

Inorganic Chemistry

Calcium Complexes Having Different Amidinate Ligands -
Synthesis and Structural DiversitySrinivas Anga,^[a] Jayeeta Bhattacharjee,^[a] Indrani Banerjee,^[a] Hari Pada Nayek,^[b] and Tarun K. Panda*^[a]Dedicated to Professor Kazushi Mashima on the occasion of his 59th Birthday.

A one-pot reaction of α -diimine ligand 1,4-disubstituted diazabutadienes (DAD) with potassium benzyl and anhydrous calcium iodide in 1:1:1 molar ratio afforded unprecedented 3-phenylprop-2-ene-di-amido calcium compound [κ^2 -(THF)₄Ca{DippNC(=CHPh)CH₂NDipp}] (1) (Dipp = 2,6-diisopropylphenyl) in good yield. The solid-state structure of the compound 1 revealed the formation of dianionic 3-phenylprop-2-ene-di-amido ligand having an exocyclic olefinic bond derived from neutral α -diimine fragment. However, analogous reactions with three different carbodiimides (RN=C=NR; R=Cy, iPr and

^tBu) with alkyl potassium and anhydrous calcium diiodide yielded corresponding homoleptic calcium compounds with amidinate ligand [κ^2 -(THF)₂Ca{RN=C(CH₂Ph)NR₂}] [R=Cy (2), ⁱPr (3) and ^tBu (4)]. A separate reaction of DAD ligand, LiCH₂SiMe₃ and anhydrous ZnCl₂ in diethylether solvent produced tri-coordinated zinc compound [κ^2 -{DippN=C(CH₂SiMe₃)CH₂NDipp}Zn[κ^1 -{DippN=C(CH₂SiMe₃)CH₂N-Dipp}] (5) having amidinate moieties in the zinc coordination sphere in high yield. Molecular structures of compounds 2–5 in their solid states were also established.

Introduction

Organometallic chemistry of alkaline earth (Ae) metal compounds largely rely on their stability in the oxidation state +2. The stable Ae metal compounds can be accomplished by using a wide variety of nitrogen-based ancillary ligands such as tris(pyrazolyl)-borates,^[1] aminotrop(on)iminates,^[2] β -diketiminates,^[3] iminopyrroles,^[4] bis(imino)pyrroles,^[5] iminoanilides,^[6] 1,4-diaza-1,3-butadiene,^[7] etc. Using these ligands as spectator ligands can enable the Ae metal compounds to act as efficient catalysts for ring-opening polymerization of cyclic esters,^[8] polymerization of styrene and dienes,^[9] and, in hydroamination and hydrophosphination reactions of alkenes and alkynes.^[6,10] Many organometallic chemists therefore use various ligands having nitrogen as donor atom to prepare Ae metal compounds.^[11] The amidinate and related guanidinate ligands have already been exploited in various main groups, and in transition metal chemistry.^[12] The electron-releasing capacity of these ligands allows them to coordinate with a wide range of metal ions across the periodic table as well as show versatile coordination modes through their donor atoms.^[13] These ligands are pseudo-allyl li-

gands and commonly act as bidentate (η^2) or bridging monodentate ($\mu:\eta^1:\eta^1$) four-electron donors through metal-nitrogen σ -bonds.^[14] In addition, these classes of ancillary ligands, which can be prepared from easily available reagents, have the possibility of substituent variation in their backbone, thus allowing in the fine tuning of their steric and electronic properties.

Harder and co-workers reported guanidinate compound of calcium and strontium - either by reaction of metal bis-amide [M{N(SiMe₃)₂}₂] to carbodiimides or through addition of potassium amide KN(SiMe₃)₂ to carbodiimides followed by the addition of AeI₂.^[15] In our recent study, we reported that, when a group 4 metal–nitrogen bond was inserted into a carbon–nitrogen double bond of carbodiimides and α -diimines, it afforded respectively, guanidinate and amido-imino ligand-supported group 4 metal compounds.^[16] We extended the same strategy to magnesium chemistry in order to obtain amidinate compounds by the insertion of a metal-carbon bond into a carbon–nitrogen double bond of carbodiimides and α -diimine ligand.^[17] To further explore the chemistry of amidinate ligands, we extended this method into calcium analogues in a straight forward synthesis and in a one-pot reaction while not isolating the metal alkyl compounds.

Here, we describe the detailed synthesis and structural investigations of bidentate 3-phenylprop-2-ene-di-amido calcium compound [κ^2 -(THF)₄Ca{DippNC(=CHPh)CH₂NDipp}] (1) along with homoleptic calcium compounds [κ^2 -(THF)₂Ca{RN=C(CH₂Ph)NR₂}] [R=Cy (2), ⁱPr (3) and ^tBu (4)] attached to amidinate ligands achieved from different carbodiimides. We also report the synthesis and solid-state structure of a three-coordinated zinc compound [κ^2 -{DippN=C-(CH₂SiMe₃)CH₂NDipp}Zn[κ^1 -

[a] S. Anga, J. Bhattacharjee, I. Banerjee, Dr. T. K. Panda
Department of Chemistry, Indian Institute of Technology Hyderabad
Kandi - 502 285, Sangareddy, Telangana, India.
E-mail: tpanda@iith.ac.in

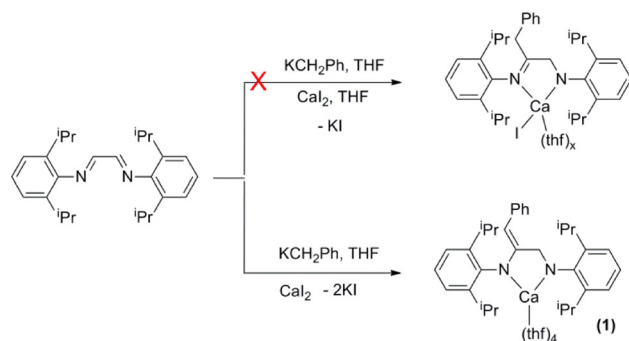
[b] Dr. H. P. Nayek
Department of Applied Chemistry,
Indian School of Mines, Dhanbad, 826004,
Jharkhand, India.

