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Synthesis and Molecular Structures of Phenylamides of Magnesium, Calcium, Strontium, and Barium – From Molecular to Polymeric Structures

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Several preparative procedures for the synthesis of the THF complexes of the alkaline earth metal bis(phenylamides) of Mg (**1**), Ca (**2**), Sr (**3**), and Ba (**4**) are presented such as metalation of aniline with strontium and barium, metathesis reactions of MI_2 with KN(H)Ph, and metalation of aniline with arylcalcium compounds or dialkylmagnesium. The THF content of these compounds is rather low and an increasing aggregation is observed with the size of the metal atom. Thus, tetrameric $[(THF)_2Ca\{\mu\text{-}N(H)Ph\}_2]_4$ (**2**) and polymeric $[(THF)_2Sr\{\mu\text{-}N(H)Ph\}_2]_\infty$ and $\{[(THF)_2Ba\{\mu\text{-}N(H)Ph\}_2]_2[(THF)Ba\{\mu\text{-}N(H)Ph\}_2]_2\}_\infty$ show six-coordinate metal atoms with increasing interactions to the π systems of the phenyl groups with increasing the radius of the alkaline earth metal atom.

Introduction

The amides of the heavy alkaline earth metals of the type $M(NH_2)_2$ have been well-known for many decades.[1] For the synthesis of these amides, the alkaline earth metals are dissolved in liquid ammonia, and $M(NH_2)_2$ forms within days or weeks. However, the heavier alkaline earth metals tend to form the amides $Sr(NH_2)_2$ and $Ba(NH_2)_2$ much more easily. Thus, the reaction of calcium with ammonia at room temperature needs several months for a complete turnover, whereas strontium and barium quantitatively form the amides in ammonia within 8 and 2 days, respectively.[2,3] For magnesium bis(amide), the reaction of Mg_3N_2 with ammonia at 350 °C and 10 atm also offers a suitable option.[1] Calcium and strontium bis(amide) crystallize isotypically with six-coordinate metal centers with Ca−N and Sr−N distances of 257 and 273 pm, respectively.[2] However, the hydrogen atoms were not located. The barium atoms in $Ba(NH_2)_2$ adopt larger coordination numbers of seven and eight with Ba−N bond lengths between 275 and 324 pm.[3] In addition, molecular structures of monomeric $M(NH_2)_2$[4] as well as their HF complexes[5] were derived from quantum chemical calculations and showed bent NMN fragments for strontium and barium as a result of (i) d-orbital participation at the metal, (ii) significant covalent M−N bond contributions, and (iii) cation polarization by the anions.[5] Soluble amides of the heavy alkaline earth metals were obtained for $M[N(SiMe_3)_2]_2$.[6,7] Because of the bulkiness of these ligands, small coordination numbers of the metal atoms are observed, for example, all of these complexes form bis(THF) complexes of the type $(THF)_2M[N(SiMe_3)_2]_2$ (M = Mg,[8] Ca,[9] Sr,[9] Ba[10]), and solvent-free compounds crystallize as $[(Me_3Si)_2N{-}M\{\mu\text{-}N(SiMe_3)_2\}_2M{-}N(SiMe_3)_2]$ with three-coordinate metal atoms (M = Mg,[11] Ca,[12] Sr,[13] Ba[10]). The substitution of one of the trimethylsilyl groups by a bulky aryl ligand led to

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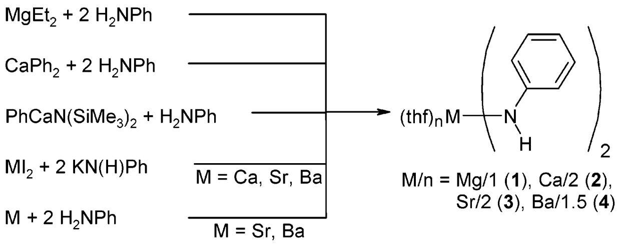
$(THF)_2M[N(Aryl)SiMe_3]_2$.[14,15] The ether adducts of $M(NPh_2)_2$ with six-coordinate alkaline earth metal atoms show bent NMN moieties,[16] which can be interpreted in agreement with the suggestion of Schleyer and co-workers[5] that the anionic ligands dominate the molecular structures and that the neutral coligands such as THF or DME occupy the vacant coordination sites, with an insignificant influence on the structure. Here, we investigated the anilides of the alkaline earth metals to study the transition from salt-like $M(NH_2)_2$ to the molecular ether complexes of $M(NPh_2)_2$.

