

Big Ligands for Stabilization of Small Functionalities in Calcium Chemistry

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Reaction of (DIPP-nacnac)CaN(SiMe₃)₂·THF (DIPP-nacnac = CH{(CMe)(2,6-*i*Pr₂C₆H₃N)}₂) with NH₃ gave the heteroleptic complex (DIPP-nacnac)CaNH₂·(NH₃)₂ which crystallized as a dimer with bridging NH₂⁻ ions. In contrast to other heteroleptic (DIPP-nacnac)calcium amides, (DIPP-nacnac)CaNH₂·(NH₃)₂ is remarkably stable toward ligand exchange. Reaction of (DIPP-nacnac)CaH·THF with Me₃SiCN gave the heteroleptic complex (DIPP-nacnac)CaCN·THF that crystallized as a trimer. The CN⁻ ions bridge in a linear fashion between the Ca²⁺ ions. In a new synthetic route (DIPP-nacnac)CaN(SiMe₃)₂·THF reacted with Et₃NH⁺Cl⁻ to give (DIPP-nacnac)CaCl·THF, which crystallized as a dimer with bridging Cl⁻ ions. The exceptional stability of these aggregates toward ligand-exchange reactions, which would give insoluble homoleptic Ca(NH₂)₂, Ca(CN)₂, or CaCl₂, is remarkable and likely due to their multinuclear nature.

Introduction

Although monoanionic β-diketiminato ligands have been known for quite some time,^{1,2} their unique properties only became apparent over the past decade.³ These chelating ligands exhibit a strong donor ability, and their straightforward modular syntheses allow for convenient variation of the substituents that control steric and electronic properties. In particular, the bulkier DIPP-nacnac ligand (DIPP-nacnac = CH{(CMe)(2,6-*i*Pr₂C₆H₃N)}₂) is renowned for stabilizing metals with low coordination numbers, a feature that partially originates from the ligand's ability to adapt its coordination mode to metal size, e.g., the same ligand allowed syntheses of the nearly complete series of rather similar monomeric alkaline-earth complexes (DIPP-nacnac)₂M (M = Mg, Ca,

Sr, Ba).⁴ The more than one thousand known compounds with DIPP-nacnac ligands include an impressive row of otherwise hardly accessible molecules^{5–8} and application in a large variety of unique well-defined single-site polymerization catalysts.^{9–16}

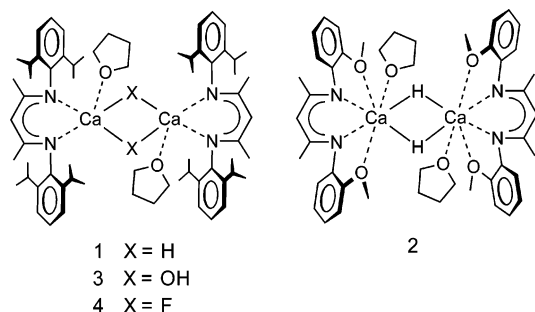
Recently we prepared a well-defined hydrocarbon-soluble calcium hydride complex (**1**) containing the DIPP-nacnac

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ligand.¹⁷ As bonds to calcium are largely ionic and weak, rapid ligand exchange is one of the major challenges in organocalcium chemistry. The DIPP-nacnac ligand in **1**, however, stabilizes the complex kinetically against disproportionation according to the Schlenk equilibrium and is of crucial importance for its successful isolation. Attempts to substitute steric shielding of the calcium coordination sphere with electronic saturation failed. The heteroleptic calcium hydride complex (**2**), containing the (2-MeO-Ph)-nacnac ligand recently introduced by Chisholm,¹⁸ is unstable and decomposes to the known homoleptic β -diketiminato calcium complex and insoluble CaH_2 .¹⁹



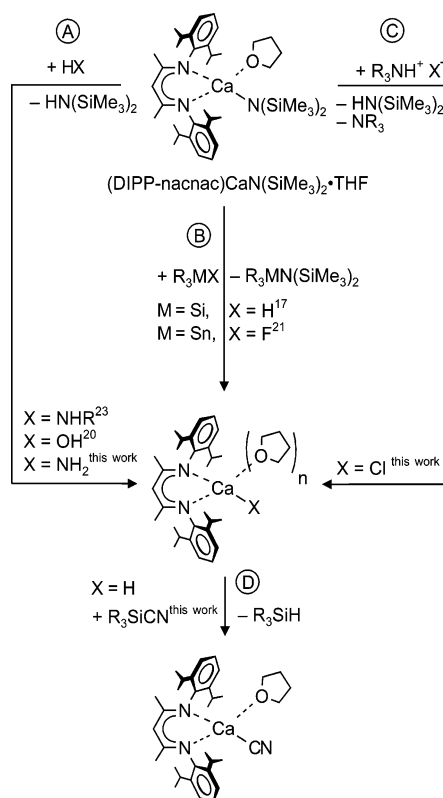
Similarly, the DIPP-nacnac ligand played a major role in the isolation of calcium hydroxide (**3**)²⁰ and fluoride (**4**)²¹ complexes, which can be used as stable hydrocarbon-soluble calcium precursors for coating surfaces with CaCO_3 or CaF_2 , respectively. Both the calcium hydroxide **3** as well as the calcium fluoride **4** are like the calcium hydride complex (**1**), exceptionally stable toward ligand-exchange reactions.

Herein we describe the syntheses and structures of stable heteroleptic calcium complexes with H_2N^- , CN^- , and Cl^- functionalities. The variety of synthetic methods hints that a much larger series of hydrocarbon-soluble calcium complexes with small “inorganic” ligands is now conveniently accessible.