Supporting information for this article is available on the WWW under
<http://dx.doi.org/10.1002/slct.201600299>

{DippN=C(CH₂SiMe₃)CH₂NDipp}] (5) having amidinate moieties in the metal coordination sphere.

Results and Discussion

We began our study with the preparation of a mono-anionic calcium compound [(DippN=C(CH₂Ph)CH₂NDipp)Ca(thf)_x], as shown in Scheme 1, analogous to the corresponding magne-



Scheme 1. Preparation of DAD calcium compound 1.

sium compound [(THF)₂Mg(CH₂Ph){2-(Ph₃CN=CH)C₄H₃N}] that was recently reported by us.^[4b] To isolate our target calcium compound, we treated DAD ligand with potassium benzyl, and followed it by the addition of anhydrous calcium diiodide at room temperature, both being in equimolar ratio in THF solvent.

To our surprise, we isolated, in good yield, an unprecedented 3-phenylprop-2-ene-di-amido calcium compound having chemical composition of [κ^2 -(THF)₄Ca{DippNC(=CHPh)CH₂NDipp}] (1). Attempts of controlled reactions using a number of methods such as of DAD ligand with calcium mono-benzyl compound (obtained from CaI₂ and KCH₂Ph in 1:1 ratio) to isolate the heteroleptic calcium mono-iodo compound were not successful. We could isolate the stable compound 1 alone in each case. The calcium compound 1 was re-crystallized from concentrated THF solution at -35 °C. The molecular structure of the air and moisture-sensitive compound 1 in the solid-state was determined by single crystal X-ray diffraction analysis. In the ¹H NMR spectra measured in C₆D₆ for the compound 1, the olefinic C–H protons appeared as a singlet at δ 6.08 ppm while the corresponding DAD ligand backbone methylene protons (CH₂) exhibited resonance signals at δ 2.11 ppm. The resonances of aromatic protons were within the expected region.^[7b] In ¹³C{¹H} NMR spectra of compound 1, the resonance signal at δ 163.5 indicated the presence of *sp*² carbon in the ligand moiety.

The calcium compound 1 was crystallized in the orthorhombic space group *Pbca* with eight individual molecules of 1 and one THF molecule as the solvent in the unit cell. Details of the structural and refinement parameters are shown in Table 1 in supporting information while the solid-state structure of compound 1 is given in Figure 1.

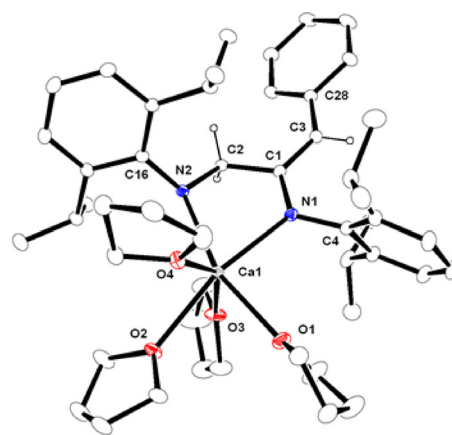
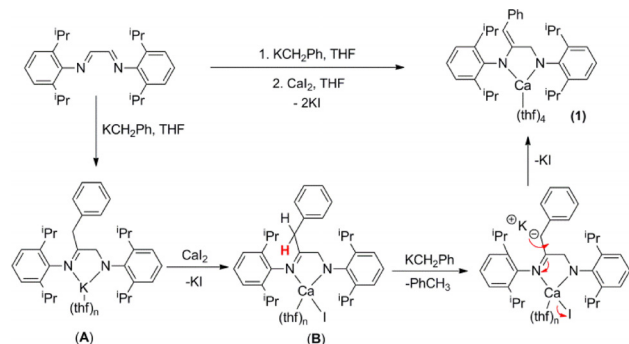


Figure 1. ORTEP drawing of solid-state structure of compound 1 and ellipsoids drawn to encompass 30% probability. Hydrogen atoms omitted for clarity (except H2a, H2b and H3a). Selected bond lengths [Å] and bond angles [°]: Ca1–N1 2.382(2), Ca1–N2 2.328(2), Ca1–C(1) 3.238(3), N1–C1 1.365(3), N1–C4 1.425(4), N2–C16 1.394(3), N2–C2 1.468(3), C1–C2 1.525(4), C1–C3 1.374(4), Ca1–O1 2.463(2), Ca1–O2 2.498(2), Ca1–O3 2.445(2), Ca1–O4 2.430(2), N2–Ca1–N1 72.89(8), C1–N1–Ca1 116.92(17), C4–N1–Ca1 125.03(18), C16–N2–C1 113.5(2), C16–N2–Ca1 132.07(17), C2–N2–Ca1 110.10(16), N1–C1–C3 124.5(3), N1–C1–C2 114.0(2), C3–C1–C2 121.52, C3–C1–Ca1 165.5(2), C2–C1–Ca1 73.03(14), N2–C2–C1 117.4(2).

Compound 1 is monomeric and the coordination polyhedron is formed by the chelation of two amido nitrogen atoms from di-anionic [DippNC(=CHPh)CH₂NDipp]²⁻ ligand moiety which is formed by the mono-benzylation of the DAD ligand followed by abstraction of a benzylic proton in the reaction medium. The Ca–N bond distances [Ca1–N1 2.382(1) and Ca1–N2 2.328(2) Å] which are consistent with Ca–N distances (2.335–2.361 Å) reported in literature,^[7a] differ slightly due to the asymmetric attachment of calcium ion to the bis-amido ligand. The single bond characters of C2–N2 and C1–C2 bonds are confirmed by the distances of C2–N2 [1.468(3) Å] and C1–C2 [1.525(4) Å]. In contrast, the distances C1–N1 [1.365(3) Å] and C1–C3 [1.374(4) Å] indicate an electron delocalization over N1–C1–N3 skeleton thus making both C1–N1 and C1–C3 distances partially double bond characters. The central calcium ion is six-fold coordinated due to the coordination of two amido nitrogens from one amidinato ligand and four oxygen atoms from four THF molecules. The geometry around the metal ion can best be described as distorted octahedral.^[7a] It is noted that the amidinato ligand backbone N1–C1–C2–N2 is not planar; rather, it is folded with a dihedral angle of 21.96° between the planes having N1, C2, C1 and N2, C2, C1 atoms.

