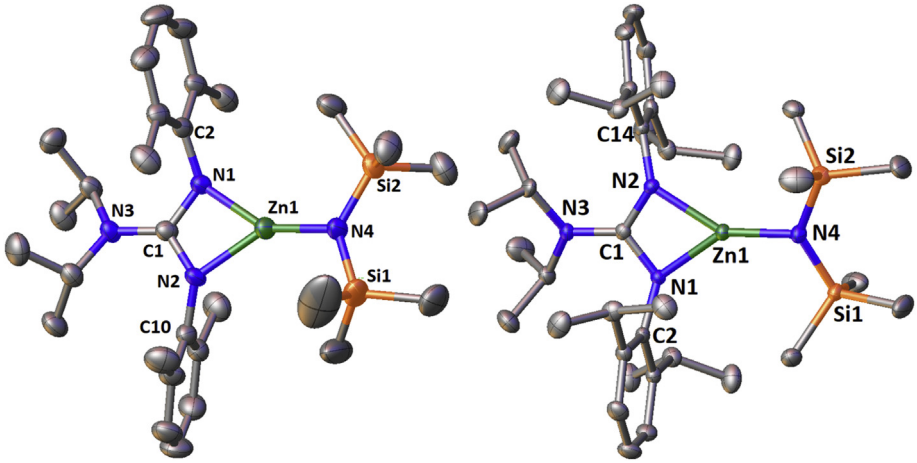


Fig. 2. Molecular structures of compounds 2 and 3. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (o) for compound 2 (left): Zn1–N1 1.993(2), Zn1–N2 2.023(3), Zn1–N4 1.858(2), Si2–N4 1.714(3), Si1–N4 1.709(3), N3–C1 1.376(4); N1–Zn1–N2 67.48(11), N4–Zn1–N1 149.26(12), N4–Zn1–N2 142.73(12), N2–C1–N1 110.8(3), Si1–N4–Si2 126.01(15) and 3 (right) Zn1–N1 2.0044(14), Zn1–N2 2.0023(15), Zn1–N4 1.8689(15), Si1–N4 1.7166(15), Si2–N4 1.7151(15), N3–C1 1.366(2); N2–Zn1–N1 67.29(6), N4–Zn1–N2 147.31(6), N4–Zn1–N1 145.39(6), N2–C1–N1109.92(14), N2–C1–N3125.20(15), Si2–N4–Zn1115.11(8), Si2–N4–Si1130.64(9).

$\{(CMe)_2(2,6\text{-}^iPr_2C_6H_3N)_2\}$] (Zn-$N_{amido}$ 1.8385(15) Å) [14]. As expected, the Ca–N (amido) bond length 2.322(3) Å (summation of the covalent radii of calcium and nitrogen = 2.47 Å) [22] is longer than the Zn–N bond distances (Zn and N = 1.93 Å) in compounds **2** and **3** 1.858(2) Å and 1.8689(15) Å, respectively. The N1–Zn1–N2 bite angles in compound **2** and **3** 67.48(11)^o 67.29(6)^o, respectively are wider than the bite angle of N1–Ca1–N2 in compound **1** (56.08(9) ^{o}).

2.2. Calcium and zinc catalysed intramolecular hydroamination reaction

In 1990's homoleptic calcium and zinc bis(amide) reagents have been reported [23]. Moreover, these reagents (derivatives) have been widely used in the coordination chemistry by the research groups of Bochmann and co-workers [24], Hill and co-workers [16c], Harder and co-workers [10a], Roesky and co-workers [11a,b], Ruhlandt-Senge and co-workers [25], Westerhausen and co-workers [26], Carpentier, Sarazin and co-workers [27] and Power and co-workers [28]. In recent years, a few examples of heteroleptic *N,N′*-chelated calcium and zinc amide complexes have been utilized as catalysts for the hydroamination reaction [16b]. In view of this we aimed to test compounds **1**, **2** and **3** for the intramolecular hydroamination/cyclization reaction of both primary and secondary amino olefins. (see, Tables 1–4).

2.2.1. Intramolecular hydroamiation of primary aminoalkenes

Initially, we began our investigation with the addition of 10 mol % of catalyst **1** to the dry and degassed 2,2-diphenylpent-4-en-1-amine in C_6D_6 at room temperature. We noticed the complete conversion of 2,2-diphenylpent-4-en-1-amine to the corresponding five-membered pyrrolidine derivative within 5 min (Table 1, entry 1).