Results and Discussion

Synthesis. The phenylamides (anilides) of magnesium (**1**) are accessible by metalation of aniline with dialkylmagnesium. Calcium bis(phenylamide) (**2**) can be prepared by several procedures. The metalation of aniline with diphenylcalcium in THF yields bis(tetrahydrofuran)calcium bis(phenylamide) (**2**). Another possibility represents the metathesis reaction of CaI_2 with KN(H)Ph or the metalation of aniline with $PhCaN(SiMe_3)_2$. This latter reaction leads to the formation of $[PhN(H)-Ca-N(SiMe_3)_2]$, which dismutates immediately to **2** and extremely soluble $(THF)_2Ca[N(SiMe_3)_2]_2$. However, a metalation of aniline with calcium powder, which was produced via the solvation of calcium in liquid ammonia and the immediate removal of NH_3, failed. The heavier and more reactive alkaline earth metals strontium and barium are able to deprotonate aniline directly. The metathesis reaction offers another option to prepare bis(tetrahydrofuran)strontium (**2**) and sesqui(tetrahydrofuran)barium bis(phenylamide) (**3**). Eq 1 gives an overview of the preparative procedures.



The NMR data support the rather-low THF content of the crystalline compounds. All of these compounds are colorless and insoluble in hydrocarbons. In diethylether, decreasing solubility is observed with increasing size of the metal atoms. Magnesium compound **1** precipitated as an amorphous solid not suitable for X-ray diffraction experiments. The THF content was determined by the integration of the ^1H NMR spectrum and from titrations. However, mono(ether) adducts of magnesium bis(amides) usually contain one bridging and one terminal amido ligand; the ether molecules occupy terminal positions, leading to distorted tetrahedral environments of the magnesium atoms. Such molecular structures were characterized by X-ray crystallography for $[(Et_2O)Mg\{o\text{-}N(SiMe_3)\}_2C_6H_4]_2$,[17] $[(THF)Mg\{N(tBu)\}_2SiMe_2]_2$,[18] $[(THF)Mg\{N(CH_2Ph)_2\}_2]_2$,[19] and $[(THF)Mg\{\mu\text{-}N(H)Ph\}\{N(SiMe_3)_2\}]_2$.[20] We could neither observe the formation of doubly deprotonated aniline nor the formation of already well-known[21] magnesium phenylimide $[(THF)MgNPh]_6$, during the stoichiometric reaction of dialkylmagnesium with aniline.

Table 1. Comparison of the NMR Data of the Alkaline Earth Metal Bis(phenylamides) of Mg (**1**), Ca (**2**), Sr (**3**), and Ba (**4**)

	H_2NPh	1	2	3	4
		^1H NMR			
δ(ortho-H)	6.65	5.92	6.25	6.21	6.43
δ(meta-H)	7.10	6.75	6.69	6.73	6.88
δ(para-H)	6.63	6.41	6.02	6.01	6.27
δ(NH)	4.32	2.17	3.02	3.19	4.13
		$^{13}C\{^1H\}$ NMR			
δ(ipso-C)	149.2	156.3	162.2	161.7	[a]
δ(ortho-C)	115.1	119.2	117.3	116.3	[a]
δ(meta-C)	129.6	129.6	129.1	129.8	[a]
δ(para-C)	117.4	116.1	110.6	110.3	[a]

[a] Compound **4** is only sparingly soluble, and reliable ^{13}C NMR data were not obtained.

The anilides of calcium (**2**), strontium (**3**), and barium (**4**) are only sparingly soluble in THF, whereas the diphenylamides of these metals were soluble in THF and 1,4-dioxane. The anilides proved to be insoluble in solvents such as 1,4-dioxane, diethylether, 1,2-dimethoxyethane as well as in aliphatic and aromatic hydrocarbons. Once crystallized, barium derivative **4** is insoluble in THF, showing that this Lewis base is not able to compete with the softer η^6-bound phenyl bases. Benzophenone is able to substitute THF in **4**, raising the solubility of barium bis(phenylamide), but no addition reaction took place. Other primary amines such as 2,4,6-trimethylphenylamine, benzylamine, and 4-aminopyridine reacted with activated barium powder; however, insoluble barium bis(amides) were obtained.

