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Article

Alkyl-Substituted Amides as Ligands in Homometallic and Heterobimetallic Calcium Complexes

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The reaction of benzylpotassium with anhydrous calcium diiodide and 2,2,6,6-tetramethylpiperidine (Tmp-H) in a molar ratio of 2:1:2 in toluene in the presence of tetramethylethylenediamine yields colorless $[(\mathrm{tmeda})\mathrm{Ca}(\mathrm{Tmp})_2]$ (**1**) with an average $\mathrm{Ca-N_{amide}}$ bond length of 227.5 pm. The metathesis reaction of $\mathrm{CaI_2}$ with 2 equiv of KN(Ph)*i*Pr in tetrahydrofuran (THF) gives $[(\mathrm{thf})_3\mathrm{Ca}\{\mathrm{N(Ph)}i\mathrm{Pr}\}_2]$ (**2**) with a Ca−N distance of 234.9 pm. An excess of KN(Ph)R (R = Me, *i*Pr) in the metathesis reaction with $\mathrm{CaI_2}$ leads to the formation of calciates of the type $\mathrm{K_2Ca[N(Ph)R]_4}$ regardless of the applied stoichiometry. The THF-free compound $[\mathrm{K_2Ca\{N(Ph)Me\}_4}]_\infty$ (**3**) forms a three-dimensional net structure, whereas the amides with the larger isopropyl group lead to the formation of molecular $[\{(\mathrm{thf})_2\mathrm{K}(\mu\text{-N-}(\mathrm{Ph})i\mathrm{Pr})_2\}_2\mathrm{Ca}]$ (**4**). In both of these heterobimetallic compounds, the potassium atoms bind to the π systems of the phenyl groups. Heterobimetallic calciates $[\mathrm{K_2Ca(NPh_2)_4(thf)_3}]_\infty$ (**5**) with R = Ph crystallize with a chain structure. In all of these calciates, the tetra-coordinate calcium atoms are in distorted tetrahedral environments.

Introduction

Calcium metal shows a rather minor tendency to deprotonate amines, even when dissolved in liquid ammonia. Utke and Sanderson[1] synthesized alkyl- and aryl-substituted amine complexes of the heavy alkaline earth metals as ammonia adducts, which were extremely air- and moisture-sensitive, even partially pyrophoric, and nearly insoluble in common organic solvents. These experiments demonstrated that neither ammonia nor alkyl- and aryl-substituted amines are deprotonated easily by calcium metal. In contrast to these observations, calcium is able to degradate ethers when codeposited with dimethylether at −196 °C.[2]

These challenges were already overcome more than 30 years ago employing the metathesis reaction of $(\mathrm{diox})_3\mathrm{KNPh_2}$ with calcium halides.[3] Nevertheless, a systematic approach for the synthesis of calcium bis(diphenylamide) was reported very recently.[4] Metalation of $\mathrm{HNPh_2}$ with phenylcalcium compounds or the metathesis reaction of $\mathrm{KNPh_2}$ with $\mathrm{CaI_2}$ proved to be valid procedures. Similar access routes were reported for calcium bis(phenylamide) (anilide).[5] Bis(carbazolyl)calcium represents a closely related calcium bis(amide) whose crystal structure was determined as a tetrakis(pyridine) complex.[6]

Another protocol allowed the synthesis of calcium bis[bis(trimethylsilyl)amide].[7] The transmetalation of $\mathrm{Sn[N(SiMe_3)_2]_2}$ with distilled calcium yielded dimeric $[\mathrm{Ca\{N(SiMe_3)_2\}_2}]_2$ or $[(\mathrm{thf})_2\mathrm{Ca\{N(SiMe_3)_2\}_2}]$, depending on the solvent used, toluene or tetrahydrofuran (THF).[8−10] The transmetalation of $\mathrm{Hg[N(SiMe_3)_2]_2}$ with the heavy alkaline earth metals also led to the formation of the corresponding bis(trimethylsilyl)amides.[11] Various metathesis reactions between alkali metal bis(trialkylsilyl)amide and $\mathrm{CaX_2}$ were

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investigated, X being a halide[12,13] or a pseudohalide such as trifluoromethylsulfonates,[14] arenesulfonates,[15] substituted phenolates,[16] and pentamethylcyclopentadienide.[17] Related to these disilylamides is the calcium complex of the octamethylcyclotetrasilazanediide.[18] The metathesis reaction of CaI_2 with $KN(Aryl)SiMe_3$ yielded the corresponding calcium bis(*N*-aryl-trimethylsilylamide), aryl being bulky 2,6-diisopropylphenyl[19] or 2,4,6-trimethylphenyl (mesityl).[20]