The possible mechanism for the formation of compound 1 is shown in Scheme 2. In the first step, addition of KCH₂Ph to the N=C bond of the DAD ligand lead to the formation of potassium amidinate compound (A). Similar migration of alkyl group with DAD ligands are already known in literature while using metal alkyls of group 2,^[16] 3,^[18] 4^[19] and 13^[20]. It was observed that the potassium amidinato compound A further reacted with calcium diiodide in a salt metathesis reaction to yield a heteroleptic calcium iodo compound (B) in the second step. However, deprotonation of the highly acidic benzylic pro-

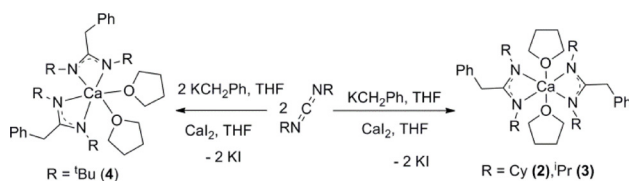


Scheme 2. Plausible mechanism to the formation of compound 1.

ton could also occur due to the second molecule of potassium benzyl, thus resulting in the generation of a benzylic anion in the amidinato ligand backbone. The free negative charge subsequently underwent delocalization from the carbon atom to the more electronegative nitrogen atom to be bonded with calcium ion to lead compound 1 through the removal of insoluble potassium iodide. Subsequently, the amidinato ligand was converted to bis-amido ligand in compound 1. Several attempts to isolate the intermediate compound B did not meet with success due to the extreme reactivity of compound B.

Reaction with Carbodiimides:

We have recently reported on the amidinato ligand-supported series of magnesium compounds obtained from the insertion of a magnesium–carbon bond into a carbon–nitrogen double bond present in carbodiimides.^[16] We have extended our study into the calcium chemistry by preparing a series of homoleptic calcium amidinato compounds using salt metathesis reaction. One-pot reaction of three different carbodiimides (RN=C=NR, R = Cy, *i*Pr, *t*Bu) with potassium benzyl followed by the addition of anhydrous calcium diiodide in 2:2:1 molar ratio in THF at room temperature (Scheme 3) afforded the desired compounds



Scheme 3. Preparation of calcium amidinato compounds 2–4.

2–4. In all cases, carbodiimides were first made to react with potassium benzyls and undergo insertion reactions analogous to group 2^[16], 3^[13], 4^[15,19] and 13^[21] metal alkyls which resulted in the yield of potassium amidinate compound which was thereafter followed by salt metathesis reaction with anhydrous calcium diiodides. Calcium compounds [Ca{CyN=C(CH₂Ph)NCy}₂(thf)₂] (2), [Ca{*i*PrN=C(CH₂Ph)-N^{*i*}Pr}₂(thf)₂] (3), and [Ca{*t*BuN=C(CH₂Ph)-N^{*t*}Bu}₂(thf)₂] (4) were isolated in good yield and re-

crystallized from a mixture of THF / pentane. The new calcium compounds 2–4 were characterized using standard analytical and spectroscopic techniques. The solid-state structures of all three calcium compounds were established by single-crystal X-ray diffraction analysis.

The ¹H NMR spectra measured in C₆D₆ of compounds 2–4 were found to be similar and exhibited only one set of signals in the solution state, thus indicating the dynamic nature of the compounds. Each of compounds 2–4 displayed a sharp singlet at δ 3.79 (2), 3.76 (3) and 4.17 ppm (4) respectively for the resonance of two benzylic protons attached to the carbon atom of amidinato ligands. These observations are in agreement with the magnesium compounds having amidinate ligand in the backbone, as recently reported by us and others.¹⁷ The multiplet resonance signals for cyclohexyl moieties attached to both the nitrogen atoms were in the expected region for compound 2 and did not show much difference with that of free carbodiimides. For compound 3, multiplets centered at δ 3.65 ppm could be assigned to both the isopropyl-CH protons present in the isopropyl groups. In addition, two doublets were observed at 1.42 ppm and 1.15 ppm respectively for chemically non-equivalent isopropyl methyl protons -CHMe₂ present in compound 3. In compound 4, a sharp singlet at 1.37 ppm could be assigned to the 18 methyl protons present in tert-butyl group of the amidinate ligand. In each spectrum, two triplets [δ 3.62 and 1.43 ppm (2), 3.63 and 1.43 ppm (3), and 3.63 and 1.39 ppm (4)] indicated the presence of coordinated THF molecules in each compound. In ¹³C{¹H} NMR spectra of compounds 2–4, the signals at δ 173.3 (2), 173.8 (3) and 172.3 ppm (4) indicated the presence of *sp*² carbon (-N-C(CH₂Ph)=N) in the solution.

Even there is ongoing interest in the amido and amidinato alkaline earth organometallics, compounds 2–4 represent a series of homoleptic calcium compounds containing amidinato ligands derived from three different carbodiimides. Their molecular structures in the solid state were confirmed by X-ray diffraction analysis. Both the compounds 2 and 3 crystallized in the centrosymmetric triclinic space group *P*-1 having two and one molecule(s) respectively in their unit cells. In contrast, compound 4 crystallized in the trigonal space group *P* 3₂1 having three individual molecules in the unit cell. The difference in space group in compound 4 can be due to the presence of bulky *tert*-butyl groups present in the amidinate backbone. The details of structural and refinement parameters of compounds 2–4 are given in Table 1 in supporting information. The molecular structures of these compounds are presented in Figures 2–4 respectively. In each case, molecular structure of the compound confirmed the attachment of two amidinate ligands to the calcium ion, thus making it homoleptic and monomeric in nature. The calcium ion in each compound is six-fold coordinated, and is bonded with four nitrogen atoms from two amidinate moieties and two oxygen atoms from two coordinated THF molecules. Thus the geometry of the calcium ions in compounds 2–4 can best be described as distorted octahedral. Both the THF molecules in compounds 2 and 3 are *trans* to each other - a *cis*- arrangement of two THF molecules can be