Results and Discussion

The easily accessible heteroleptic complex $(\text{DIPP-nacnac})\text{CaN}(\text{SiMe}_3)_2 \cdot \text{THF}$ (Scheme 1) is a very convenient starting material for a wide variety of heteroleptic β -diketiminato calcium complexes.¹⁸ Synthetic routes can be generally classified in the categories summarized in Scheme 1. Route A, reaction with acidic protic substrates, has been applied in the preparation of heteroleptic cyclopentadienides,²² primary amides,²³ and a hydroxide complex.²⁰ Well-defined hydrocarbon-soluble calcium hydride and fluoride complexes

Scheme 1



have been obtained by nucleophilic displacement reactions with silanes and stannanes, respectively (route B).^{17,21} Here we introduce route C in which the Ca amide precursor reacts with an ammonium salt to introduce the small ligand and route D which is a variation on route B.

(DIPP-nacnac)CaNH₂·(NH₃)₂ and (DIPP-nacnac)CaNH₂·THF. Amide ligands in calcium chemistry are generally bulky for steric saturation of the relatively large Ca^{2+} ion (e.g., $(\text{Me}_3\text{Si})_2\text{N}^-$ or $(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2)(\text{Me}_3\text{Si})\text{N}^-$).²⁴ Whereas the simplest amide ligand NH_2^- plays an increasing role in the chemistry of late-main-group-metal complexes,²⁵ complexes of the early-main-group metals are only known as polymeric salts $[\text{M}(\text{NH}_2)_x]_\infty$. The calcium amide $[\text{Ca}(\text{NH}_2)_2]_\infty$ has been used in polymerization catalysis.²⁶ In combination with its thermal decomposition product, the related imide CaNH , it also receives attention in hydrogen-storage research.²⁷

The molecular complex $(\text{DIPP-nacnac})\text{CaNH}_2$ was synthesized by route A (Scheme 1): a solution of (DIPP-

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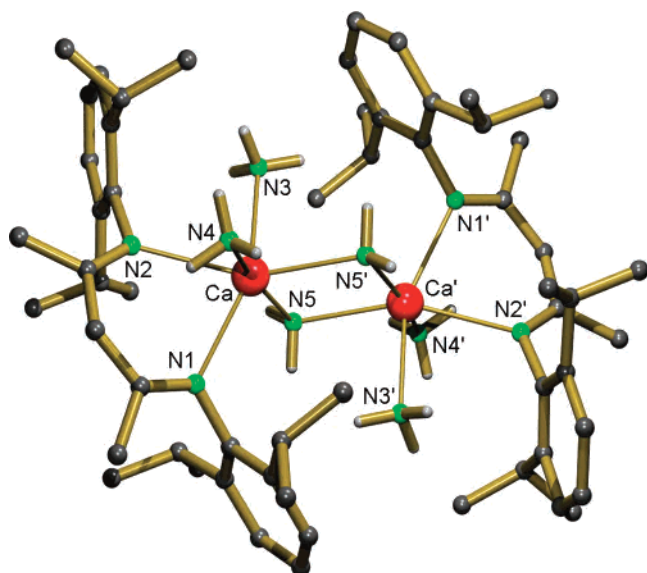


Figure 1. Crystal structure of $[(\text{DIPP-nacnac})\text{CaNH}_2 \cdot (\text{NH}_3)_2]_2$. Hydrogen atoms (except those on the NH_2^- and NH_3 groups) have been omitted for clarity. Selected bond distances and angles are given in Table 1.

Table 1. Selected Bond Distances (Å) and Angles (deg) for $(\text{DIPP-nacnac})\text{CaNH}_2 \cdot (\text{NH}_3)_2$, $(\text{DIPP-nacnac})\text{CaCN} \cdot \text{THF}$, and $(\text{DIPP-nacnac})\text{CaCl} \cdot \text{THF}$

$(\text{DIPP-nacnac})\text{CaNH}_2 \cdot (\text{NH}_3)_2$					
Ca–N1	2.5049(9)	Ca–N5–Ca	99.52(4)	N3–Ca–N5	82.14(5)
Ca–N2	2.5465(8)	N5–Ca–N5	80.48(4)	N4–Ca–N5	164.35(4)
Ca–N3	2.546(1)	N1–Ca–N2	75.85(3)	H–N5–H	104(2)
Ca–N4	2.608(1)	N3–Ca–N4	106.92(5)		
Ca–N5	2.430(1)				
Ca–N5	2.448(1)				
$(\text{DIPP-nacnac})\text{CaCN} \cdot \text{THF}$					
Ca1–N1	2.385(2)	Ca2–N3	2.380(2)	Ca3–N5	2.379(2)
Ca1–N2	2.387(2)	Ca2–N4	2.364(2)	Ca3–N6	2.398(2)
Ca1–O1	2.398(2)	Ca2–O2	2.444(2)	Ca3–O3	2.414(2)
Ca1–CN1	2.461(3)	Ca2–CN2	2.512(3)	Ca3–CN1	2.449(3)
Ca1–CN2	2.510(3)	Ca2–CN3	2.545(3)	Ca3–CN3	2.430(3)
$(\text{DIPP-nacnac})\text{CaCl} \cdot \text{THF}$					
Ca1–Cl1	2.676(1)	Ca2–Cl1	2.679(1)	Ca1–Cl1–Ca2	98.71(4)
Ca1–Cl2	2.681(1)	Ca2–Cl2	2.685(1)	Ca1–Cl2–Ca2	98.44(5)
Ca1–N1	2.345(3)	Ca2–N3	2.368(3)	Cl1–Ca1–Cl2	81.49(4)
Ca1–N2	2.357(3)	Ca2–N4	2.378(3)	Cl1–Ca2–Cl2	81.37(4)
Ca1–O1	2.435(4)	Ca2–O2	2.324(3)		

$\text{nacnac})\text{CaN}(\text{SiMe}_3)_2 \cdot \text{THF}$ in hexane reacted at room temperature instantaneously with 1 bar of gaseous NH_3 . The light-yellow precipitate that immediately formed in near quantitative yield was analyzed as $(\text{DIPP-nacnac})\text{CaNH}_2 \cdot (\text{NH}_3)_2$. Recrystallization from hot hexane gave the analytically pure product in the form of light-yellow crystalline plates.