Further, the same reaction was performed by using lower catalyst loadings (5 mol %, and 2 mol %). A complete conversion of 2,2-diphenylpent-4-en-1-amine into cyclic amine was noticed within 15–30 min (Table 1, entries 2–3). Moreover, the same reaction was performed by using a catalyst **4** with catalyst loadings 5 mol % and 2 mol %. We observed that compound **4** exhibits similar catalytic activity as that of the compound **1**. Further, we decided to test the catalytic activity of compounds **2** and **3.** First, the intramolecular hydroamination of primary amino alkene *i.e*, 2,2-diphenylpent-4-en-1-amine with catalyst **2** (5 mol%) was performed in C_6D_6 at 80 °C. After heating for 8 h, there was no cyclized product, as revealed by ^{1}H NMR spectrum of the reaction mixture. Next, this reaction was performed with an equimolar amount (with respect to catalyst) of the activator, [$PhNMe_2H$] [$B(C_6F_5)_4$]. A quantitative conversion of amino alkene into cyclized product was noticed within 120 min. This improvement in the catalytic activity may be attributed to the *in situ* generation of the coordinatively unsaturated cationic zinc species, in which the activator acts as amide $-NH(SiMe_3)_2$ abstracting agent. However, the same reaction was performed at 80 °C in C_6D_6 with lower catalysts loadings (2.5 mol %) by using catalysts **2** and **3**. In both the cases, longer reaction time is required for the quantitative conversion.

With optimized reaction conditions for the intramolecular hydroamination of 2,2-diphenylpent-4-en-1-amine in hand, the reaction scope was expanded to various other primary amino olefin substrates by using catalysts **1** and **2** (see, Table 2).

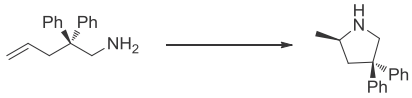
As expected, a higher catalyst loading and elevated temperature are required for the preparation of six-membered piperidine and seven-membered azepane derivatives, when compared to five-membered pyrrolidine derivatives. It is known that catalytic turnover increases for smaller ring sizes (5 > 6 > 7) (Baldwin's guidelines) [29]. The intramoleular hydroamination reactions of 2,2-diphenylhex-5-en-1-amine and (1-(but-3-en-1-yl)cyclohexyl) methanamine with complex **1** or **2** yielded the corresponding six-membered piperidine derivatives of 97% (Table 2, entry 11), 95% (Table 2, entry 12) and 99% (Table 2, entry 13), 96% (Table 2, entry 14), respectively.

2.2.2. Intramolecular hydroamination of secondary aminoalkenes

After the successful conversion of various primary amino olefins into cyclized amines by using catalysts **1** and **2,** we aimed to test compounds **1** and **2** catalysed intramolecular hydroamination reaction of secondary amines. The intramolecular hydroamination reaction of secondary aminoalkene was carried out by using N-benzyl-2,2-diphenylpent-4-en-1-amine as a model substrate (see, Table 3).

We carried out with addition of 5 mol % catalyst **1** and equimolar amount (with respect to catalyst) of activator [$PhNMe_2H$] [$B(C_6F_5)_4$] (5 mol %) to a N-benzyl-2,2-diphenylpent-4-en-1-amine in C_6D_6 in a J Young valve NMR tube. The above reaction mixture was heated to 120 °C for 24 h. We noticed the formation of 1-benzyl-2-methyl-

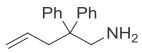
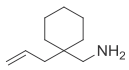
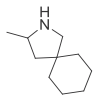
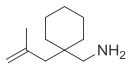
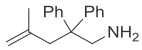
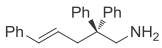
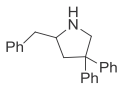
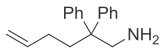
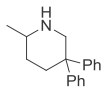
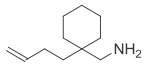
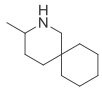
Table 1
Cyclization of 2,2-diphenylpent-4-en-1-amine[a].2



Entry	Precatalyst	Cat. (mol%)	Time (min)	Temp (°C)	Conv. (%)[b]
1	$LCaN(SiMe_3)_2 \cdot 2THF$ (**1**)	10	5	25	>99
2	**1**	5	15	25	>99
3	**1**	2	30	25	>99
4	$L^1CaN(SiMe_3)_2 \cdot THF$ (**4**)	5	15	25	>99
5	**4**	2	30	25	>99
6	$LZnN(SiMe_3)_2$ (**2**)	5	120	80	>99[c]
7	**2**	2.5	480	80	>99[c]
8	$L^1ZnN(SiMe_3)_2$ (**3**)	2.5	480	80	>99[c]

[a] Conditions: primary amino olefin (20 μL), 0.5 mL C_6D_6 on the NMR scale.
[b] Calculated by ^1H NMR spectroscopy and hexamethylbenzene added as an internal standard.
[c] Co-catalyst $[PhNMe_2H]$ $[B(C_6F_5)_4]$ equimolar amount (with respect to catalyst).