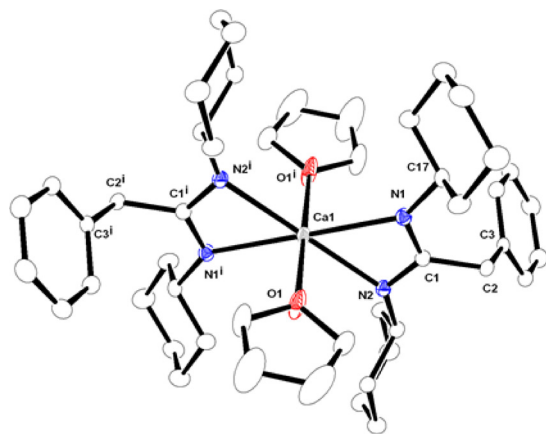


Figure 2. ORTEP drawing of solid-state structure of compound **2** and ellipsoids - drawn to encompass 30% probability. Hydrogen atoms omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Ca1-N1 2.420(3), Ca1-N1ⁱ 2.420(3), Ca1-N2 2.437(3), Ca1-N2ⁱ 2.437(3), Ca1-O1 2.411(3), Ca1-O1ⁱ 2.411(3), Ca1-C1 2.856(3), Ca1-C1ⁱ 2.856(3), N1-C1 1.335(4), N1ⁱ-C1ⁱ 1.335(4), N2-C1 1.327(4), N2ⁱ-C1ⁱ 1.327(4), C1-C2 1.538(4), C1ⁱ-C2ⁱ 1.538(4), N1-Ca1-N2 55.40(9), N1ⁱ-Ca1-N2ⁱ 55.40(9), N2-C1-N1 115.9(3), N2ⁱ-C1-N1ⁱ 115.9(3), O1ⁱ-Ca1-O1 180.000(1), O1ⁱ-Ca1-N1 91.68(10), O1-Ca1-N1 88.32(10), O1ⁱ-Ca1-N1ⁱ 88.32(10), O1-Ca1-N1ⁱ 91.68(10), N1-Ca1-N1ⁱ 180.0, O1ⁱ-Ca1-N2 91.50(9), O1-Ca1-N2 88.50(9), N1ⁱ-Ca1-N2 124.60(9), O1ⁱ-Ca1-N2ⁱ 88.50(9), O1-Ca1-N2ⁱ 91.50(9), N1-Ca1-N2ⁱ 124.60(9), N2-Ca1-N2ⁱ 180.000(1), N1-Ca1-C1ⁱ 152.20(9), N1ⁱ-Ca1-C1ⁱ 27.80(8), N2-Ca1-C1ⁱ 152.39(8), N1ⁱ-Ca1-C1 152.20(9), N2-Ca1-C1 27.61(8), N2ⁱ-Ca1-C1 152.39(8), C1ⁱ-Ca1-C1 180.0, N2-C1-C2 122.3(3), N1-C1-C2 121.8(3).

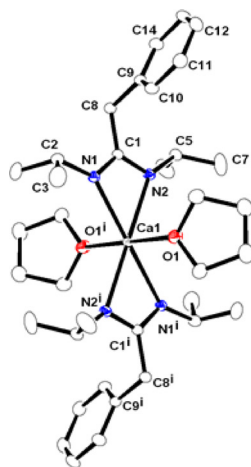


Figure 3. ORTEP drawing of solid-state structure of compound **3** and ellipsoids drawn to encompass 30% probability. Hydrogen atoms omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Ca1-N1 2.4247(14), Ca1-N1ⁱ 2.4247(14), Ca1-N2 2.4285(14), Ca1-N2ⁱ 2.4285(13), Ca1-O1 2.4282(12), Ca1-O1ⁱ 2.4282(12), Ca1-C1 2.8455(16), Ca1-C1ⁱ 2.8455(16), N1-C1 1.335(2), N2-C1 1.334(2), C1-C8 1.534(2), N2-C1-N1 116.18(14), N1-Ca1-N2 55.65(5), N1ⁱ-Ca1-N2ⁱ 55.65(5), O1-Ca1-O1ⁱ 180.00(4), C8-C1-Ca1 174.87(11), N1-Ca1-N1ⁱ 180.00(6), N1-Ca1-N2ⁱ 124.35(5), N1ⁱ-Ca1-N2 124.35(5), N2ⁱ-Ca1-N2 180.00(10), N1ⁱ-Ca1-C1 152.09(4), N2ⁱ-Ca1-C1 152.12(4), N1-Ca1-C1 152.09(4), N2-Ca1-C1ⁱ 152.12(4), C1-Ca1-C1ⁱ 180.00(6), C1-N1-Ca1 93.86(10), C1-N2-Ca1 93.72(9), N2-C1-C8 121.46(14), N1-C1-C8 122.35(14).

observed in compound **3** due to the presence of sterically bulky *tert*-butyl groups in the amidinate moieties. The similar Ca–