The crystal structure (Figure 1 and Table 1) shows a dimeric complex with terminal DIPP-nacnac ligands and symmetrically bridging NH_2^- ions. Two additional NH_3 ligands complete the distorted octahedral coordination sphere around Ca^{2+} .

All Ca–N distances are rather long for their kind. The Ca–N bonds to the DIPP-nacnac ligand (average 2.5257(9) Å) are much longer than those observed in sterically congested $(\text{DIPP-nacnac})_2\text{Ca}$ (average 2.379(9) Å)⁴ and also longer than in the dimeric complexes **1**, **3**, and **4** (range 2.372(2)–2.426(2) Å). Likewise, the average Ca– NH_3 bond

distance of 2.572(1) Å is significantly longer than that of 2.496(2) Å in $(\text{Me}_4\text{Cp})_2\text{Ca} \cdot (\text{NH}_3)_2$.²⁸ Although there is no precedence for a Ca– NH_2 bond, the average bond distance of 2.439(1) Å is only slightly smaller than that for the much bulkier $(\text{Me}_3\text{Si})_2\text{N}^-$ anion bridging two Ca^{2+} ions (2.475(6) Å).^{24a} The dihedral angle between the NH_2 plane and the Ca–N5–Ca'–N5' plane is 81.5(1)°, i.e., a typical perpendicular orientation that allows for maximum interaction between the N lone pairs and the Ca^{2+} ions.

The ^1H NMR spectrum of $(\text{DIPP-nacnac})\text{CaNH}_2 \cdot (\text{NH}_3)_2$ dissolved in C_6D_6 shows one broad resonance for the NH_2^- and NH_3 ligands at -0.55 ppm. This suggests rapid exchange of protons between amine and amide ligands which would involve a transient species with a bridging NH_3 ligand and a terminal NH_2^- ligand. Indeed, cooling a toluene solution gave decoalescence of the signal into two resonances: the smaller signal at -1.57 ppm is attributed to NH_2^- and the larger signal at -0.29 ppm to the NH_3 ligands. The 1:2 ratio of their respective integrals indicates that part of the NH_3 eliminated upon solvation in benzene. A rough estimate of the activation energy for proton exchange is 11.3(1) kcal/mol ($T_{\text{coal.}} = 258$ K). The chemical shift for NH_2^- (-1.57 ppm) is at higher field than the shifts observed in late-main-group metal amides, e.g., Ge-NH_2 (0.55–0.75 ppm),^{25c,d} Al-NH_2 (-0.55 ppm),^{25b} or Ga-NH_2 (-0.58 ppm).^{25a} This is in line with considerable negative charge on the NH_2^- ligand and underscores the highly ionic nature of the Ca– NH_2 bond.

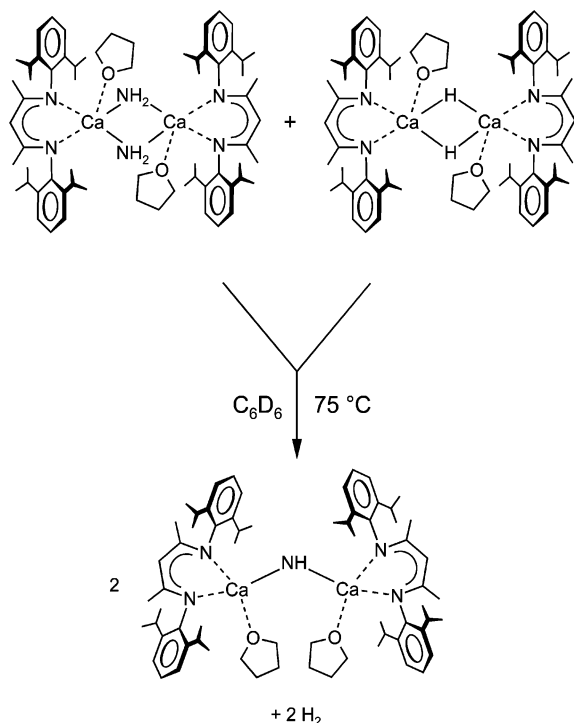
The IR spectrum of $(\text{DIPP-nacnac})\text{CaNH}_2 \cdot (\text{NH}_3)_2$ shows a weak somewhat broadened signal at 3366 cm^{-1} which is assigned to the N–H stretch vibrations of NH_2^- and NH_3 ligands. This value is in a similar range as N–H frequencies observed for Al-NH_2 (3396 – 3468 cm^{-1})^{25b} or Ge-NH_2 (3325 – 3402 cm^{-1})^{25c} complexes.