Table 2
Intramolecular hydroamination reaction of aminoalkenes catalysed by 1 and 2.[a].

Entry	Substrate	Product	Catalyst (mol%)	Time (min)	Temp (°C)	Conv. (%)[b]
1			1(2)	20	25	>99
2			2(5)	120	80	>99
3			1(2)	20	25	99
4			2(5)	120	80	99
5			1(2)	25	25	99
6			2(5)	120	80	98
7			1(2)	25	25	98
8			2(5)	120	80	97
9			1(2)	20	25	99
10			2(5)	120	80	98
11			1(10)	120	60	97[c]
12			2(5)	180	80	95
13			1(10)	150	60	99[c]
14			2(5)	180	80	96

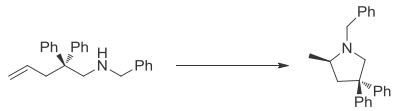
[a] Conditions: For catalyst **1;** amine (20 μL) and catalyst (2 mol %); for catalyst **2** amine (20 μL) catalyst (5 mol %) and activator $[PhNMe_2H]$ $[B(C_6F_5)_4]$ (5 mol%) in 0.5 mL C_6D_6 on NMR scale.
[b] Determined by ^1H NMR spectroscopy using hexamehyl benzene as an internal standard.
[c] Catalyst **1** (10 mol%).

4,4-diphenylpyrrolidine in 95%, which is confirmed by ^1H NMR spectrum of the reaction mixture. Catalyst **4** shows similar catalytic activity for the above reaction. However, both catalysts **2** and **3** show better catalytic activity for the conversion of N-benzyl-2,2-diphenylpent-4-en-1-amine into 1-benzyl-2-methyl-4,4-diphenylpyrrolidine when compared to catalysts **1** and **4**. (Table 3, entries 3–6).

Moreover, both compounds **2** and **3** exhibit similar catalytic activity compare to aminotroponiminate zinc complexes **5** and **6** (Table 3, entries, 7 & 8). Furthermore, it is worthy to mention that catalysts **2** and **3** are showing much superior catalytic activity compare to compounds **7**–**9** (Entries 9–11) [30].

As summarized in Table 4, a variety of secondary aminoalkenes underwent intramolecular hydroamination reaction in the presence of catalysts **1** and **2** and equimolar amount of activator (Table 4, entries 1–14) in C_6D_6. In each case, a quantitative conversion was noticed. Progress of the reaction was monitored by ^1H NMR spectroscopy of the reaction mixture using internal standard hexamethyl benzene. As is the case in primary amino olefins, a longer reaction time is required for the formation of six-membered piperidine derivatives (Table 4, entries 11–14). For the conversion of primary amines into cyclized amines calcium amide is superior

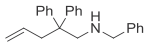
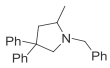
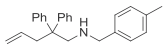
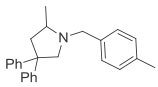
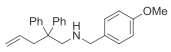
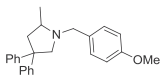
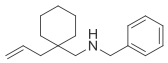
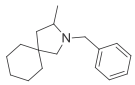
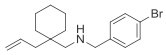
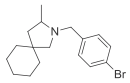
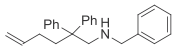
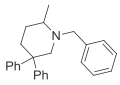
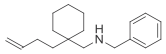
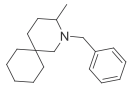
Table 3
Cyclization of N-benzyl-2,2-diphenylpent-4-en-1-amine [a]