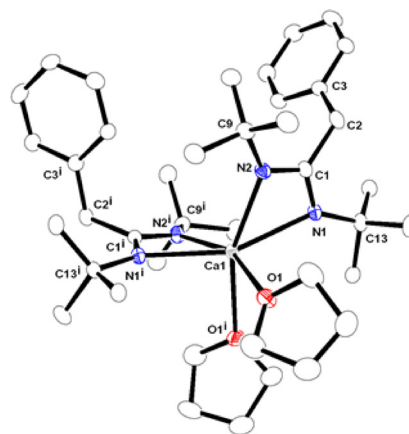


Figure 4. ORTEP drawing of solid-state structure of compound **4** and ellipsoids - drawn to encompass 30% probability. Hydrogen atoms omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Ca1-N1 2.454(3), Ca1-N1ⁱ 2.454(3), Ca1-N2 2.437(3), Ca1-N2ⁱ 2.437(3), Ca1-O1 2.444(3), Ca1-O1ⁱ 2.444(3), Ca1-C1 2.8773, Ca1-C1ⁱ 2.877(3), N1-C1 1.337(5), N1ⁱ-C1ⁱ 1.337(5), N2-C1 1.334(5), N2ⁱ-C1ⁱ 1.334(5), C1-C2 1.550(5), C1ⁱ-C2ⁱ 1.550(5), N2-C1-N1 114.8(3), N2-Ca1-N1 54.79(11), N2ⁱ-Ca1-N1ⁱ 54.79(11), N2ⁱ-Ca1-N2 111.54(16), N2ⁱ-Ca1-O1ⁱ 86.81(10), N2-Ca1-O1ⁱ 57.62(10), N2ⁱ-Ca1-O1 157.62(10), N2-Ca1-O1 86.81(10), O1ⁱ-Ca1-O1 78.85(14), N2-Ca1-N1ⁱ 110.30(11), O1ⁱ-Ca1-N1ⁱ 90.55(10), O1-Ca1-N1ⁱ 107.80(10), N2ⁱ-Ca1-N1 110.30(11), O1ⁱ-Ca1-N1 107.80(10), O1-Ca1-N1 90.55(10), N1ⁱ-Ca1-N1 156.44(16), N2-Ca1-C1ⁱ 110.56(11), O1-Ca1-C1ⁱ 91.66(9), O1-Ca1-C1ⁱ 134.97(10), N1-Ca1-C1ⁱ 133.77(12), N2ⁱ-Ca1-C1 110.56(11), O1ⁱ-Ca1-C1 134.97(10), O1-Ca1-C1 91.66(9), N1ⁱ-Ca1-C1 133.77(12), C1ⁱ-Ca1-C1 123.12(15), C1-N1-Ca1 94.1(2), C1-N2-Ca1 94.9(2), N2-C1-C2 121.9(3), N1-C1-C2 123.1(3), C2-C1-Ca1 166.8(2).

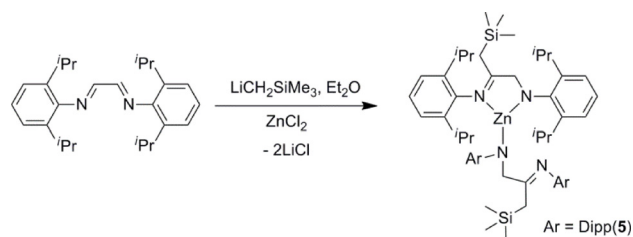
N distances in compounds **2–4**, ranging from 2.420–2.454 Å, indicate the delocalization of negative charge over N–C–N backbone of the respective amidinate ligands. They are also in agreement with Ca–N distances as previously reported by us and others.^[7a,14] This observation is further confirmed by similar N–C bond distances [N1–C1 1.336 (4), N2–C1 1.327(4) for **2**, N1–C1 1.335(4), N2–C1 1.334(4) for **3**, and N1–C1 1.337(4), N2–C1 1.324(4) Å for **4**] of the amidinate ligand. The Ca1–C1 distance in each compound [2.856(3) (**2**), 2.845(2) (**3**) and 2.877(3) Å (**4**)] is significantly longer for one to be able to consider any interaction between *sp*² carbon C1 of amidinate ligand and Ca1 atom.

Two four-membered calcium metallacycles Ca1–N1–C1–N2 and Ca1–N1ⁱ–C1ⁱ–N2ⁱ were formed due to the η²-coordination mode of two amidinato ligands with the calcium ion in each compound (**2–4**). The Ca–O distances [2.411(3) (**2**), 2.428(1) (**3**) and 2.445(3) Å (**4**)] are similar and fall within the reported values.^{7a} The plane containing N1, C1 and N2 is coplanar with the plane having N1ⁱ, C1ⁱ and N2ⁱ atom in compounds **2** and **3**; however an 88.45° arrangement of the same planes are observed in compound **4**.

Zinc compound:

Recently, Schultz et al. explored the reactivity of zinc alkyls with various carbodiimides which led to the formation of zinc amidinate compounds.^[22] We were therefore interested to make an structural analogy between calcium and zinc compounds hav-

ing amidinate ligand formed from α -diimine 1,4-disubstituted diazabutadienes (DAD). The treatment of neutral DAD ligand with lithium alkyl ($\text{LiCH}_2\text{SiMe}_3$) in diethylether at room temperature, followed by the addition of anhydrous ZnCl_2 , afforded a tri-coordinated zinc compound [κ^2 -{DippN=C(CH₂SiMe₃)CH₂NDipp}Zn] κ^1 -{DippN=C(CH₂SiMe₃)CH₂N-Dipp}] (5) having amidinate and amido moieties in the metal coordination sphere (Scheme 4). The reaction of DAD with $\text{LiCH}_2\text{SiMe}_3$ underwent



Scheme 4. Synthesis of zinc compound 5.

insertion reaction to yield an intermediate lithium amidinate compound analogous to potassium amidinates (*vide supra*) which further reacted with zinc dichloride to give compound 5.

The zinc compound 5 was characterized by spectroscopic and analytical methods, and the solid-state structure of the compound 5 was confirmed by single crystal x-ray diffraction analysis. In the ¹H NMR spectra of compound 5 measured in D₆-benzene, the singlet signal at δ 4.61 ppm can be assigned to the resonance of two methylene (CH₂) protons present in the [DippN=C(CH₂SiMe₃)CH₂NDipp]⁻ ligand backbone. The resonance of the methylene protons of CH₂SiMe₃ was observed at δ 1.72 ppm which was in the high-field region as compared to that of benzylic protons which were present in compounds 1–4. Two distinct septet signals centered at δ 3.85 ppm and 3.14 ppm respectively, and three doublet resonances at δ 1.47, 1.38 and 1.09 ppm respectively, were observed due to the -CH proton and isopropyl methyl protons present in the amidinate ligand moiety [DippN=C(CH₂SiMe₃)CH₂NDipp]⁻. The sharp singlet at δ 0.12 ppm was observed as a result of the resonance of the protons present in the -SiMe₃ group. In the ¹³C{¹H} spectra, resonance at δ 173.5 can be assigned to imine carbon atom [-N=C(CH₂SiMe₃)] present in the [DippN=C(CH₂SiMe₃)CH₂NDipp]⁻ moiety.