The NH_3 ligands in $(\text{DIPP-nacnac})\text{CaNH}_2 \cdot (\text{NH}_3)_2$ can easily be exchanged for THF ligands by solvation in THF and removal of all volatiles to give a solid compound of formula $(\text{DIPP-nacnac})\text{CaNH}_2 \cdot (\text{THF})$. The ^1H NMR signal for the NH_2^- (-1.62 ppm) is observed at a similar frequency as for $(\text{DIPP-nacnac})\text{CaNH}_2 \cdot (\text{NH}_3)_2$ (-1.57 ppm). This indicates that the NH_2^- in $(\text{DIPP-nacnac})\text{CaNH}_2 \cdot (\text{THF})$ is also bridging and that the complex is presumably dimeric like **1**, **3**, and **4**. The ^1H NMR resonance for the NH_2^- ligand could be observed as a relatively sharp singlet at -1.62 ppm.

$(\text{DIPP-nacnac})\text{CaNH}_2 \cdot (\text{THF})$ is exceptionally stable toward ligand exchange: heating a benzene solution to reflux temperature gave only minor formation of the homoleptic complex $(\text{DIPP-nacnac})_2\text{Ca}$. This strongly contrasts with the instability of several similar primary amides toward the Schlenk equilibrium.²³ Deprotonation of the primary amines $t\text{BuNH}_2$, CyNH_2 , and PhNH_2 with $(\text{DIPP-nacnac})\text{CaN}(\text{SiMe}_3)_2 \cdot \text{THF}$ gave unidentified products along with formation of $(\text{DIPP-nacnac})_2\text{Ca}$. Stable heteroleptic complexes could only be obtained by reaction with 2,6- $i\text{Pr}_2\text{-C}_6\text{H}_4\text{NH}_2$ or $\text{MeOCH}_2\text{CH}_2\text{NH}_2$, which gave either a sterically

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Scheme 2



encumbered product or an amide stabilized by the chelate effect. It was concluded that the steric demands and/or denticity of the ligand is of major importance for the stability of heteroleptic β -diketiminate calcium complexes.²³

In light of the latter conclusion, the exceptional stability of $(DIPP-nacnac)CaNH_2 \cdot THF$ (as well as **1**, **3**, and **4**) is more than remarkable. As these species with rather small NH_2^- , H^- , OH^- , and F^- ligands are all of dimeric nature, the nuclearity of these complexes seems to be another factor of major importance for the stability of heteroleptic β -diketiminate calcium complexes. The small ligands occupy bridging positions and essentially behave as bidentate ligands filling two coordination sites at the metal, thus explaining their stability toward ligand exchange.

Synthesis of a calcium complex containing the simple imido ligand, NH^{2-} , was attempted according to Scheme 2. Reaction of $(DIPP-nacnac)CaNH_2 \cdot THF$ with $(DIPP-nacnac)CaH \cdot THF$ at $75\text{ }^\circ\text{C}$ gave slow conversion to a new species with a singlet at -1.73 ppm , which might be attributed to the NH^{2-} ion. As this reaction was incomplete and extensive heating also gave decomposition to homoleptic $(DIPP-nacnac)_2Ca$, the desired product could not be isolated by crystallization. Apparently, the second deprotonation of the amine ligand is not easily accomplished and needs more drastic reaction conditions.²⁹ Also, the $Ca-OH$ functionality in $(DIPP-nacnac)CaOH \cdot THF$ was resistant to a second deprotonation. This is in striking contrast with late-main-group-metal- NH_2 and early-transition-metal- NH_2 com-

plexes, which often spontaneously eliminate NH_3 to form the imido products.^{25,30}

(DIPP-nacnac)CaCN \cdot (THF). Calcium cyanide is an industrially important cyanide source for which even today new synthetic routes are developed.³¹ Despite its extreme lethal properties for humans it is classically used in a variety of applications, e.g., insecticides,³² polymerization catalysts,³³ in the catalytic production of vinyl cyanide,³⁴ or in mine leaching operations and froth flotation processes. Whereas the CN^- ligand is well established in the coordination chemistry of transition metals,³⁵ early-main-group-metal cyanide complexes are few. Crystal structures of the dimeric complex $[LiCN \cdot DMF]_2$ and the cation $[Li-C \equiv N-Li]^+$ as part of a cyanocuprate have been reported.³⁶ Although syntheses and IR spectra of $(tBuO)_4Be_3(CN)_2$ ^{37a} and the "ate" complex $[Me_4N^+][Me_2MgCN^-]$ ^{37b} have been described, we are not aware of any structurally characterized alkaline-earth-metal cyanide complex.

Despite this lack of information, the latter group of complexes is interesting from a theoretical point of view.³⁸ Whereas $Be(CN)_2$ should be described as an isocyanide with an energy minimum for the linear structure $CN-Be-NC$, a negligible energy difference between cyanide (C coordination) and isocyanide (N coordination) was calculated for $Mg(CN)_2$. Rather interestingly, the heavier alkaline-earth metals Ca, Sr, and Ba prefer a side-on coordination mode and can be described neither as cyanide nor as isocyanide.^{38a}

Synthesis of a well-defined calcium cyanide complex was attempted by bubbling HCN gas through a solution of $(DIPP-nacnac)CaN(SiMe_3)_2 \cdot THF$ in hexane (route A) and reaction of $(DIPP-nacnac)CaN(SiMe_3)_2 \cdot THF$ with Me_3SiCN . In both cases no clean conversion could be observed, and no defined products have been isolated. Reaction of $(DIPP-nacnac)CaH \cdot THF$ with Me_3SiCN in benzene, however, at room temperature gave clean conversion to $(DIPP-nacnac)CaCN \cdot THF$ and Me_3SiH . After cooling a concentrated solution the product could be isolated as colorless crystalline blocks in 50% yield (this route, D in Scheme 1, is a variation of route B).