Entry	Precatalyst	Cat. (mol%)	Time (h)	Temp (°C)	Conv. (%)[b]
1	$LCaN(SiMe_3)_2 \cdot 2THF$ (**1**)	5	24	120	95
2	$L^1CaN(SiMe_3)_2 \cdot THF$ (**4**)	5	23	120	93
3	$LZnN(SiMe_3)_2$ (**2**)	5	2	80	99
4	**2**	2.5	12	80	94
5	$L^1ZnN(SiMe_3)_2$ (**3**)	5	2	80	98
6	**3**	2.5	12	80	94
7	$[\{ATI(iPr)_2\}ZnMe]$[c] (**5**)	2.5	1.59	80	quant. 99[d]
8	$[\{ATI(iPr)_2\}ZnPh]$[c] (**6**)	2.5	1.59	80	92
9	$[\{ATI(iPr)_2\}Zn\{N(SiMe_3)_2\}]$[c] (**7**)	2.5	1.59	80	29
10	$[\{ATI(Cy)_2\}Zn\{N(SiMe_3)_2\}]$[c] (**8**)	2.5	12	80	64
11	$[\{PhS\text{-}ATI(iPr)_2\}Zn\{N(SiMe_3)_2\}]$[c] (**9**)	2.5	12	80	87

[a] Conditions: secondary amino olefin (20 μL), equimolar amount (with respect to catalyst) of co-catalyst $[PhNMe_2H]$ $[B(C_6F_5)_4]$, 0.5 mL C_6D_6 on the NMR scale.
[b] Calculated by ^1H NMR spectroscopy and hexamethylbenzene added as an internal standard.
[c] See Ref. 30.
[d] Isolated yield.

Table 4
Intramolecular hydroamination reaction of secondary aminoalkenes catalysed by 1 and 3.[a].

Entry	Substrate	Product	Catalyst	Time (h)	Temp (°C)	Conv. (%)[b]
1			1	24	120	>95
2			2	2	80	99
3			1	34	120	95
4			2	4	80	96
5			1	36	120	94
6			2	4	80	97
7			1	24	120	98
8			2	2	80	99
9			1	26	120	96
10			2	3	80	98
11			1	34	120	93
12			2	4	80	94
13			1	36	120	94
14			2	4	80	95

[a] Conditions: For catalysts **1** and **2** amine (20 μL), catalyst (5 mol %) and activator $[PhNMe_2H]$ $[B(C_6F_5)_4]$ (5 mol %) in 0.5 mL C_6D_6 on NMR scale.
[b] Determined by ^1H NMR spectroscopy using hexamethy lbenzene as an internal standard.

catalyst when compared zinc amides. However, in the case of secondary amines, zinc amides are better catalyst than calcium amides.

3. Conclusion

Three new heteroleptic calcium and zinc complexes (**1**–**3**) bearing bulky guanidinato and amido ligands have been synthesized and structurally characterized. Furthermore, we have demonstrated the formation of carbon-nitrogen bonds in both primary and secondary aminoalkenes by intramolecular cyclization (hydroamination) reaction catalysed by heteroleptic calcium and zinc amide complexes. These catalysts show similar catalytic activity with reported calcium/zinc amide and other main group metal complexes. These complexes (**1**–**3**) are important precursors for isolation of guanidinate supported hydride and hydroxides, alkoxides etc. Such studies are in progress in our laboratory and we publish in due course.

4. Experimental section

All manipulations were carried out using standard Schlenk line technique and glove box under an inert atmosphere of nitrogen. Solvents were collected from MBraun Solvent Purification System and degassed prior to use. Benzene-d_6 was dried over potassium mirror and freeze-thaw was performed twice prior to use. NMR spectroscopic data were recorded on a Bruker AV-400 spectrometer (^{1}H NMR, 400 MHz; ^{13}C{^{1}H} NMR, 101 MHz, ^{29}Si{^{1}H} NMR, 80 MHz). Deuterated benzene was used for NMR measurements; chemical shift values (δ) are reported in parts per million relative to the residual signals of the solvent (δ 7.16 for ^{1}H and δ 128.0 for ^{13}C). Elemental analyses were performed in a Vario Micro Cube Elementar CHNS/O analyzer. All the chemicals were purchased from Sigma-Aldrich, Alfa Aesar, Acros organics and used as received. [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] was purchased from Strem chemicals and used without any further purification. Precursors such as LH [17], L^{1}H [31] and L^{1}Ca(NSiMe$_3$)$_2$.THF [19c] were prepared according to literature procedures. Aminoalkenes substrates both primary and secondary such as 2,2-diphenylpent-4-en-1-amine [32], (1-allylcyclohexyl)methylamine [33], (1-(2-methylallyl)cyclohexyl) methanamine [33], 4-methyl-2,2-diphenylpent-4-en-1-amine [33], (*E*)-2,2,5-triphenylpent-4-en-1-amine [34], 2,2-diphenylhex-5-en-1-amine [35], (1-(but-3-en-1-yl)cyclohexyl)methanamine [34], N-benzyl-2,2-diphenylpent-4-en-1-amine [34], N-(4-methylbenzyl)-2,2-diphenylpent-4-en-1-amine [36], N-(4-methoxybenzyl)-2,2-diphenylpent-4-en-1-amine [13c], 1-(1-allylcyclohexyl)–N-benzylmethanamine [13c], 1-(1-allylcyclohexyl)–N-(4-bromobenzyl) methanamine, N-benzyl-2,2-diphenylhex-5-en-1-amine [37], N-benzyl-1-(1-(but-3-en-1-yl)cyclohexyl)methanamine [34] were prepared according to the literature procedures and dried by distilling. All hydroamination products are known compounds and were identified by comparing to the reported literature ^{1}H NMR spectroscopic data.