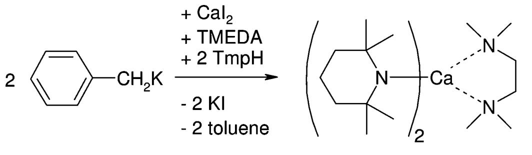
The metathesis reaction (salt elimination reaction) of calcium dihalide with an alkali metal amide enforces a strict stoichiometric ratio of the starting materials in order to avoid halide-containing products. An excess of alkali metal amide can lead to heterobimetallic complexes which form "inverse" crowns in the case of alkali metal−magnesium amides.[21−23] Heterobimetallic complexes also form from equimolar mixtures of $Ca[N(SiMe_3)_2]_2$ and $MN(SiMe_3)_2$. However, "inverse" crowns were not observed, but complexes of the type $[(Me_3Si)_2N{-}Ca\{\mu\text{-}N(SiMe_3)_2\}_2M]$ were isolated, M being Li,[24] Li(thf),[25] K(thf),[26] and $MgN(SiMe_3)_2$.[27]

Bidentate diaza ligands such as $[(Me_3SiN)_2E]^-$, with E being SPh (sulfinates),[28] $SN(SiMe_3)_2$ (sulfites),[28] CPh,[29] and PPh_2,[30] are also well-known and bind via the nitrogen bases to the calcium atom. The bidentate diketiminato ligand *N*-tert-butyl-4-(tert-butylimino)-2-penten-2-amide coordinated in an η^5 fashion to the calcium cation, whereas the replacement of the tert-butyl groups by isopropyl substituents led to an η^2 binding mode.[31,32] Bulky bidentate β-diketiminato ligands are able to stabilize small coordination numbers at the alkaline earth metal centers, as shown for homoleptic $Ca[\{N(2,6\text{-}iPr_2C_6H_3)C(Me)\}_2CH]_2$ with a tetra-coordinate calcium atom.[33]

The substituents of these calcium amides were chosen in order to achieve (i) solubility in common organic solvents, (ii) small aggregation degrees, and (iii) reduction of the anionic charge on the nitrogen base. The last aspect also reduces the nucleophilicity of the amide and can be realized by employing phenyl groups (delocalization of anionic charge) or trialkylsilyl substituents (negative hyperconjugation of charge from the $p_z(N)$ orbital into the $\sigma^*(Si{-}C)$ bond). Bulky substituents at the periphery of the molecule hinder aggregation and shield the reactive Ca−N bonds. Here, we present our first investigations on alkylated amides of homoleptic calcium and heteroleptic calcium−potassium complexes.

Results and Discussion

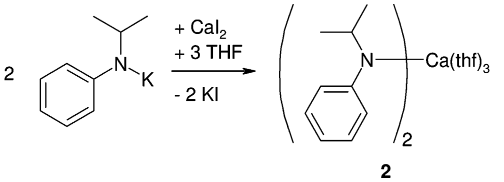
Synthesis. The reaction of benzylpotassium with anhydrous calcium diiodide in toluene yielded dibenzylcalcium, according to a known procedure,[34] which reacted immediately with 2,2,6,6-tetramethylpiperidine (Tmp-H) in the presence of tetramethylethylenediamine (TMEDA), according to eq 1. Colorless $[(tmeda)Ca(Tmp)_2]$ (**1**) is extremely sensitive toward moisture and air and combusts spontaneously through contact with the air. In the absence of TMEDA, no formation of calcium bis(2,2,6,6-tetramethylpiperidide) was observed.



1

(1)

N-Alkylated anilides of calcium were obtained from the metathesis reaction of CaI_2 with KN(Ph)*i*Pr in THF, yielding tris(tetrahydrofuran)calcium bis(*N*-isopropylanilide) (**2**) according to eq 2. Toluene and pentane were added in order to reduce the solubility. Storage at −20 °C afforded the precipitation of crystals of **2**.



2

(2)

Mixtures of KN(Ph)R (R = Me, *i*Pr) and anhydrous CaI_2 in a molar ratio of 4:1 in toluene led to the formation of $K_2Ca[N(Ph)R]_4$. However, this calciate formed with molar ratios larger than 2:1 regardless of the applied stoichiometry, and calciates such as $KCa[N(Ph)R]_3$ were not accessible by this procedure. The THF-free compound $[K_2Ca\{N(Ph)Me\}_4]_\infty$ (**3**) formed a three-dimensional net structure, whereas the larger isopropyl group gave molecular $[\{(thf)_2K(\mu\text{-}N(Ph)iPr)_2\}_2Ca]$ (**4**) in THF solution, as shown in eq 3. In