The crystal structure shows a nonsymmetrical trimeric complex in which CN^- anions bridge the three Ca^{2+} ions as bidentate ligands (Figure 2, Table 1). Although the coor-

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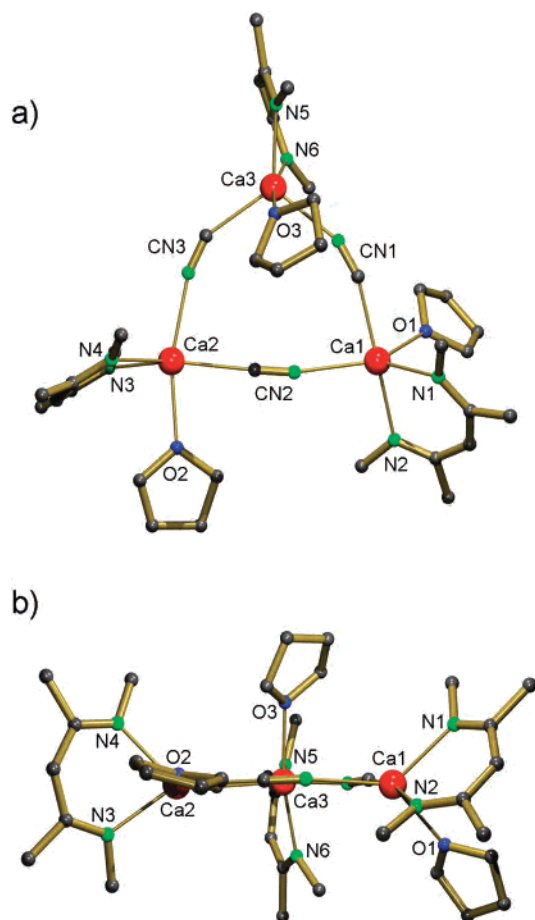


Figure 2. Crystal structure of [(DIPP-nacnac)CaCN·THF]₃: (a) view perpendicular on the Ca1–Ca2–Ca3 plane; (b) view along the Ca1–Ca2–Ca3 plane. Hydrogen atoms and the 2,6-*i*Pr₂-phenyl substituents (except the *C*_{ipso} atom) have been omitted for clarity. The CN[−] ions are disordered, and no discrimination between C and N could be made (the figure shows one of the isomers). Selected bond distances and angles are given in Table 1.

dination geometries around the Ca²⁺ ions are distorted trigonal bipyramidal, all are different and unique with respect to occupation of equatorial and axial positions. Lack of symmetry is also reflected in the different Ca⋯Ca' distances: Ca1⋯Ca2 = 6.1551(8) Å, Ca1⋯Ca3 = 5.7907(7) Å, and Ca2⋯Ca3 5.7589(7) Å. The cyanide anions are disordered over two positions, and in the difference Fourier map it is not possible to discriminate between C and N. Likewise, no clear pattern in metal–cyanide bond distances could be observed. Therefore, the cyanide anion was refined as a diatomic entity in which both positions have 50% C and 50% N occupation. As the bond between Ca²⁺ and CN[−] is largely ionic, it seems likely that the orientation of the CN ligand is independent from that of its neighbors. Consequently, two different isomers are possible, i.e., one with all CN ligands oriented head-to-tail and one with a head-tail/head-tail/tail-head orientation (a statistical distribution of 1/3 is expected, respectively). Similar disorder of bridging cyanide ligands is quite common³⁹ and has been observed in the oligomeric rings [(Me₃SiCH)₂AlCN]₃,⁴⁰ [Cp*₂SmCN·CyNC]₃,⁴¹ [Cp*₂SmCN]₆⁴² and in the linear coordination

polymers [Me₃SnCN]_∞⁴³ or [Me₂InCN]_∞.⁴⁴ This type of disorder is also in line with recent calculation results: the energy difference between the *C*_{4h} and *D*_{2h} isomers of the ring [X₂AlCN]₄ is less than 1 kJ/mol.⁴⁵

The C–N bond distances in the cyanide ligands vary from 1.164(4) to 1.173(4) Å and are consistent with CN triple bond character.⁴⁶ The bonds between Ca and the cyanide ligands vary from 2.430(3) to 2.510(3) Å and are consistent with the Ca–NC bond of 2.434(3) Å for a cyanide ligand bridging between Ca²⁺ and Nb.⁴⁷ The Ca–C–N and Ca–N–C geometries deviate slightly from linearity with angles ranging from 150.6(2)° to 177.3(2)° (average 163.4(3)°). The Ca–N bond distances to the DIPP-nacnac ligands (range 2.364(2)–2.398(2) Å) and the Ca–O(THF) bonds (range 2.398(2)–2.444(2) Å) are as expected.

The linear bridging of the cyanide ligands between two Ca²⁺ ions is apparently favored over side-on bridging. Experimental proof for a computationally predicted side-on-coordinated cyanide anion possibly could be found in a monomeric calcium cyanide complex.