4.1. Synthesis of compound 1

To a mixture of bulky guanidine free ligand, LH [L = {ArNC(-N^{i}Pr$_2$)NAr}; (Ar = 2,6-Me$_2$-C$_6$H$_3$)] (0.5 g, 1.42 mmol) and KN(SiMe$_3$)$_2$ (0.574 g, 2.87 mmol) was added THF (20 mL) and stirred at room temperature for 4 h. The resultant reaction mixture was then added drop by drop to a stirred suspension of CaI$_2$ (0.417 g, 1.42 mmol) in THF (5 mL) at −78 °C. The reaction mixture was slowly allowed to warm to room temperature and stirred for 24 h. All the volatiles were removed under vacuum. Finally, the solid was dried under high vacuum and extracted with *n*-hexane (~40 mL) and filtered through Celite. The clear solution was reduced approximately to 10 mL and colorless single crystals of the desired product were obtained after one day at 0 °C Yield: 0.83 g (84%); mp = 140–145 °C. ^{1}H NMR (C$_6$D$_6$, 298 K, 400 MHz) δ 7.11 (d, J = 7.4 Hz, 4H, Ar–*H*), 6.93 (t, J = 7.4 Hz, 2H, Ar–*H*), 3.87 (sept, J = 8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.52 (br, 8H, OC*H*$_2$CH$_2$), 2.59 (s, 12H, C*H*$_3$), 1.39 (br, 8H, OCH$_2$C*H*$_2$), 0.75 (d, J = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 0.10 (s, 18H, Si(C*H*$_3$)$_3$); ^{13}C {^{1}H} NMR (C$_6$D$_6$, 298 K, 100 MHz): δ 172.5 (NCN), 151.1 (Ar–*C*), 132.6 (Ar–*C*), 130.1 (Ar–*C*), 121.4 (Ar–*C*), 67.9 (OCH$_2$CH$_2$), 50.2 (N-^{i}Pr-*C*H), 25.7 (OCH$_2$*C*H$_2$), 24.7 (Ar–*C*H$_3$), 23.0 (Ar–*C*H$_3$), 20.5 (^{i}Pr-*C*H$_3$), 20.2 (^{i}Pr-*C*H$_3$), 6.4 (Si–*C*); ^{29}Si {^{1}H} NMR (C$_6$D$_6$, 298 K, 79 MHz): δ 1.89 (N*Si*(CH$_3$)$_3$). Despite several attempts, accurate elemental analysis could not be obtained for compound **1**.