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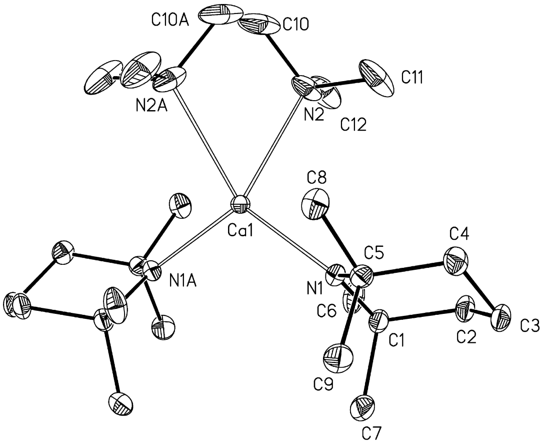
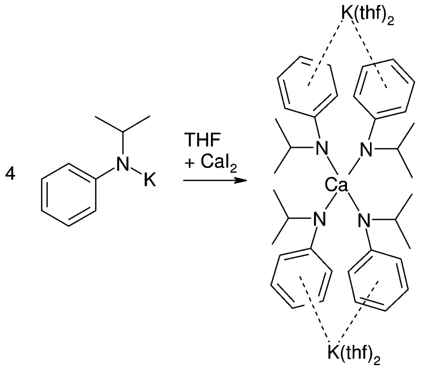


Figure 1. Molecular structure and numbering scheme of [(tmeda)Ca(Tmp)$_2$] (**1**). The ellipsoids represent a probability of 40%. Hydrogen atoms are neglected for clarity reasons. Symmetry-related atoms are marked with “A”.

both of these heterobimetallic compounds, the potassium atoms bind to the π systems of the phenyl groups (see below). In compound **4**, the isopropyl groups hinder further aggregation. In order to study the influence of these alkyl substituents, we also prepared [K$_2$Ca(NPh$_2$)$_4$(thf)$_3$]$_\infty$ (**5**), which precipitated with a chain structure.



(3)

4

Molecular Structures. Molecular structures and numbering schemes of **1** and **2** are represented in Figures 1 and 2. The tetra-coordinate calcium atom of **1** is in a tetrahedral environment which is distorted due to a rather small bite of the TMEDA ligand, leading to a small N2−Ca−N2A angle of 70.4(2)°. Due to electrostatic attraction, the Ca−N1 bond length of 227.5(2) pm to the anionic amide ligand is much smaller than the Ca−N2 distance of 264.5(2) pm to the neutral TMEDA ligand. The nitrogen atoms of the 2,2,6,6-tetramethylpiperidide ligands show angle sums of 359.9° and, hence, are in a trigonal-planar environment.

The 2,2,6,6-tetramethylpiperidide anion shows a chair conformation, as is also observed for the alkali metal derivatives [(tmeda)NaTmp]$_2$ and [(tmeda)KTmp]$_2$ with central M$_2$N$_2$ rings.[35] The average N−C bond length shows a value of 146.3(3) pm.

In [(thf)$_3$Ca{N(Ph)*i*Pr}$_2$] (**2**), the calcium atom shows a distorted trigonal-bipyramidal environment with the bulkier amido ligands in the equatorial plane. In addition, the axial THF molecules are bent toward the smaller equatorial THF ligand, leading to a O1−Ca−O3 angle of 155.98(7)°. Enhancement of the coordination number of the calcium atom also leads to a slight but significant elongation of the Ca−N1 bond. Selected bond lengths of mononuclear calcium bis(amides) are compared in Table 1. In several cases, the coordination number of the calcium atom is extended by additional weak interactions to alkyl and aryl groups (agostic bonds). These interactions gain importance with a decreasing coordination number, and therefore, the Ca−N distances correlate only weakly with the coordination number of the alkaline earth metal atom. Alkylated amides exhibit a larger nucleophilicity, leading to short Ca−N distances. The strong Ca−N$_{\mathrm{amide}}$ interactions of [(tmeda)Ca(Tmp)$_2$] (**1**) lead to large Ca−N distances of the TMEDA coligand. An extremely small Ca−N bond length was found in chainlike [(thf)$_2$Ca(NH$_2$−BH$_3$)$_2$]$_\infty$ with two significantly different values of 206.9(7) and 236.2(7) pm.[38]

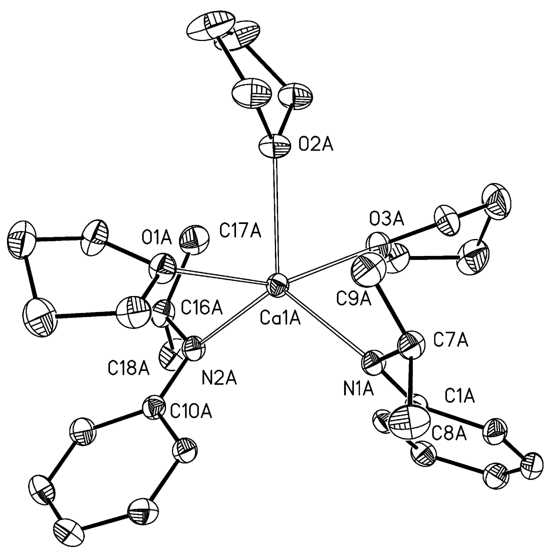


Figure 2. Molecular structure and numbering scheme of molecule A of [(thf)$_3$Ca{N(Ph)*i*Pr}$_2$] (**2**). The ellipsoids represent a probability of 40%. The second molecule B and all hydrogen atoms are omitted for clarity reasons.