The IR spectrum of (DIPP-nacnac)CaCN·THF shows two signals for the cyanide stretching vibrations at 2142 and 2117 cm^{−1} in a ratio of 1:3. The larger absorbance splits in at least two signals in a second-derivative spectrum (2120 and 2114 cm^{−1} in a ratio of 2:1). This is consistent with the observed disorder of the cyanide ligands and the presence of isomers. The observed frequencies compare well to those reported for [Cp*₂SmCN·CyNC]₃ (2105–2110 cm^{−1}).⁴¹

A solution of [(DIPP-nacnac)CaCN·(THF)]₃ in C₆D₆ shows one set of ¹H NMR signals for the DIPP-nacnac ligands, implying that all ligands are equal on the NMR time scale. The ¹³C NMR signal for the CN ligand is observed at 158.1 ppm, which corresponds to the resonance of NaCN in water (166.9 ppm).⁴⁸

(DIPP-nacnac)CaCl·(THF). As many organocalcium complexes are prepared by a metathesis reaction with a calcium halide, heteroleptic calcium complexes containing a halogenide ion are rather common. Usually in synthesis the THF-soluble CaI₂ is preferred over the less soluble lighter halides. Consequently, calcium complexes with the lighter halide ions are less known. The first well-defined heteroleptic calcium fluoride complex, (DIPP-nacnac)CaF·(THF), was only recently reported.²¹ While few organocalcium chloride

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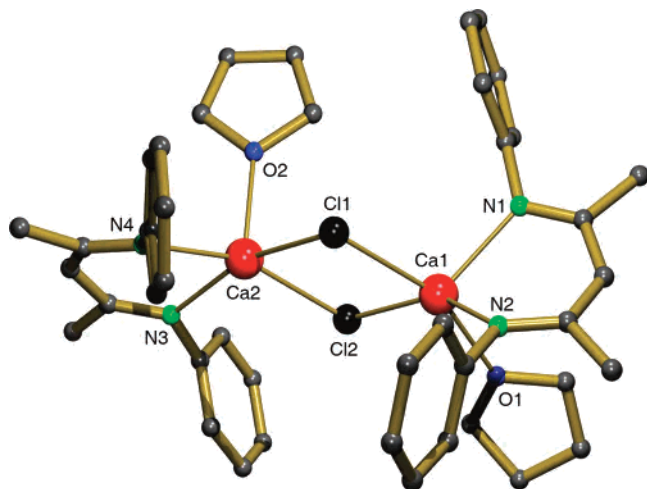


Figure 3. Crystal structure of [(DIPP-nacnac)CaCl·THF]₂. Hydrogen atoms and *iPr* substituents have been omitted for clarity. Selected bond distances and angles are given in Table 1.

complexes have been reported,⁴⁹ the main purpose for our research on (DIPP-nacnac)CaCl·(THF) is its synthetic method.

Partial protolysis of (DIPP-nacnac)CaN(SiMe₃)₂·THF by diffusion of gaseous HCl into a benzene solution (route A) was expectedly unselective and gave a mixture of products. Therefore, we reacted the calcium amide precursor with the much weaker acid Et₃NH⁺Cl⁻ in THF (Scheme 1, route C). In the course of 1 h the solid ammonium salt slowly disappeared. After removal of all volatiles and crystallization from toluene, (DIPP-nacnac)CaCl·THF could be obtained in 70% crystalline yield.

These crystals are isomorphous with some of the different crystal modifications found for (DIPP-nacnac)CaH·THF and (DIPP-nacnac)CaOH·THF.⁵⁰ The crystal structure of (DIPP-nacnac)CaCl·THF (Figure 3, Table 1) shows the typically nonsymmetric dimeric aggregate in which the Ca²⁺ ions are bridged by chloride ions. A similar dimeric structure was not only observed for the lightest halogen analogue in the series, (DIPP-nacnac)CaF·THF, but also for a comparable iodine analogue.⁵¹ This underscores the flexibility of the β -diketiminato ligand to adapt its coordination mode to the other ligands in the coordination sphere. The Ca–Cl bonds are in the narrow range of 2.676(1)–2.685(1) Å and considerably shorter than those published for [1,2,4-(*t*Bu)₃CpCaCl·(DME)]₂ (average 2.7460(9) Å) or several phosphacyclopentadienyl or arsacyclopentadienylcalcium chloride complexes (range 2.714(1)–2.826(5) Å).⁴⁹ The Ca–N and Ca–O bond distances in (DIPP-nacnac)CaCl·THF are in the normal range.

Conclusions

Although ligand size plays an important role in stabilization of heteroleptic β -diketiminato calcium complexes,²³ three

new stable β -diketiminato complexes with small ligands are introduced: (DIPP-nacnac)CaNH₂·(NH₃)₂, (DIPP-nacnac)CaCN·THF, and (DIPP-nacnac)CaCl·THF. These complexes crystallize as either a dimer or a trimer in which the small functionalities NH₂⁻, CN⁻, or Cl⁻ bridge two Ca²⁺ ions. This way they essentially behave as bidentate ligands that considerably fill the coordination sphere of the Ca²⁺ ions, thus explaining the extraordinary stabilities of these heteroleptic complexes. As similar dimeric complexes with bridging H⁻, OH⁻, and F⁻ functionalities are known, this seems to be a general principle.

In addition, the synthetic methods toward these complexes have been extended with a new method: reaction of the heteroleptic β -diketiminato calcium amide precursor with an ammonium salt (Scheme 1, route C). Since the β -diketiminato anion is stable toward protolysis by NH₃, not only R₃NH⁺ but also NH₄⁺ salts can be used. This enables access to a large variety of hydrocarbon-soluble calcium complexes containing small ligands. Furthermore, it allows a study of these functional groups at a molecular level and promises possible application in material chemistry (as demonstrated for the hydrocarbon-soluble calcium hydroxide²⁰ and fluoride²¹ complexes).