In Table 1, the NMR data of these anilides are listed, and the parameters of aniline are included for comparison reasons.[22] Large dependency between the chemical shifts and the alkaline earth metals was observed for the nitrogen-bound protons, which showed a shift to higher δ values, as the size of the metal atom increases. The ^{13}C NMR data show a weaker influence of the metal atoms on these δ values. All of these anilides of the alkaline earth metals contain chemically inequivalent anilide groups. However, in the NMR spectra only one set of resonances was observed. The insolubility in many organic solvents suggests aggregation.

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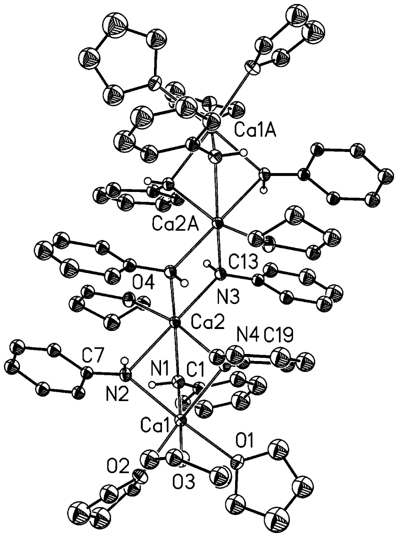

Figure 1. Molecular structure of tetranuclear $[(THF)_2Ca\{N(H)Ph\}_2]_4$ (**2**). Hydrogen atoms are omitted for clarity reasons, except N−H ones. Symmetry-related atoms ($-x + 1$, $-y$, $-z + 2$) are marked with "A". Selected bond lengths (pm): Ca1−O1 241.1(2), Ca1−O2 244.0(2), Ca1−O3 240.1(2), Ca1−N1 242.5(2), Ca1−N2 240.7(2), Ca1−N4 241.8(2), Ca2−O4 243.5(2), Ca2−N1 250.7(2), Ca2−N2 261.7(2), Ca2−N3 245.8(2), Ca2−N4 249.2(2), Ca2−N3A 247.0(2), N1−C1 138.5(3), N2−C7 138.2(3), N3−C13 138.2(3), N4−C19 137.9(3), Ca1···Ca2 331.01(7), Ca2···Ca2A 367.08(9).

However, on the NMR time scale a rapid exchange leads to one set of resonances for the anilide groups. In addition, a breaking up of the aggregates in solution cannot be excluded. The NMR experiments of barium derivative **4** has to be performed from freshly prepared solutions because after crystallization the solubility was too low to obtain unambiguous NMR spectra. This fact suggests that the solution contained smaller units than the solid phase.

Molecular Structures. The low THF content and the fact that these compounds are sparingly soluble in THF and insoluble in hydrocarbons point to oligomeric structures of the alkaline earth metal bis(phenylamides). Even though the ether content is rather similar for all of the derivatives of the heavier alkaline earth metals, the molecular structures differ significantly.

The molecular structure of tetranuclear $(THF)_2Ca[N(H)Ph]_2$ (**2**) is represented in Figure 1. In this centrosymmetric molecule with a central planar Ca_2N_2 ring, the outer calcium atoms show three bridging amide substituents, thus forming trigonal Ca_2N_3 bipyramids with the metal atoms in apical positions. Although the calcium atoms are in different environments, the octahedral coordination spheres are completed by additional THF molecules.