The molecular structure of zinc compound 5 in its solid state was established by single-crystal X-ray diffraction analysis. It confirmed the attachment of two amidinate ligands to the zinc ion. The crystals of compound 5 obtained from toluene, and having two independent molecules in the unit cell, were found to crystallize in the triclinic space group *P*-1. The details of structural and refinement parameters of compound 5 are given in Table 1 (see supporting information). The molecular structure of compound 5 is shown in Figure 5. Homoleptic zinc compound 5 is monomeric, and the coordination polyhedron is formed by the chelation of one amido and one imine nitrogen atom of a single monoionic amidinate ligand with only one amido nitrogen atom from the second amidinate ligand moi-

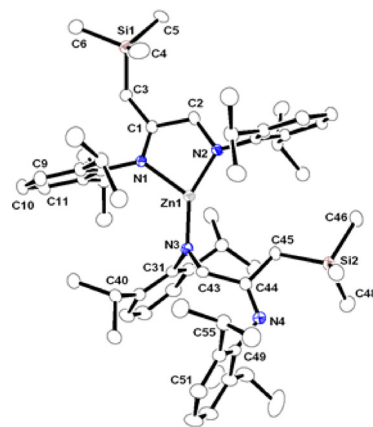


Figure 5. ORTEP drawing of solid-state structure of compound 5 and ellipsoids drawn to encompass 30% probability. Hydrogen atoms omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Zn1–N1 2.092(3), Zn1–N2 1.871(3), Zn1–N3 1.852(3), N1–C1 1.292(4), C1–C2 1.508(5), C1–C3 1.497(5), C2–N2 1.449(4), N3–C43 1.466(4), C43–C44 1.517(5), C44–N4 1.277(4), N1–Zn1–N2 84.68(12), N1–Zn1–N3 124.04(12), N2–Zn1–N3 151.14(13).

ety. The presence of sterically bulky 2,6-diisopropylphenyl groups of the amidinate ligand prevent the imine nitrogen from the second ligand from coordinating with the calcium ion, and as a result, the corresponding imine nitrogen is seen dangling away from the metal center. Thus, the zinc ion is three-fold coordinated, and the geometry around the zinc ion can be best described as distorted trigonal planar. The zinc atom Zn1 is perfectly coplanar with the plane containing N1, N2 and N3 atoms. The trigonal planar geometry in the case of zinc (II) ion is very rare and observed in only a few cases in literature.^[23] There are two types of Zn–N [Zn1–N1 2.092(3); Zn1–N2 1.871(3) and Zn1–N3 1.852(3)] bond distance are present which indicate Zn–N2 and Zn1–N3 bonds as amido, and Zn1–N1 bond as imino bond in the monoionic ligand. The C–N and C–C bond distances of C1–N1 1.292(4), C1–C2 1.508(5), C2–N2 1.449(4), and C1–C3 1.497(5) Å were observed to be within the monoionic amidinate moiety. However, the angles N1–Zn1–N2 (84.68°), N1–Zn1–N3 (124.04°) and N2–Zn1–N3 (151.14°) were found to have deviated by 120° due to the formation of a five membered zinc metallacycle Zn1–N1–C1–C2–N2.

Conclusions

In summary, we have demonstrated an unusual 3-phenylprop-2-ene-di-amido calcium compound that was derived from the amidinate ligand. In addition, we have described the synthetic and structural details of a series of calcium amidinato compounds. In each case, the amidinato moieties were obtained from benzyl migration from potassium benzyl to the back bone imine carbon atom of 1,4-diaza-1,3-butadiene and carbodiimides. In compound 1, 1,4-diaza-1,3-butadiene was converted to a di-anionic 3-phenylprop-2-ene-di-amido ligand [DippNC(=CHPh)CH₂NDipp]²⁻ with unusual C–H bond abstraction, and coordinated to the calcium ion via two amido nitrogen atoms. However, in compounds 2–4, the pro-ligand carbodiimides

were converted to a mono-anionic amidinato moiety which bonded to the calcium ion in an asymmetric fashion through amido and imino nitrogen atoms acting as a bidentate ligand. The calcium ion was hexa-coordinated in each case and adopted distorted octahedral geometry. In addition we have presented the very rare tri-coordinated zinc compound, coordinated via two amido and one imino nitrogen atoms from two amidinate ligands.

Supporting information

Experimental procedures for the preparation of compound and characterization details are given in the electronic supporting information.

Acknowledgements

This work was supported by 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, India and J.B. thanks UGC India for their PhD fellowship. Generous supports from Prof. Kazushi Mashima and Dr. Hayato Tsurugi of Osaka University, Japan are gratefully acknowledged.