Experimental Section

General Methods. Solvents were dried by standard methods and distilled prior to use. All moisture- and air-sensitive reactions were carried out under an inert argon atmosphere using standard Schlenk techniques. Samples prepared for spectral measurements as well as for reactions were manipulated in a glovebox. NMR spectra were recorded on Bruker DPX300 and Bruker DRX500 spectrometers. IR spectra were measured as a Nujol mull between KBr plates. Compounds (DIPP-nacnac)CaN(SiMe₃)₂·THF¹⁸ and (DIPP-nacnac)CaH·THF¹⁷ were prepared according to literature methods.

Synthesis of (DIPP-nacnac)CaNH₂·(NH₃)₂. (DIPP-nacnac)CaN(SiMe₃)₂·THF (1.30 g; 1.88 mmol) was dissolved in 12 mL of hexane. The solution was charged with NH₃ gas, whereupon a light yellow solid precipitated. After centrifugation the solid was dried under vacuum (25 °C, 1 Torr, 30 min). Yield: 830 mg, 1.69 mmol, 90%. The product can be recrystallized by slowly cooling a hot hexane solution to –27 °C. Melting point: 317 °C (decomposition). ¹H NMR (300 MHz, C₆D₆): δ –0.54 (8H, NH₂ and NH₃), 1.09 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂), 1.18 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂), 1.66 (s, 6H, Me-backbone), 3.20 (sept, *J* = 6.9 Hz, 4H, CH(CH₃)₂), 4.71 (s, 1H, CH-backbone), 7.04 (m, 6H, Ar–H). ¹³C NMR (75 MHz, C₆D₆): δ 23.5 (*iPr*–CH), 24.4 (*iPr*–CH), 25.3 (*iPr*–Me), 28.2 (Me-backbone), 93.0 (CH-backbone), 123.6 (Ar), 125.9 (Ar), 141.6 (Ar), 149.1 (Ar), 164.4 (backbone). IR (Nujol): $\tilde{\nu}$ = 3366, 3272, 3251, 3201, 3055, 2956, 2924, 2855, 1544, 1509, 1460, 1422, 1381, 1310, 1253, 1224, 1095, 1019, 922, 782, 756 cm⁻¹. Anal. Calcd for C₂₉H₄₉CaN₅ (*M* = 507.81): C, 68.59; H, 9.73. Found: C, 68.28; H, 9.81.

Synthesis of (DIPP-nacnac)CaNH₂·THF. (DIPP-nacnac)CaNH₂·(NH₃)₂ (1.00 g, 1.97 mmol) was dissolved in 10 mL of THF. After evaporation of the solvent (DIPP-nacnac)CaNH₂·(THF) was obtained as a light yellow solid. Yield: 1.08 g, 1.97 mmol, 100%. Melting point: 308 °C (decomposition). ¹H NMR (300 MHz, C₆D₆): δ –1.62 (s, 2H, NH₂), 1.16 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂), 1.20 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂), 1.40 (m, 4H, THF), 1.69 (s, 6H, Me-backbone), 3.14 (sept, *J* = 6.9 Hz,

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Table 2. Crystal Data

compound	(DIPP-nacnac)CaNH ₂ ·(NH ₃) ₂	(DIPP-nacnac)CaCN·THF	(DIPP-nacnac)CaCl·THF
formula	C ₅₈ H ₉₈ Ca ₂ N ₁₀	C ₁₀₂ H ₁₄₇ Ca ₃ N ₉ O ₃ (C ₆ H ₆) ₂	C ₆₆ H ₉₈ Ca ₂ Cl ₂ N ₄ O ₂
M _w	1015.62	1823.75	1130.54
size (mm ³)	0.4 × 0.4 × 0.3	0.5 × 0.4 × 0.3	0.5 × 0.4 × 0.3
cryst syst	triclinic	monoclinic	monoclinic
space group	P $\bar{1}$	P2 ₁	I2/a
a (Å)	9.1128(3)	12.5335(3)	22.4227(13)
b (Å)	12.7164(5)	27.9272(7)	12.1193(7)
c (Å)	14.2182(5)	16.6225(4)	49.354(3)
α (deg)	107.305(2)	90	90
β (deg)	104.709(2)	109.086(1)	94.150(3)
γ (deg)	93.217(2)	90	90
V (Å ³)	1506.0(1)	5498.5(2)	13377(1)
Z	1	2	8
ρ (g·cm ⁻³)	1.120	1.102	1.123
μ(Mo Kα) (mm ⁻¹)	0.233	0.202	0.293
T (°C)	-90	-70	-70
θ(max)	30.1	25.4	24.2
reflns total, unique	103 194, 8857	127 997, 20 108	44 663, 10 655
R _{int}	0.041	0.060	0.099
obsd reflns (I > 2σ(I))	7857	15 335	6961
R ₁	0.0390	0.0472	0.0709
wR ₂	0.1146	0.1182	0.2136
GOF	1.05	1.02	1.03
max/min resd (e Å ⁻³)	-0.38/0.40	-0.24/0.46	-0.71/0.41

4H, CH(CH₃)₂), 3.51 (m, 4H, THF), 4.78 (s, 1H, CH-backbone), 7.09 (m, 6H, Ar-H). ¹³C NMR (75 MHz, C₆D₆): δ 24.3 (*i*Pr-CH), 24.5 (*i*Pr-Me), 25.0 (*i*Pr-Me), 25.7 (THF), 28.3 (Me-backbone), 68.2 (THF), 93.9 (CH-backbone), 123.8 (Ar), 124.2 (Ar), 141.8 (Ar), 146.8 (Ar), 164.9 (backbone).