The six-coordinate calcium atoms Ca1 and Ca2 are bridged by three anilide substituents. These nitrogen atoms, N1, N2, and N3, represent the common face of the two coordination octahedra. As a result of the common face, the calcium atoms show a rather small Ca1···Ca2 distance of only 330.9(2) pm, whereas the transannular Ca2···Ca2A contact shows a value of 365.1(2) pm. In contrast to the molecular structure of **2**, the ether adducts of the alkaline earth metal bis(diphenylamides) are monomeric and show bent NMN units. Schleyer and co-workers[5] concluded from theoretical and experimental studies on carbazoles of the alkaline earth metals that the molecular structures depend mainly on the anionic ligands and that the neutral coligands occupy vacant coordination sites without influence on the structure. Deviations from the expected valence-shell electron-pair repulsion (VSEPR) geometries still initiate plenty of investigations on d^0 systems.[4,5,23] Molecules of the type $M(NH_2)_2$ and cations $[M(NH_3)_2]^{2+}$ show bent NMN fragments for the heavy alkaline earth metals.[4,5,24] Keeping these investigations in mind, the bent NMN moieties of the bis(diphenylamides) can be explained by d-orbital participation at the alkaline earth metal atoms. Similar considerations are valid for dimeric compounds and show for the dihydrides that nonclassical structures such as $H{-}M(\mu\text{-}H)_3M$ and $M(\mu\text{-}H)_4M$ are low in energy.[25] Comparable structural features were also observed for some phosphanides[7] of the type $X{-}M(\mu\text{-}PRR')_3M$ with M as Ca,[26] Sr,[27] and Ba.[28] The Ca1−N bond lengths in **2** are smaller than the Ca2−N values because Ca1 is bound to three amides, whereas Ca2 is surrounded by five anilide groups. The intramolecular electrostatic repulsion increases with the number of anions at the metal atom. Enhanced strain at Ca2 can be excluded on the basis of similar Ca1−O and Ca2−O distances.

Strontium derivative **3** crystallized as a polymer of the type $[(THF)_2Sr\{\mu\text{-}N(H)Ph\}_2]_\infty$, with six-coordinate metal atoms in a distorted octahedral environment with the THF molecules in a cis arrangement. Part of this chain is shown in Figure 2. The Sr−O bond lengths vary between 259.6(3) and 270.9(3) pm (average Sr−O 264.0 pm) depending on the intramolecular repulsion between the phenyl groups and the THF ligands. Because of the fact that all of the anilide anions are in bridging positions between strontium atoms, rather small endocyclic N−Sr−N angles (N1−Sr1−N2 77.9(1), N3−Sr1−N4 78.2(1), N3−Sr2−N4 77.0(1), N5−Sr2−N6 79.9(1), N5−Sr3-N6 79.0(1)°) are observed, leading to rather strong distortions of the octahedral environment of the metal centers.

The structure of barium derivative **4** is very similar to the strontium compound. However, the molecular structure has to be described as $\{[(THF)_2Ba\{\mu\text{-}N(H)Ph\}_2]_2[(THF)Ba\{\mu\text{-}N(H)Ph\}_2]_2\}_\infty$ because half of the barium atoms bind only to one THF molecule. Another coordination site is covered by a π-arene contact of the phenyl ring to the barium atom. Counting this π-arene bond as one ligand, a distorted octahedral environment can also be assumed for the metal atoms with the neutral coligands (THF and π-bound arenes) in cis positions. Part of this chain is represented in Figure 3.

On the basis of theoretical investigations of the alkaline

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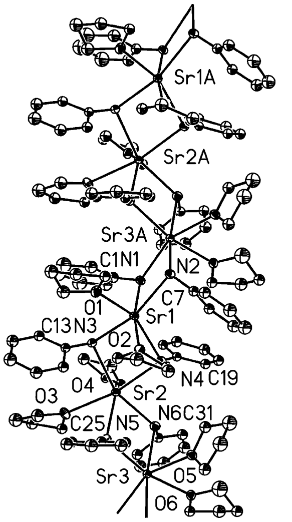

Figure 2. Molecular structure of polymeric $[(THF)_2Sr\{N(H)Ph\}_2]_\infty$ (**3**). Hydrogen atoms are neglected for clarity reasons. Symmetry-related atoms (A: $x + 1$, y, z; B: $x - 1$, y, z) are marked with "A" and "B". Selected bond lengths (pm): Sr1−O1 259.6(3), Sr1−O2 262.7(3), Sr1−N1 263.1(4), Sr1−N2 268.3(4), Sr1−N3 262.0(4), Sr1−N4 262.4(4), Sr2−O3 270.9(3), Sr2−O4 262.6(3), Sr2−N3 262.3(4), Sr2−N4 268.8(4), Sr2−N5 267.6(4), Sr2−N6 259.3(4), Sr3−O5 265.2(3), Sr3−O6 260.3(3), Sr3−N5 264.3(4), Sr3−N6 267.3(4), Sr3−N1A 259.2(3), Sr3−N2A 263.1(4), N1−C1 137.8(6), N2−C7 136.9(6), N3−C13 137.1(6), N4−C19 137.8(5), N5−C25 137.6(6), N6−C31 138.0(6), Sr1⋯Sr2 408.0(1), Sr1⋯Sr3B 406.8(1), Sr2⋯Sr3 407.07(8).