Keywords: Calcium · amidinate · 1,4-diaza-butadiene · zinc · carbodiimides

- [1] a) M. H. Chisholm, J. Gallucci, K. Phomphrai, *Chem. Commun.* **2003**, 48. b) M. H. Chisholm, J. Gallucci, K. Phomphrai, *Inorg. Chem.* **2004**, 43, 6717. c) M. H. Chisholm, *Inorg. Chim. Acta.* **2009**, 362, 4284. d) M. J. Saly, M. J. Heeg, C. H. Winter, *Inorg. Chem.* **2009**, 48, 5303.
- [2] a) S. Datta, P.W. Roesky, S. Blechert, *Organometallics* **2007**, 26, 4392. b) S. Datta, M. T. Gamer, P. W. Roesky, *Organometallics* **2008**, 27, 1207.
- [3] a) C. F. Caro, P. B. Hitchcock, M. F. Lappert, *Chem. Commun.* **1999**, 1433. b) S. Harder, *Organometallics* **2002**, 21, 3782. c) M. S. Hill, P. B. Hitchcock, *Chem. Commun.* **2003**, 1758. d) M. R. Crimmin, I. J. Casely, M. S. Hill, *J. Am. Chem. Soc.* **2005**, 127, 2042. e) S. Harder, J. Brettar, *Angew. Chem., Int. Ed.* **2006**, 45, 3474. f) M. R. Crimmin, M. Arrowsmith, A. G. M. Barrett, I. J. Casely, M. S. Hill, P. A. Procopiou, *J. Am. Chem. Soc.* **2009**, 131, 9670. g) S. P. Sarish, A. Jana, P. W. Roesky, T. Schulz, M. John, S. Datta, *Inorg. Chem.* **2010**, 49, 3816. h) M. Arrowsmith, M. R. Crimmin, A. G. M. Barrett, M. S. Hill, G. Kociok-Köhn, P. A. Procopiou, *Organometallics* **2011**, 30, 1493. i) S. P. Sarish, S. Nembenna, S. Nagendran, H. W. Roesky, *Acc. Chem. Res.* **2011**, 44, 157.
- [4] a) T. K. Panda, K. Yamamoto, K. Yamamoto, H. Kaneko, Y. Yang, H. Tsurugi and K. Mashima, *Organometallics* **2012**, 31, 2268.; b) R. K. Kottalanka, A. Harinath, S. Rej and T. K. Panda, *Dalton Trans.* **2015**, 44, 19865.
- [5] a) J. Jenter, R. Koeppe, P. W. Roesky, *Organometallics* **2011**, 30, 1404. b) H. Hao, S. Bhandari, Y. Ding, H. W. Roesky, J. Magull, H. G. Schmidt, M. Noltemeyer and C. Cui, *Eur. J. Inorg. Chem.* **2002**, 1060.
- [6] a) B. Liu, T. Roisnel, J.-F. Carpentier, Y. Sarazin, *Angew. Chem. Int. Ed.* **2012**, 51, 4943; *Angew. Chem.* **2012**, 124, 5027; b) B. Liu, T. Roisnel, J.-F. Carpentier, Y. Sarazin, *Chem. Eur. J.* **2013**, 19, 13445.
- [7] a) T. K. Panda, H. Kaneko, O. Michel, H. Tsurugi, K. Pal, K. W. Toernroos, R. Anwander and K. Mashima, *Organometallics* **2012**, 31, 3178. b) V. Lorenz, C. G. Hrib, Dirk Grote, L. Hilfert, M. Krasnopolski, and F. T. Edelmann, *Organometallics* **2013**, 32, 4636.
- [8] a) O. Dechy-Cabaret, B. Martin-Vaca and D. Bourissou, *Chem. Rev.* **2004**, 104, 6147; b) B. J. O'Keefe, M. A. Hillmyer and W. B. Tolman, *J. Chem. Soc., Dalton Trans.* **2001**, 2215; c) C. A. Wheaton, P. G. Hayes and B. Ireland, *Dalton Trans.* **2009**, 4832; d) C. M. Thomas, *Chem. Soc. Rev.* **2010**, 39, 165.
- e) S. M. Li, I. Rashkov, J. L. Espartero, N. Manolova and M. Vert, *Macromolecules* **1996**, 29, 57; f) P. Dobrzyński, J. Kasperczyk and M. Bero, *Macromolecules* **1999**, 32, 4735; g) Z. Zhong, P. J. Dijkstra, C. Birg, M. West-erhausen and J. Feijen, *Macromolecules* **2001**, 34, 3863; h) M. Westerhausen, S. Schneiderbauer, A. N. Kneifel, Y. Sörtl, P. Mayer, H. Nöth, Z. Zhong, P. J. Dijkstra and J. Feijen, *Eur. J. Inorg. Chem.* **2003**, 3432; i) M. H. Chisholm, J. Gallucci and K. Phomphrai, *Chem. Commun.* **2003**, 48; j) M. H. Chisholm, J. C. Gallucci and K. Phomphrai, *Inorg. Chem.* **2004**, 43, 6717; k) Y. Sarazin, R. H. Howard, D. L. Hughes, S. M. Humphrey and M. Bochmann, *Dalton Trans.* **2006**, 340; l) D. J. Darensbourg, W. Choi, P. Ganguly and C. P. Richers, *Macromolecules* **2006**, 39, 4374; m) M. G. Davidson, C. T. O'Hara, M. D. Jones, C. G. Keir, M. F. Mahon and G. Kociok-Köhn, *Inorg. Chem.* **2007**, 46, 7686; n) D. J. Darensbourg, W. Choi and C. P. Richers, *Macromolecules* **2007**, 40, 3521; o) D. J. Darensbourg, W. Choi, O. Karroonnirun and N. Bhuvanesh, *Macromolecules* **2008**, 41, 3493; p) V. Poirier, T. Roisnel, J.-F. Carpentier and Y. Sarazin, *Dalton Trans.* **2009**, 9820; q) X. Xu, Y. Chen, G. Zou, Z. Ma and G. Li, *J. Organomet. Chem.* **2010**, 695, 1155; r) Y. Sarazin, D. Rosca, V. Poirier, T. Roisnel, A. Silvestru, L. Maron and J.-F. Carpentier, *Organometallics* **2010**, 29, 6569; s) Y. Sarazin, B. Liu, T. Roisnel, L. Maron and J.-F. Carpentier, *J. Am. Chem. Soc.* **2011**, 133, 9069.
- [9] a) S. Harder, F. Feil and K. Knoll, *Angew. Chem., Int. Ed.* **2001**, 40, 4261; b) S. Harder and F. Feil, *Organometallics* **2002**, 21, 2268; c) P. Jochmann, T. S. Dols, T. P. Spaniol, L. Perrin, L. Maron and J. Okuda, *Angew. Chem., Int. Ed.* **2009**, 48, 5715.
- [10] a) A. G. M. Barrett, M. R. Crimmin, M. S. Hill and P. A. Procopiou, *Proc. R. Soc. London, Ser. A*, **2010**, 466, 927; b) S. Harder, *Chem. Rev.* **2010**, 110, 3852. c) S. Harder, *Topics in Organometallic Chemistry*, Springer: Berlin, **2013**; Vol. 45. d) H. Hu, C. Cui, *Organometallics* **2012**, 31, 1208.
- [11] a) R. K. Kottalanka, K. Naktode, S. Anga, H. P. Nayek and T. K. Panda, *Dalton Trans.* **2013**, 42, 4947; b) R. K. Kottalanka, S. Anga, K. Naktode, P. Laskar, H. P. Nayek and T. K. Panda, *Organometallics* **2013**, 32, 4473; c) R. K. Kottalanka, A. Harinath, J. Bhattacharjee, H. V. Babu and T. K. Panda, *Dalton Trans.* **2014**, 8757; d) J. Bhattacharjee, R. K. Kottalanka, A. Harinath and T. K. Panda, *J. Chem. Sci.* **2014**, 126, 1463; (f) R. K. Kottalanka, A. Harinath and T. K. Panda, *RSC Adv.* **2015**, 5, 37755.
- [12] a) F. T. Edelmann, *Advances in Organometallic Chemistry*, **2008**, 57, 183 ;b) J. Barker, M. Kilner, *Coord. Chem. Rev.* **1994**, 133, 219; c) F. T. Edelmann, *Coord. Chem. Rev.* **1994**, 137, 403. d) P. J. Bailey, S. Pace, *Coord. Chem. Rev.* **2001**, 214, 91. e) P. J. Bailey, L. A. Mitchell, S. Parsons, *J. Chem. Soc., Dalton Trans.* **1996**, 2839. f) P. J. Bailey, S. F. Bone, L. A. Mitchell, S. Parsons, S. J. Taylor, L. J. Yellowlees, *Inorg. Chem.* **1997**, 36, 867. g) J. Bailey, R. O. Gould, C. N. Harmer, S. Pace, A. Steiner, D. S. Wright, *Chem. Commun.* **1997**, 1161. h) S. J. Aeilts, M. P. Coles, D. C. Swenson, R. F. Jordan, V. G. Young, *Organometallics* **1998**, 17, 3265. i) A. P. Kenney, G. P. A. Yap, D. S. Richeson, S. T. Barry, *Inorg. Chem.* **2005**, 44, 2926. j) G. R. Giesbrecht, A. Shafir, J. Arnold, *J. Chem. Soc. Dalton Trans.* **1999**, 3601.
- [13] See the following and references cited therein: S. T. Barry, *Coord. Chem. Rev.* **2013**, 257, 3192.
- [14] See the following and references cited therein: F. T. Edelmann, *Chem. Soc. Rev.* **2009**, 38, 2253.
- [15] F. Feil and S. Harder, *Eur. J. Inorg. Chem.* **2005**, 4438.
- [16] a) T. K. Panda, H. Tsurugi, K. Pal, H. Kaneko and K. Mashima, *Organometallics* **2010**, 29, 34; b) K. Naktode, S. Das, J. Bhattacharjee, H. P. Nayek and T. K. Panda, *Inorg. Chem.* **2010**, 49, 1142.
- [17] S. Anga, J. Bhattacharjee, A. Harinath, and T. K. Panda, *Dalton Trans.* **2015**, 44, 955.
- [18] a) H. Kaneko, H. Tsurugi, T. K. Panda, and K. Mashima, *Organometallics* **2010**, 29, 3463; b) G. Du, Y. Wei, L. Ai, Y. Chen, Q. Xu, X. Liu, S. Zhang, Z. Hou, and X. Li, *Organometallics* **2011**, 30, 160.
- [19] a) H. Tsurugi, R. Ohnishi, H. Kaneko, T. K. Panda, K. Mashima, *Organometallics* **2009**, 28, 680. b) P. De Waele, B. A. Jazdzewski, J. Klosin, R. E. Murray, C. N. Theriault, and P. C. Vosejka, *Organometallics* **2007**, 26, 3896.
- [20] a) A. M. Felix, D. A. Dickie, I. S. Horne, G. Page, and R. A. Kemp, *Inorg. Chem.* **2012**, 51, 4650; b) D. Pappalardo, C. Tedesco, and C. Pellicchia, *Eur. J. Inorg. Chem.* **2002**, 621.
- [21] a) A. P. Kenney, G. P. A. Yap, D. S. Richeson, S. T. Barry, *Inorg. Chem.* **2005**, 44, 2926; b) A. L. Brazeau, Z. Wang, C. N. Rowley and S. T. Barry, *Inorg. Chem.* **2006**, 45, 2276; c) A. L. Brazeau, G. A. DiLabio, K. A. Kreisel, W. H.