In **2**, very different N−C bond lengths were found. The N−C$_{\mathrm{Ph}}$ distances are much smaller (average value 137.1 pm) than the N−C$_{i\mathrm{Pr}}$ values (average 146.0 pm). This fact and the coplanar orientation of the phenyl and amido moieties can be explained by delocalization of the anionic charge into the aryl substituent.

Due to this fact, the more electron-rich phenyl groups can easily act as Lewis bases to rather soft cations. This principle is realized in the mixed K/Ca amides [K$_2$Ca{N(Ph)Me}$_4$]$_\infty$ (**3**), [{(thf)$_2$K(μ-N(Ph)*i*Pr)$_2$}$_2$Ca] (**4**), and [K$_2$Ca(NPh$_2$)$_4$(thf)$_3$]$_\infty$ (**5**). The molecular structure and numbering scheme of **4** are shown in Figure 3. All amido groups are bound to calcium, leading to the calciate anion [Ca{N(Ph)*i*Pr}$_4$]$^{2-}$ with

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Table 1. Comparison of Selected Bond Lengths (Average Values, pm) of Mononuclear Calcium Bis(amides) Dependent on the Coordination Number of the Calcium Atom (CN(Ca))

compound[a]	CN(Ca)	$Ca-N_{amide}$	$Ca-O_{coligand}$	$Ca-N_{coligand}$	ref
$(thf)Ca[N(SiMe_3)(SiPh_2tBu)]_2$	3[b]	232.3	238.2		13
$(dme)Ca[N(SiMe_3)_2]_2$	4	227.1	239.7		36
$(thf)_2Ca[N(SiMe_3)_2]_2$	4	230.2	237.7		10
$(thf)_2Ca[N(SiMe_3)(SiPh_3)]_2$	4	236.0	237.3		13
$(py)_2Ca[N(SiMe_3)(SiMe_2tBu)]_2$	4	235.3		253.7	13
$(hmpa)_2Ca[N(SiMe_3)(SiMe_2tBu)]_2$	4	239.0	228.0		13
$(thf)_2Ca[N(Ar')SiMe_3]_2$	4	231.4	236.7		19
$(thf)_2Ca[N(Ar'')SiMe_3]_2$	4	230.4	234.3		20
$(tmeda)Ca[N(Ar'')SiMe_3]_2$	4	231.1		252.9	20
$(tmeda)Ca(Tmp)_2$	4	227.5		264.5	this work
$(thf)_3Ca[N(SiMe_2CH_2)_2]_2$	5	233.6	240.2		9
$(thf)_3Ca[N(Ph)iPr]_2$	5	234.9	242.7		this work
$(dme)_2Ca(NPh_2)_2$	6	236.9	247.7		4
$(py)_4Ca(carbazolyl)_2$	6	244.3		252.5	6
$(dme)_2Ca[\{N(tol)C(Ph)\}_2]_2$	6	233.3	242.1		37

[a] $Ar' = 2,6\text{-}iPr_2C_6H_3$; $Ar'' = 2,4,6\text{-}Me_3C_6H_2$ (mesityl); dme = 1,2-dimethoxyethane; hmpa = $OP(NMe_2)_3$; py = pyridine; thf = tetrahydrofuran; tmeda = $Me_2N(CH_2)_2NMe_2$; Tmp = $N(CMe_2CH_2)_2CH_2$ (2,2,6,6-tetramethylpiperidyl); tol = *para*-tolyl. [b] Coordination number is enhanced due to intramolecular agostic interactions.

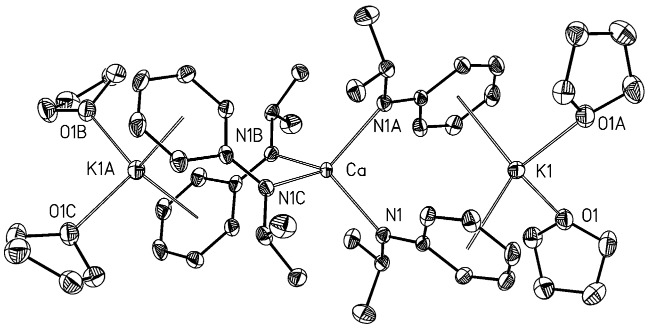

Figure 3. Molecular structure and numbering scheme of $[\{(thf)_2K(\mu\text{-}N(Ph)iPr)_2\}_2Ca]$ (**4**). Hydrogen atoms are not shown for clarity reasons. The ellipsoids represent a probability of 40%. Symmetry-related atoms are marked with capital letters "A", "B", and "C". Selected bond lengths (pm): Ca−N1 241.8(2), K1−O1 268.7(2). Angles (deg): N1−Ca−N1A 99.91(7), N1−Ca−N1B 114.45(4), O1−K1−O1A 108.55(7).