4.2. Synthesis of compound 2

To a mixture of free ligand LH (0.5 g, 1.422 mmol) and KN(SiMe$_3$)$_2$ (0.57 g, 2.87 mmol) was added THF (20 mL) and stirred at room temperature for 4 h. The resultant reaction mixture was then added drop by drop to a stirred suspension of ZnCl$_2$ (0.194 g, 1.422 mmol) in THF (~5 mL) at −78 °C. The reaction mixture was slowly allowed to warm to room temperature and stirred for 24 h. All the volatiles were removed under vacuum. The solid residue was extracted with *n*-hexane (~40 mL) and filtered through Celite. The volume of the clear solution was reduced approximately to 10 mL and few drops of THF was added. The colorless single crystals of the desired product were obtained after three days day at −30 °C.Yield: 0.69 g (84%); mp = 120–125 °C. ^{1}H NMR (C$_6$D$_6$, 298 K, 400 MHz) δ 6.97 (d, J = 7.4 Hz, 4H, Ar–*H*), 6.91–6.87 (m, 2H, Ar–*H*), 3.87 (sept, J = 6.6 Hz 2H, C*H*(CH$_3$)$_2$), 2.40 (s, 3H, Ar–C*H*$_3$), 2.27 (s, 9H, Ar–C*H*$_3$), 0.68 (d, J = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 0.20 (s, 18H, Si(C*H*$_3$)$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 298 K, 100 MHz): δ 169.9 (NCN), 147.0 (Ar–*C*), 133.5 (Ar–*C*), 128.4 (Ar–*C*), 123.0 (Ar–*C*), 51.0 (N-^{i}Pr-*C*H), 24.1 (Ar–CH$_3$), 18.9 (^{i}Pr-*C*H$_3$), 5.1 (Si–*C*); ^{29}Si {^{1}H} NMR (C$_6$D$_6$, 298 K, 79 MHz): δ 0.51 (N*Si*(CH$_3$)$_3$). Anal Calcd for C$_{29}$H$_{50}$N$_4$Si$_2$Zn; C, 60.44; H, 8.75; N, 9.72. Found C, 60.29; H, 8.31, N, 10.09.

4.3. Synthesis of compound 3

The compound was synthesized by using a similar procedure to that employed for the preparation of **2**, but by using L^{1}H [L^1 = {Ar'NC(N^{i}Pr$_2$)NAr'} (Ar' = 2,6- ^{i}Pr$_2$-C$_6$H$_3$)] (0.5 g, 1.08 mmol), KN(SiMe$_3$)$_2$ (0.435 g, 2.18 mmol) and ZnCl$_2$ (0.147 g, 1.07 mmol).Yield: 0.65 g (88%).^{1}H NMR (C$_6$D$_6$, 298 K, 400 MHz) δ 7.10 (d, J = 1.8 Hz, 2H, Ar–*H*), 7.05 (t, J = 4 Hz, 4H, Ar–*H*), 3.65 (sept, 6H, C*H*(CH$_3$)$_2$), 1.40 (d, J = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.29 (d, J = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 1.24 (d, J = 6.9 Hz, 24H, CH(C*H*$_3$)$_2$), 0.75 (d, J = 7.1 Hz, 3H, CH(C*H*$_3$)$_2$), 0.20 (s, 18H, Si(C*H*$_3$)$_3$); ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$, 25 °C): δ 170.4 (NCN), 143.4(Ar-*C*), 143.0 (Ar–*C*), 133.7 (Ar–*C*), 125.5 (Ar–*C*), 124.0 (Ar–*C*), 123.7 (Ar–*C*), 51.0 (N-^{i}Pr-*C*H), 29.5 (^{i}Pr-*C*H$_3$), 28.2 (^{i}Pr-*C*H$_3$), 25.4 (^{i}Pr-*C*H$_3$), 23.9 (^{i}Pr-*C*H$_3$), 23.4 (^{i}Pr-*C*H$_3$), 22.9 (^{i}Pr-*C*H$_3$), 5.6 (Si–*C*); ^{29}Si{^{1}H} NMR (80 MHz, C$_6$D$_6$, 25 °C): δ 0.80 (N*Si*(CH$_3$)$_3$). Anal Calcd for C$_{37}$H$_{66}$N$_4$Si$_2$Zn: C, 64.55; H, 9.66; N, 8.14. Found C, 64.39; H, 9.82; 7.75.

4.4. General procedure for the intramolecular hydroamination of primary aminoalkenes

4.4.1. Compound **1** catalysed hydroamination reactions

Primary aminoalkene (20 μL), catalyst (2–10 mol %), hexamethylbenzene (known amount used as internal standard) and C$_6$D$_6$ (0.5 mL) were charged in a J. Young valve NMR tube inside the glove box. The progress of the reaction was monitored by ^{1}H NMR spectroscopy and NMR yields were calculated by comparing the integration of well resolved ^{1}H NMR signal of cyclic amine with that of internal standard (hexamethyl benzene).

4.4.2. Compounds 2 and 3 catalysed hydroamination reactions

Primary aminoalkene (20 μL), catalyst (2.5–5 mol %), equimolar amount of co-catalyst [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (2.5–5 mol %) hexamethylbenzene (known amount used as internal standard) and C$_6$D$_6$ (0.5 mL) were charged in a J. Young valve NMR tube inside the glove box.