- Monillas, G.P.A. Yap and S.T. Barry, *Dalton Trans.* **2007**, 30, 3297; d) L.C. Ziffle, A.P. Kenney, S.T. Barry, J. Müller, *Polyhedron* **2008**, 27, 1832.
- [22] a) S. Schmidt, S. Schulz, D. Bläser, R. Boese and M. Bolte, *Organometallics* **2010**, 29, 6097; b) T. Eisenmann, J. Khanderi, S. Schulz and U. Flörke, *Z. Anorg. Allg. Chem.* **2008**, 634, 507; c) M. Münch, U. Flörke, M. Bolte, S. Schulz and D. Gudat, *Angew. Chem. Int. Ed.* **2008**, 47, 1512; d) M. P. Coles and P. B. Hitchcock *Eur. J. Inorg. Chem.* **2004**, 2662; e) S. Schmidt, B. Gutschank, S. Schulz, D. Bläser, R. Boese and C. Wölper, *Eur. J. Inorg. Chem.* **2011**, 4464.
- [23] a) K. Naktode, S. Anga, R. K. Kottalanka, H. P. Nayek and T. K. Panda, *J. Coord. Chem.* **2014**, 67, 236; b) K. Pang, Y. Rong, G. Parkin, *Polyhedron*, **2010**, 29, 1881; c) C. A. Wheaton and P. G. Hayes, *Dalton Trans.*, **2010**, 39, 3861; d) M. H. Chisholm, J. C. Gallucci and H. Zhen, *Inorg. Chem.* **2001**, 40, 5051.

Submitted: April 1, 2016

Accepted: May 30, 2016