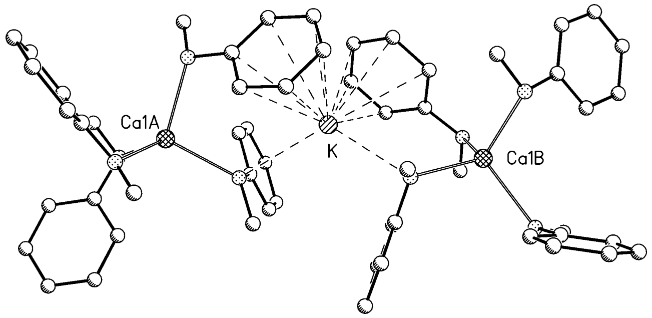

Figure 4. Part of the crystal structure of polymeric $[K_2Ca\{N(Ph)Me\}_4]_\infty$, **3**, which forms a three-dimensional structure. The balls are shown with arbitrary radii. Hydrogen atoms are neglected for clarity reasons.

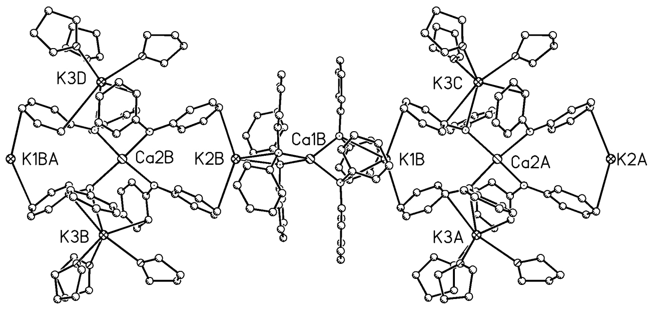

Figure 5. Part of the chainlike structure of $[K_2Ca(NPh_2)_4(thf)_3]_\infty$ (**5**). For clarity reasons, the atoms are drawn with arbitrary radii. Symmetry-related atoms are marked with capital letters "A" and "B". Hydrogen atoms are omitted for clarity reasons.

a tetra-coordinate calcium center and a Ca−N bond length of 241.8(2) pm. This rather large value results from intramolecular electrostatic repulsion between the amido groups. A smaller coordination number of 3, as observed in the calciate anion $[Ca\{N(SiMe_3)_2\}_3]^-$, reduces these repulsive forces, and Ca−N distances of only 230.46(7) pm were determined.[39]

Attached to this $[Ca\{N(Ph)iPr\}_4]^{2-}$ anion are two $K(thf)_2$ units, with each potassium atom bound to two π systems of phenyl groups. These K−C distances vary between 315.6(2) and 325.9(2) pm. The K−O bond length of 268.7(2) pm appears to be in the expected range.

The crystal structure of $[K_2Ca\{N(Ph)Me\}_4]_\infty$ (**3**) is damaged due to disordering of the amido ligands and twinning problems and will not be discussed in further detail. However, the same structural principle as observed in **4** was observed. Due to a smaller alkyl group (methyl in **3** instead of isopropyl in **4**), the formation of a three-dimensional network was observed. The structural motif is shown in Figure 4 and also consists of tetrakis(amido)calciate anions which are interconnected by potassium ions that interact with the π systems of the phenyl groups.

Enhancing the number of phenyl groups by replacement of the isopropyl group with another phenyl substituent leads to the formation of the calciate anion $[Ca(NPh_2)_4]^{2-}$ with a tetra-coordinate calcium center and an average Ca−N bond length of 240.3 pm. The potassium cations K1 and K2 interconnect these calciate anions via bonds to the amido nitrogen atoms and to the π systems of the phenyl groups, leading to a chainlike structure. Additional $K(thf)_3$ moieties with an average K−O distance of 265.2 pm are attached at the periphery of this one-dimensional coordination polymer, as shown in Figure 5. Comparable structural fragments were already observed in the homometallic complex $[(thf)_3\text{-}KNPh_2]_2$, with an average K−O bond length of 272.0 pm,[40]

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and in $\{[(\mathrm{diox})_2\mathrm{KNPh}_2]\cdot\mathrm{diox}\}_\infty$ (diox = 1,4-dioxane), with an average K−O value of 272.2 pm.[41]

Summary and Conclusion

Salt elimination reactions offer suitable access routes to calcium bis(amides) regardless of the substituents at the nitrogen atoms. Another suitable access route resembles the metalation of 2,2,6,6-tetramethylpiperidine with in situ prepared dibenzylcalcium. This compound class now includes compounds such as dialkylamides, bis(trialkylsilyl)amides, diphenylamides, *N*-alkyl-phenylamides, and *N*-phenyl-trialkylsilylamides of calcium. In all of these derivatives, the coordination sphere of the calcium center is sterically saturated by additional neutral coligands such as ethers, HMPA, or amines and often by intramolecular agostic interactions. The coordination number is limited by the bulkiness of the ligands, varying between three and six.