earth metal hydrides,[29,30] halides,[4,31,32] hydroxides,[4] amides,[4] and methanides,[4] one would expect an increasing influence of the metal-centered d orbitals on the molecular structures. However, at first glance strontium and barium derivatives **3** and **4** seem to agree better with the VSEPR model[33] than calcium compound **2**. On the one hand, the increasing electronegativity difference between nitrogen and the alkaline earth metals with their increasing radii leads to a more-ionic bonding situation for the heavier metals, which lowers the importance of the covalent-bond contribution and hence the significance of the d orbitals. On the other hand, the larger cations prefer coordination to soft bases, according to the Pearson concept.[34] These preferences lead to short contacts to carbon atoms of the phenyl groups. For calcium derivative **2**, no short Ca−C contacts are observed. In strontium compound **3**, small distances are found between strontium and the ipso-carbon atoms: Sr1−C1 326.1(5), Sr1−C7 323.0(4), Sr2−C13 333.2(4), Sr2−C19 330.9(4), and Sr3−C31 323.3(4) pm. These contacts lead to a tilting of the anilide substituents and to strongly different Sr−N−C angles. In derivative **4**, the soft π system of a phenyl group is even able to replace a THF molecule. Whereas examples of neutral arenes side-on coordinated to calcium are rather rare,[35,36] there are several examples for barium compounds.[37,38] The