Synthesis of (DIPP-nacnac)CaCN·THF. Me₃SiCN (64.5 mg from a 10 wt % solution of Me₃SiCN in C₆D₆, 65.9 μmol) was added to a solution of (DIPP-nacnac)CaH·THF (35.0 mg, 65.9 μmol) in 0.5 mL of C₆D₆. After 5 min at room temperature the ¹H NMR spectrum showed full conversion without formation of side products. Concentration of the solution and cooling to +6 °C led to formation of colorless blocks (yield 18.3 mg, 33.0 μmol, 50%). Melting point: 95 °C (decomposition). ¹H NMR (300 MHz, C₆D₆): δ 1.23 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂), 1.25 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂), 1.39 (m, 4H, THF), 1.61 (s, 6H, Me-backbone), 3.18 (sept, *J* = 6.9 Hz, 4H, CH(CH₃)₂), 3.37 (m, 4H, THF), 4.73 (s, 1H, CH-backbone), 7.05–7.16 (m, 6H, Ar-H). ¹³C NMR (75 MHz, C₆D₆): δ 24.6 (*i*Pr-Me), 24.7 (*i*Pr-CH), 25.4 (THF), 25.8 (*i*Pr-Me), 27.9 (Me-backbone), 69.3 (THF), 94.8 (CH-backbone), 123.6 (Ar), 124.1 (Ar), 142.2 (Ar), 147.3 (Ar), 158.1 (CN), 165.5 (backbone). IR (Nujol): $\tilde{\nu}$ = 3054, 2953, 2852, 2142, 2117, 1539, 1514, 1462, 1405, 1314, 1260, 1170, 1100, 1020, 926, 788, 760, 723 cm⁻¹. Anal. Calcd for C₃₄H₄₉CaN₃O (M = 555.85): C, 73.47; H, 8.89. Found: C, 73.15; H, 8.99.

Synthesis of (DIPP-nacnac)CaCl·THF. (DIPP-nacnac)CaN-(SiMe₃)₂·THF (600 mg; 869 μmol) was added to a suspension of Et₃NH⁺Cl⁻ (120 mg; 869 μmol) in 8 mL of THF. Stirring for 1 h resulted in a clear solution. The volatile components were removed under vacuum (25 °C, 1 Torr, 30 min), and the resulting sticky solid was washed with pentane (10 mL). Drying under vacuum gave the product as a white solid. Yield: 344 mg, 609 μmol, 70%. The product can be recrystallized by cooling a saturated toluene solution to -27 °C. Melting point: 165 °C (decomposition). ¹H NMR (300 MHz, C₆D₆): δ 1.18 (d, *J* = 6.8 Hz, 12H, CH(CH₃)₂), 1.23 (d, *J* = 6.8 Hz, 12H, CH(CH₃)₂), 1.33 (m, 4H, THF), 1.64 (s, 6H, Me-backbone), 3.15 (sept, *J* = 6.8 Hz, 4H, CH(CH₃)₂), 3.64 (m, 4H, THF), 4.74 (s, 1H, CH-backbone), 7.12 (m, 6H, Ar-H). ¹³C NMR (75 MHz, C₆D₆):

δ 24.4 (*i*Pr-CH, THF), 24.5 (*i*Pr-Me), 25.1 (*i*Pr-Me), 28.0 (Me-backbone), 69.6 (THF), 94.1 (CH-backbone), 123.1 (Ar), 124.0 (Ar), 141.6 (Ar), 146.7 (Ar), 165.2 (backbone). Anal. Calcd for C₃₃H₄₉CaClN₂O (M = 565.29): C, 70.12; H, 8.74. Found: C, 69.77; H, 8.80.

Crystal Structure Determinations. Single crystals have been measured on a Siemens SMART CCD diffractometer. Structures have been solved and refined using SHELXS-97 and SHELXL-97, respectively.⁵² All geometry calculations and graphics have been performed with PLATON.⁵³

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 655378 (DIPP-nacnac)-CaNH₂·(NH₃)₂, 655379 (DIPP-nacnac)CaCN·THF, and 655380 (DIPP-nacnac)CaCl·THF. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Crystal Structure Determination for (DIPP-nacnac)CaNH₂·(NH₃)₂. Selected data for crystal, measurement, and refinement are summarized in Table 2. Hydrogen atoms at the NH₂⁻ and one of the NH₃ ligands have been observed and refined isotropically. All other hydrogen atoms have been placed on calculated positions and refined in a riding mode.

Crystal Structure Determination for (DIPP-nacnac)CaCN·THF. Selected data for crystal, measurement, and refinement are summarized in Table 2. Checks for higher symmetry were negative. The Flack parameter refined to -0.021(18). All hydrogen atoms have been placed on calculated positions and refined in a riding mode. The C and N positions in the cyanide anions were disordered. Both atoms were isotropically refined with 50% C and 50% N occupation.

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Crystal Structure Determination for (DIPP-nacnac)CaCl·THF. Selected data for crystal, measurement, and refinement are summarized in Table 2. Part of the hydrogens was located in the difference Fourier map and refined isotropically. The other part was placed on calculated positions and refined in a riding mode. The relatively poor crystal structure quality is due to twinning of the plate-like crystals. Reflections of two crystal lattices have been measured and separated.

Acknowledgment. D. Bläser and Prof. Dr. R. Boese are kindly acknowledged for collection of the X-ray data.

Supporting Information Available: Crystallographic data for (DIPP-nacnac)CaNH₂·(NH₃)₂, (DIPP-nacnac)CaCN·THF, and (DIPP-nacnac)CaCl·THF as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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