The preparation of these calcium bis(amides) affords special care regarding the stoichiometry. An excess of potassium amide during the metathesis reaction of KNR_2 with CaI_2 leads to the formation of calciates of the type $[(\mathrm{L})_n\mathrm{K}_2\mathrm{Ca}\{\mathrm{N(Ph)R}\}_4]$ regardless of the stoichiometry, L being neutral coligands such as ethers. These calciate anions contain distorted tetrahedrally coordinated calcium centers with enhanced Ca−N bond lengths due to electrostatic repulsion between the amido ligands. The soft potassium atoms bind to the nitrogen atoms as well as the π systems of the phenyl groups. These coordination modes can lead to aggregation polymers such as chainlike structures or three-dimensional networks. Inverse crown structures as observed for heterobimetallic magnesium amides were not yet observed for the heavier calcium congeners. For larger amides, tris(amido)calciates with three-coordinate calcium atoms were also observed and structurally characterized.[24−26]

Experimental Section

General Remarks. All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. The solvents were dried according to common procedures and distilled under argon. Deuterated solvents were dried over sodium, degassed, and saturated with argon. The ^{1}H and ^{13}C{^{1}H} spectra were obtained either on a Bruker AC 400 MHz or on a Bruker 200 MHz spectrometer. Mass spectra were obtained on a Finnigan MAT SSQ 710 system, and IR measurements were carried out using a Perkin-Elmer System 2000 FTIR. The IR spectra were taken as Nujol mulls between KBr windows. Melting and decomposition points were measured with a Reichert-Jung type 302102 apparatus and are uncorrected. Most of the compounds were pyrophoric, and therefore we were unable to perform reliable CHN analyses. The THF adduct **2** lost THF during handling and weighing, and a reliable CHN analysis was not obtained.

Synthesis of $[(\mathrm{tmeda})\mathrm{Ca}(\mathrm{Tmp})_2]$ (1). Benzyl potassium (793 mg, 6.09 mmol) was suspended in 15 mL of toluene, and 2,2,6,6-tetramethylpiperidine (1.20 mL, 7.11 mmol), solid CaI_2 (885 mg, 3.01 mmol), and TMEDA (2.5 mL, 16.78 mmol) were added successively at room temperature. After stirring overnight, a precipitate of colorless KI was removed, and the volume of the resulting dark red solution was reduced to a third of its original volume. At −20 °C, **1** precipitated in colorless crystals suitable for X-ray structure analysis (237 mg, 0.54mmol, 17,9%). Another crop of crystals of **1** was obtained after the removal of all volatile materials, the addition of 4 mL of benzene, the removal of all solids, and storage at 4 °C (168 mg, 0.38 mmol, 12,7%). Mp: 157.5 °C (dec.). ^{1}H NMR (25 °C, [D$_6$]benzene): δ 1.45 (CH_3 (Tmp)), 1.53 (β-CH_2 (Tmp)), 1.87 (CH_2 (tmeda) + CH_3 (tmeda)), 2.06 (γ-CH_2 (Tmp)). ^{13}C NMR (25 °C, [D$_6$]benzene): δ 21.1 (γ-CH_2 (Tmp)), 35.3 (CH_3 (Tmp)), 40.9 (β-CH_2 (Tmp)), 47.3 (CH_3 (tmeda)), 52.7 (α-C (Tmp)), 56.7 (CH_2 (tmeda).

Synthesis of $[(\mathrm{thf})_3\mathrm{Ca}\{\mathrm{N(Ph)}i\mathrm{Pr}\}_2]$ (2). The addition of 444 mg of solid CaI_2 (1.51 mmol) at room temperature to a stirred solution of 524 mg of KN(Ph)*i*Pr (3.02 mmol) in 15 mL of THF led to the precipitation of colorless KI. After 3 h, all solids were removed, and the volume of the filtrate was reduced to half of the original volume. Then, 3 mL of toluene and 3 mL of pentane were added, and a precipitate of **2** formed at −78 °C. Another crop of crystals of **2** was obtained at −20 °C after the addition of another 4 mL of pentane. Yield: 855 mg (1.63 mmol, 54%). ^{1}H NMR ([D$_8$]THF): δ 6.73 (4H, dd, $^3J_{\mathrm{H,H}} = 7.6$ Hz, *m*-H); 6.11 (4H, d, $^3J_{\mathrm{H,H}} = 7.8$ Hz, *o*-H); 5.85 (2H, t, $^3J_{\mathrm{H,H}} = 6.8$ Hz, *p*-H); 3.58 (m, THF); 3.42 (2H, hept, $^3J_{\mathrm{H,H}} = 6.2$ Hz, CH); 1.73 (m, THF); 1.13 (12H, d, $^3J_{\mathrm{H,H}} = 6.4$ Hz, CH_3). ^{13}C{^{1}H} NMR ([D$_8$]THF): 157.1 (*i*-C); 126.6 (*m*-C); 109.6 (*o*-C); 104.9 (*p*-C); 65.0 (THF); 44.8 (CH); 23.1 (THF); 21.4 (CH_3). MS [DEI; *m*/*z* (%)]: 401 (39); 386 (6) $[401 - \mathrm{CH}_3]^+$; 358 (18) $[401 - i\mathrm{Pr}]^+$; 268 (21); 253 (14); $[268 - \mathrm{CH}_3]^+$; 225 (11) $[268 - i\mathrm{Pr}]^+$; 135 (42) $[i\mathrm{PrHNPh} + \mathrm{H}]^+$; 120 (100) $[135 - \mathrm{CH}_3]^+$. IR: 3414 vw, 3046 w, 2924 vs, 2854 vs, 2591 vw, 1592 s, 1541 w, 1504 m, 1482 vs, 1465 s, 1375 m, 1344 m, 1305 vs, 1271 m, 1255 s, 1182 m, 1136 m, 1077 vw, 1028 m, 987 w, 962 w, 770 m, 745 s, 696 m, 493 w.