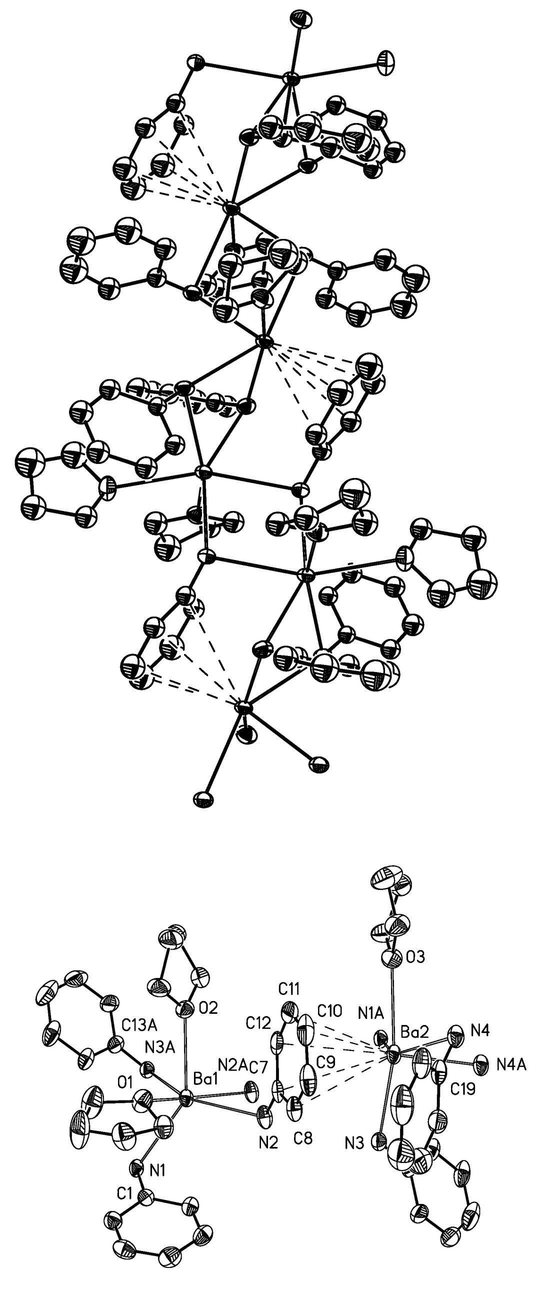

Figure 3. Molecular structure of polymeric $[(THF)_{1.5}Ba\{N(H)Ph\}_2]_\infty$ (**4**). Hydrogen atoms are neglected for clarity reasons. Symmetry-related atoms (A: $-x$, $-y$, $-z + 1$; B: $-x$, $-y + 1$, $-z + 1$) are marked with "A" and "B". Selected bond lengths (pm): Ba1−O1 278.5(5), Ba1−O2 275.0(5), Ba1−N1 276.8(5), Ba1−N2 281.6(5), Ba1−N2A 282.6(5), Ba1−N3A 280.4(5), Ba1−C1 326.7(6), Ba1−C13A 336.2(6), Ba2−O3 275.8(5), Ba2−N3 279.3(6), Ba2−N4 277.7(5), Ba2−N1A 279.1(5), Ba2−N4A 276.0(5), Ba2−C7 351.4(7), Ba2−C9 330.2(8), Ba2−C10 325.1(8), Ba2−C11 329.3(7), Ba2−C12 340.4(6), Ba2−C19 325.0(7), Ba1⋯Ba1A 444.57(7), Ba1⋯Ba2A 412.31(5).

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role of secondary interactions is discussed in detail for the alkaline earth metal pyrazolates.[39]

Summary

The phenylamides (anilides) of the alkaline earth metals adopt behavior and structures that lie between the amides of the types $M(NH_2)_2$ and $M(NPh_2)_2$. All of these amides are colorless solids. The alkaline earth metal bisamides $M(NH_2)_2$ are salt-like solids with solid-state structures, which can be regarded as a packing of cations and anions. They are insoluble in common organic solvents. The ether adducts of the alkaline earth metal bis(diphenylamides) are monomeric molecules, which are soluble in THF and 1,4-dioxane, whereas the anilides are only sparingly soluble in THF and insoluble in hydrocarbons. This fact can be explained by aggregation. Tetranuclear $[(THF)_2Ca\{\mu\text{-}N(H)Ph\}_2]_4$ (**2**), polymeric $[(THF)_2Sr\{\mu\text{-}N(H)Ph\}_2]_\infty$, and $\{[(THF)_2Ba\{\mu\text{-}N(H)Ph\}_2]_2[(THF)Ba\{\mu\text{-}N(H)Ph\}_2]_2\}_\infty$ contain metal atoms in an environment of six ligands and all of the phenylamide ligands are in bridging positions. The strontium and barium atoms show short contacts to the soft π system of the phenyl groups, whereas calcium prefers coordination to the hard oxygen and nitrogen bases, THF and anilide. The phenylamides of magnesium, calcium, strontium, and barium are extremely moisture and air sensitive; contact with air leads to an immediate color change to brown. These amides are not volatile, and efforts to detect molecular ions in mass spectrometric experiments yielded only decomposition products.

The reactivity of activated metal powders increases from magnesium to barium. Light metals magnesium and calcium are not able to deprotonate aniline, whereas strontium and barium react with aniline to the corresponding phenylamides. The metathesis reaction of KN(H)Ph with MI_2 in THF offers an alternative as a result of the insolubility of KI in this solvent. Calcium bis(phenylamides) are also accessible via the metalation of aniline with diarylcalcium or with $PhCaN(SiMe_3)_2$, followed by a dismutation reaction that yields poorly soluble $Ca[N(H)Ph]_2$ and soluble $Ca[N(SiMe_3)_2]_2$.

Experimental Section

All of the manipulations were carried out in an argon atmosphere under anaerobic conditions. The reported compounds are extremely moisture sensitive and lose coordinated THF easily once isolated. It was not possible to weigh out a definite amount because the weight of the substances changed permanently during handling and weighing. Therefore, the analysis is limited to NMR and IR spectroscopic investigations as well as X-ray structure determinations. ^1H NMR and ^{13}C NMR spectra were recorded in $[D_8]THF$ solutions at ambient temperature on a Bruker AC 200 MHz or a Bruker AC 400 MHz spectrometer. All of the spectra were referenced to deuterated THF as an internal standard. DEI-mass spectra were obtained on a Finnigan MAT SSQ 710 system (2,4-dimethoxy-benzylalcohol as matrix), IR measurements were carried out on a PerkinElmer System 2000 FTIR. Decomposition points were measured with a Reichert−Jung apparatus Type 302102. Prior to use, all of the solvents were thoroughly dried and distilled in an argon atmosphere. Aniline was purchased from Alfa Aesar and used without further purification. Barium (99.7%) was purchased form ABCR GmbH & Co. KG and strontium (99+ %) were purchased from Aldrich. Both metals were activated prior to use. $(THF)_4CaI_2$ was obtained from the elements in THF.

