Calcium Complexes Having Different Amidinate Ligands - Synthesis and Structural Diversity

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Dedicated to Professor Kazushi Mashima on the occasion of his 59th Birthday.

A one-pot reaction of α-dimine 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 \( [\kappa^2-(\text{THF})_4 \text{Ca} \{\text{Dipp} \text{NC-CHPh} \text{CH}_2 \text{NDipp}\}] \) (1) (Dipp = 2,6-disopropylphenyl) in good yield. The solid-state structure of the compound revealed the formation of dianionic 3-phenylprop-2-ene-di-amido ligand having an exocyclic olefinic bond derived from neutral α-dimine fragment. However, analogous reactions with three different carbodiimides (RN = C = NR; R = Cy, iPr and Bu) with alkyl potassium and anhydrous calcium diiodide yielded corresponding homoleptic calcium compounds with amidinate ligand \( [\kappa^2-(\text{THF})_2 \text{Ca} \{\text{RN-CH}_2 \text{Ph} \text{NR}\}] \) (\( R = \text{Cy} \) (2), \( \text{Pr} \) (3) and \( \text{Bu} \) (4)). A separate reaction of DAD ligand, LiCH$_2$SiMe$_3$ and anhydrous ZnCl$_2$ in diethylether solvent produced tri-coordinated zinc compound \( [\kappa^2- (\text{Dipp} \text{N} \text{Cy}) \text{Zn}] \) (1:1-DippN=−C(CH$_2$SiMe$_3$)CH$_2$N-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 diazabutadienes (DAD) with potassium benzyl and anhydrous calcium diiodide yield corresponding homoleptic calcium compounds with amidinate ligand \( [\kappa^2-(\text{THF})_2 \text{Ca} \{\text{RN-CH}_2 \text{Ph} \text{NR}\}] \) (\( R = \text{Cy} \) (2), \( \text{Pr} \) (3) and \( \text{Bu} \) (4)). A separate reaction of DAD ligand, LiCH$_2$SiMe$_3$ and anhydrous ZnCl$_2$ in diethylether solvent produced tri-coordinated zinc compound \( [\kappa^2- (\text{Dipp} \text{N} \text{Cy}) \text{Zn}] \) (1:1-DippN=−C(CH$_2$SiMe$_3$)CH$_2$N-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.

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sium compound [(THF)₂Mg(CH₂Ph)[2-(Ph₃CN=CH)CH₂H₄N]] that was recently reported by us. 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 amidinate moieties [(DippNC(=CHPh)CH₂NDipp)] (1). Attempts of controlled reactions using a number of methods such as of DAD ligand with calcium monobenzyl 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 resonance signal at δ 163.5 indicated the presence of sp² carbon in the ligand moiety.

The calcium compound 1 was crystalized in the orthorhombic space group Pbcn 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.

Compound 1 is monomeric and the coordination polyhedron is formed by the chelation of two amido nitrogen atoms from di-anionic [DippNC(=CHPh)CH₂NDipp]⁻⁻ 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 [Ca–N 2.382(1) and Ca–N 2.328(2) Å] which are consistent with Ca–N distances (2.335–2.361 Å) reported in literature, differ slightly due to the asymmetric attachment of calcium ion to the bis-amido ligand. The single bond characters of C=N and C–N bonds are 1.23 and 1.39 Å, respectively. The central calcium ion is six-fold coordinated due to the coordination of two amidinate ligands and four oxygen atoms from four THF molecules. The geometry around the metal ion can best be described as distorted octahedral. It is noted that the amidinate ligand backbone N1-C1-N3 is not planar; rather, it is folded with a dihedral angle of 21.96° between the planes having N1, C1 and N3 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, 3, 4 and 13. It was observed that the potassium amidinate 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-
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 amidinato ligand backbone. 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 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, iPr, tBu) 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 2–4. In all cases, carbodiimides were first made to react with potassium benzyls and undergo insertion reactions analogous to group 2,[16] 3,[19], 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 diiodide. Calcium compounds [Ca(Cy)N=C(CH2Ph)NCy]2(thf)2] (2), [Ca(iPrN=C(CH2Ph)-NPr]2(thf)2] (3), and [Ca(BuN=C(CH2Ph)-NBu]2(thf)2] (4) were isolated in good yield and recrystallized 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 nonequivalent isopropyl methyl protons -CH2Me2 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 sp2 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 back bone. 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 motifs 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
observed in compound 3 due to the presence of sterically bulky tert-butyl groups in the amidinate moieties. The similar Ca–

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.\textsuperscript{[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 sp² carbon C1 of amidinate ligand and Ca1 atom.

Two four-membered calcium metallacycles Ca1-N1-C1-N2 and Ca1-N1′-C1′-N2′ were formed due to the η⁰ coordination mode of amidinate 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.\textsuperscript{[14]} The plane containing N1, C1 and N2 is coplanar with the plane having N1′, C1′ and N2′ 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.\textsuperscript{[22]} We were therefore interested to make an structural analogy between calcium and zinc compounds hav-
ing amidinate ligand formed from α-dilimine 1,4-disubstituted diazabutadienes (DAD). The treatment of neutral DAD ligand with lithium alkyl (LiCH₂SiMe₃) in diethylether at room temperature, followed by the addition of anhydrous ZnCl₂ afforded a tri-coordinated zinc compound \([\text{DippN}^-\text{C(CH₂SiMe₃)CH₂N-Dipp}]\) (5) having amidinate and amido moieties in the metal coordination sphere (Scheme 4). The reaction of DAD with LiCH₂SiMe₃ underwent 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 \(^1\)H NMR spectra of compound 5 measured in \(\text{D}_2\) benzene, the singlet signal at \(\delta 4.61\) ppm can be assigned to the resonance of two methylene (CH₂) protons present in the \([\text{DippN}^-\text{C(CH₂SiMe₃)CH₂N-Dipp}]\) ligand backbone. The resonance of the methylene protons of CH₂SiMe₃ was observed at \(\delta 1.72\) 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 \(\delta 3.85\) ppm and 3.14 ppm respectively, and three doublet resonances at \(\delta 1.47\), 1.38 and 1.09 ppm respectively, were observed due to the –CH proton and isopropyl methyl protons present in the amidinate ligand moiety \([\text{DippN}^-\text{C(CH₂SiMe₃)CH₂N-Dipp}]\). The sharp singlet at \(\delta 0.12\) ppm was observed as a result of the resonance of the protons present in the -SiMe₃ group. In the \(^1\)C{\(^1\)H} spectra, resonance at \(\delta 173.5\) can be assigned to imine carbon atom \([-\text{N}=\text{C(CH₂SiMe₃)}]\) present in the \([\text{DippN}^-\text{C(CH₂SiMe₃)CH₂N-Dipp}]\) 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 \(\text{P}-1\). 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 trigonal planar. The 

The presence of sterically bulky 2,6-disisoproplyphenyl 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. There are two types of Zn–N [Zn1-N1 2.092(3); Zn1-N2 1.871(3) and Zn1-N3 1.852(3)] bond distances 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–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-en-diamido 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 amidinate 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-en-diamido ligand \([\text{DippNC}^-\text{C(Ph)CH₂N-Dipp}]\) 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 monoo-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.

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