Synthesis of $[\mathrm{K}_2\mathrm{Ca}\{\mathrm{N(Ph)Me}\}_4]_\infty$ (3). Solid anhydrous CaI_2 (464 mg, 1.55 mmol) was added to a stirred solution of KN(Ph)Me (899 mg, 6.19 mmol) in 10 mL of THF. After stirring overnight, all precipitates (mainly KI) were removed. After reduction of the volume of the solution to 30% of its original volume, 3 mL of toluene was added. Storage at −20 °C led to the crystallization of **3**. Yield: 361 mg (0.66 mmol; 43%). ^{1}H NMR ([D$_8$]THF): δ 6.80 (8H, dd, $^3J_{\mathrm{H,H}} = 7.8$ Hz, *m*-H); 6.29 (8H, d, $^3J_{\mathrm{H,H}} = 6.6$ Hz, *o*-H); 5.94 (4H, t, $^3J_{\mathrm{H,H}} = 6.6$ Hz, *p*-H); 2.75 (12H, s, CH_3). ^{13}C{^{1}H} NMR ([D$_8$]THF): δ 160.5 (*i*-C); 128.8 (*m*-C); 112.3 (*o*-C); 108.8 (*p*-C); 35.4 (CH_3). IR: 3436 w, 3047 m, 2921 vs, 2853 vs, 2814 s, 2766 s, 2607 vw, 2548 vw, 1908 w, 1765 w, 1583 vs, 1540 s, 1508 s, 1481 vs, 1417 m, 1376 m, 1334 vs, 1315 vs, 1274 s, 1181 vs, 1151 m, 1078 m, 1040 m, 1017 m, 971 vs, 845 m, 792 s, 753 vs, 700 vs, 577 m, 523 m.

Synthesis of $[\{(\mathrm{thf})_2\mathrm{K}(\mu\text{-}\mathrm{N(Ph)}i\mathrm{Pr})_2\}_2\mathrm{Ca}]$ (4). To a stirred solution of KN(Ph)*i*Pr (527 mg, 3.04 mmol) in 12.5 mL THF was added anhydrous CaI_2 (223 mg, 0.76 mmol). After stirring overnight, the resulting colorless precipitate of KI was removed by filtration. Reduction of the volume of the filtrate, the addition of 3 mL of toluene, and storage at −20 °C led to the crystallization of **4**. Yield: 378 mg (0.4 mmol; 53%). Mp: 80 °C (dec.). ^{1}H NMR ([D$_8$]THF): 6.81 (8H, b, *m*-H); 6.32 (8H, b, *o*-H); 5.89 (4H, b, *p*-H); 3.59 (THF); 3.46 (4H, hept, $^3J_{\mathrm{H,H}} = 6.2$ Hz, CH); 1.77 (THF); 1.18 (24H, d, $^3J_{\mathrm{H,H}} = 6.0$ Hz, CH_3). ^{13}C{^{1}H} NMR ([D$_8$]THF): 159.9 (*i*-C); 129.9 (*m*-C); 112.7 (*o*-C); 107.7 (b, *p*-C); 47.9 (CH); 26.2 (CH_3). IR: 3441 w, 3068 m, 3037 m, 2939 vs, 2668 w, 2586 w, 2550 w, 1888 w, 1797 w, 1587 vs, 1528 vs, 1489 vs, 1458 vs, 1377 s, 1341 vs, 1321 vs, 1277 s, 1192 vs, 1166 s, 1137 s, 1118 m, 1052 vs, 1024 s, 984 s, 957 s, 904 m, 823 m, 812 s, 744 vs, 690 vs, 604 m, 535 m, 491 m.