Sealed NMR tube was taken out from the glovebox and heated at 80 °C on a pre-heated oil bath. The progress of the reaction was monitored by ^{1}H NMR spectroscopy.

4.5. General procedu re for the intramolecular hydroamination of secondary aminoalkenes

Secondary aminoalkene (20 μL), catalyst (5 mol %), co-catalyst [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (5 mol %) and internal standard hexamethyl benzene (known amount) C$_6$D$_6$. (0.5 mL) were charged in a J. Young valve NMR tube inside the glove box. Sealed NMR tube was taken out from the glovebox and heated at 80–120 °C on a pre-heated oil

Table 5
Crystal data and structure refinement details of compounds 1, 2 and 3.

	1	2	3
CCDC	1835652	1835654	1835653
Empirical formula	$C_{37}H_{66}CaN_4O_2Si_2$	$C_{29}H_{50}N_4Si_2Zn$	$C_{37}H_{66}N_4Si_2Zn$
Formula weight	695.20	576.28	688.49
Temperature	100(2) K	100(2) K	100(2) K
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	$Pca2_1$	$P\overline{1}$	$P2_1/c$
a (Å)	18.302(18)	9.710(4)	17.428(7)
b (Å)	12.818(12)	11.479(4)	12.746(5)
c (Å)	17.682(15)	16.187(7)	18.721(7)
α (°)	90	70.395(2)	90
β (°)	90	84.806(2)	101.187(2)
γ (°)	90	77.247(2)	90
V (Å^3)	4148(2)	1657.4(12)	4080(2)
Z, Calculated density	4, 1.113 Mg/m^3	2, 1.155 Mg/m^3	4, 1.121 Mg/m^3
μ/mm^{-1}	0.243	0.835	0.689
F(000)	1520	620	1496
Theta range for data collection/°	2.23 to 25.30	1.34 to 25.75	1.19 to 25.50
Index ranges	$-22 \le h \le 14$, $-10 \le k \le 5$, $-21 \le l \le 20$	$-11 \le h \le 11$, $-13 \le k \le 14$, $-19 \le l \le 19$	$-21 \le h \le 21$, $-15 \le k \le 15$, $-22 \le l \le 22$
Reflections collected/unique	21514/6619 [R(int) = 0.0599]	17884/6231 [R(int) = 0.1456]	48524/7598 [R(int) = 0.0434]
Completeness to theta	99.1%	98.6%	99.9%
Absorption correction	Empirical	Empirical	Empirical
Max. and min. transmission	0.7452 and 0.6422	0.7453 and 0.5967	0.7461 and 0.6652
Data/restraints/parameters	6619/1/429	6231/0/339	7598/0/415
Goodness-of-fit on F^2	1.019	0.923	1.040
Final R indices [I > 2sigma(I)]	R1 = 0.0451, wR$_2$ = 0.1014	R1 = 0.0471, wR$_2$ = 0.1059	R1 = 0.0307, wR$_2$ = 0.0745
R indices (all data)	R$_1$ = 0.0602, wR$_2$ = 0.1087	R1 = 0.0785, wR$_2$ = 0.1335	R1 = 0.0395, wR$_2$ = 0.0796
Largest diff. peak and hole	0.19 and −0.22 e.Å^{-3}	0.654 and −0.643 e.Å^{-3}	0.376 and −0.491 e.Å^{-3}
Flack parameter	0.96(4)		

bath. The progress of the reaction was monitored by ^{1}H NMR spectroscopy and NMR yields were calculated by comparing the integration of well resolved ^{1}H NMR signal of cyclic amine with that of internal standard (hexamethyl benzene).

4.6. Crystallographic details

Crystallographic data for compounds **1, 2** and **3** are summarized in Table 5. Suitable crystals of compounds **1, 2** and **3** were removed from the Schlenk flask under an inert atmosphere and immediately coated with silicon oil on a glass slide and mounted on a glass fiber, and then placed quickly in a stream of liquid nitrogen on an X-ray diffractometer. X-ray diffraction data were collected using a Bruker APEX-II CCD diffractometer equipped with an Oxford low-temperature device, operating at T = 100 K. Data collection was monitored with Apex II software, and preprocessing was done with SADABS [38] integrated with Apex II. Using Olex2 [39] the structures were solved with the ShelXT structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation [40]. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.02.005.

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