Synthesis of $[\mathrm{K}_2\mathrm{Ca}(\mathrm{NPh}_2)_4(\mathrm{thf})_3]_\infty$ (5). A solution of $\mathrm{KN(Ph)}_2$ (1.035 g, 4.99 mmol), 15 mL of THF, and anhydrous CaI_2 (366

Table 2. Crystal Data and Refinement Details for the X-ray Structure Determinations of the Calcium Bis(amides) **1** and **2** As Well As of the Tetrakis(amino)calciates **3**, **4**, and **5**

compound	**1**	**2**	**3**	**4**	**5**
formula	$C_{24}H_{52}CaN_4$	$C_{30}H_{48}CaN_2O_3$	$C_{28}H_{32}CaK_2N_4$	$C_{36}H_{48}CaN_4$*2($C_8H_{16}KO_2$)	$C_{60}H_{62}CaK_2N_4O_3$
fw (g·mol^{-1})	436.78	524.78	542.86	943.48	1005.42
T/°C	−90(2)	−90(2)	−90(2)	−90(2)	−90(2)
cryst syst	monoclinic	orthorhombic	cubic	tetragonal	orthorhombic
space group	$C2/c$	$P2_12_12_1$	$I\bar{4}3d$	$I\bar{4}2d$	$Fdd2$
a/Å	17.7149(7)	13.0476(3)	28.4956(4)	18.0194(8)	30.6638(6)
b/Å	10.5141(4)	14.8263(3)	28.4956(4)	18.0194(8)	33.8849(8)
c/Å	15.6061(5)	31.6952(5)	28.4956(4)	16.4929(7)	20.4672(4)
α/deg	90.00	90.00	90.00	90.00	90.00
β/deg	110.466(2)	90.00	90.00	90.00	90.00
γ/deg	90.00	90.00	90.00	90.00	90.00
V/Å^3	2723.26(17)	6131.4(2)	23138.4(6)	5355.2(4)	21266.2(8)
Z	4	8	24	4	16
ρ (g cm^{-3})	1.065	1.137	0.935	1.170	1.256
μ (cm^{-1})	2.46	2.35	3.95	3.17	3.23
measured data	9415	29736	70429	18171	35570
data with $I > 2\sigma(I)$	2557	9435	3113	2568	8375
unique data/R_{int}	3111/0.0	13687/0.0565	4401/0.1023	3058/0.0398	11630/0.0599
wR_2 (all data, on F^2)^a	0.1848	0.1251		0.0975	0.1496
R_1 ($I > 2\sigma(I)$)^a	0.0665	0.0548		0.0373	0.0567
s^b	1.157	1.015		1.021	1.015
res. dens./e·Å^{-3}	0.451/−0.380	0.336/−0.349		0.270/−0.153	1.229/−0.413
Flack parameter		−0.02(3)		0.01(5)	0.02(4)
abs method	none	none		none	none
CCDC No.	702724	702725		702726	702727

[a] Definition of the R indices: $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$. $wR_2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o{}^2) + (aP)^2$. [b] $s = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/(N_o - N_p)\}^{1/2}$.

mg, 1.24 mmol) was stirred overnight. The resulting colorless KI was removed by filtration, and the volume of the filtrate was reduced to half of the original volume. The addition of 2 mL of toluene and 2 mL of pentane as well as storage at −78 °C led to the precipitation of **5**. Yield: 718 mg (0.71 mmol, 57%). ^{1}H NMR ([D$_8$]THF): 6.91 (16H, b, *m*-H); 6.91 (16H, b, *o*-H); 6.34 (8H, broad, *p*-H); 3.61 (THF); 1.78 (THF). ^{13}C{^{1}H} NMR ([D$_8$]THF): 153.9 (*i*-C); 129.5 (*m*-C); 118.0 (b, *o*-C); 114.9 (b, *p*-C); 68.1 (THF); 26.3 (THF).

X-Ray Structure Determinations. The intensity data for compounds **1**−**5** were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects.[42,43] The structures were solved by direct methods (SHELXS)[44] and refined by full-matrix least-squares techniques against $F_o{}^2$ (SHELXL-97;[45] Table 2). The hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[45] The crystals of **3** were extremely thin and of low quality, resulting in a substandard data set; however, the structure is reliable enough to show connectivity and geometry despite the high final R value. We will only publish the conformation of the molecule and the crystallographic data. We will not deposit the data in the Cambridge Crystallographic Data Centre. The crystal of **1** was a nonmerohedral twin. The twin law was determined by PLATON[46] to (−1,0,0/0,−1,0/0.616,0,1). The contribution of the main component was refined to 0.799(4). XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

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Supporting Information Available: CIF files giving data collection and refinement details as well as positional coordinates of all atoms. This material is available free of charge via the Internet at http://pubs.acs.org. In addition, crystallographic data (excluding structure factors) have also been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-702724 for **1**, CCDC-702725 for **2**, CCDC-702726 for **4**, and CCDC-702727 for **5**. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U. K. (e-mail: deposit@ccdc.cam.ac.uk).

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