Synthesis of $[Mg(NHPh)_2\cdot THF]_2$ (1). A solution of 1.51 g of $(diox)MgEt_2$ (8.85 mmol) in 30 mL of diethyl ether was stirred at room temperature, and aniline (1.65 g, 17.72 mmol) was added dropwise. Upon warming, a colorless precipitate of $[Mg(NHPh)_2]_n$ was formed, and the resulting suspension was stirred for an additional hour. The precipitate was collected and washed with two portions of 10 mL of diethyl ether. After drying in vacuo, 2.22 g (6.15 mmol, 70%) of a colorless, air- and moisture-sensitive solid was isolated. Recrystallization from THF/diethyl ether yielded colorless microcrystalline $[(THF)Mg(NHPh)_2]_2$ (**1**) at −90 °C. The solid decomposed above 50 °C.

^1H NMR (25 °C, 400 MHz): δ 1.73 (THF), 2.17 (2H, s, br, NH), 3.58 (THF), 5.92 (4H, s, br, *o*-CH), 6.41 (2H, s, br, *p*-CH), 6.75 (4H, s, br, *m*-CH). ^{13}C NMR (25 °C, 100 MHz): δ 26.3 (THF), 68.1 (THF), 116.1 (2C, *p*-C), 119.2 (4C, *o*-C), 129.6 (4C, *m*-C), 156.3 (2C, *i*-C). MS (DEI, *m/z*, [%]): 66 [28], 71 [5], 77 (Ph) [3], 93 ($PhNH_2$) [100]. IR (Nujol, KBr, cm^{-1}): 3070 w, 1596 vs, 1484 vs, 1357 m, 1320 w, 1252 vs, 1175 s, 1151 vw, 1070 w, 1025 m, 993 m, 872 m, 817 m, 756 vs, 692 vs, 567 s, 507 m. THF content (by acidic titration): 1.07 per Mg.

Synthesis of $[(THF)_2Ca(NHPh)_2]_4$ (2). $(THF)_4CaI_2$ (1.65 g, 2.83 mmol) was suspended in THF (10 mL), and a solution of potassium phenylamide (potassium anilide) in THF (0.125 M, 45.34 mL, 5.67 mmol) was added dropwise at ambient temperature. During the reaction, $(THF)_4CaI_2$ dissolved completely, whereas a precipitate of KI was formed. The reaction mixture was stirred for 1 h, filtered, and the volume of the filtrate was reduced to half of its original volume. Colorless crystals of $[(THF)_2Ca(NHPh)_2]_4$ (**2**) (0.92 g, 0.624 mmol, 88%) suitable for X-ray structure analysis were obtained during storage of the solution at ambient temperature for 3 days. These crystals were isolated and dried in vacuo. The solid decomposed above 50 °C.

^1H NMR (25 °C, 200 MHz): δ 1.73 (THF), 3.02 (8H, s, br, NH), 3.57 (THF), 6.02 (8H, s, br, *p*-CH), 6.25 (16H, s, br, *o*-CH), 6.69 (16H, s, br, *m*-CH). ^{13}C NMR (25 °C, 50 MHz): δ 26.3 (THF), 68.2 (THF), 110.6 (8C, *p*-C), 117.3 (16C, *o*-C), 129.1 (16C, *m*-C), 162.2 (8C, *i*-C). MS (DEI, *m/z*, [%]): 42 [44], 66 [34], 77 (Ph) [60], 93 ($PhNH_2$) [100], 105 (PhN_2) [15], 182 (PhN═NPh) [40]. IR (Nujol, KBr, cm^{-1}): 1619 vw, 1603 w, 1588 vs, 1499 w, 1346 vw, 1317 vw, 1278 vs, 1171 w, 1037 w, 985 w, 859 vw, 818 vw, 747 m, 693 m, 661 vw, 519 vw, 468 vw.

Synthesis of $[(THF)_2Sr(NHPh)_2]_\infty$ (3). Activated strontium (1.76 g, 20.09 mmol) was suspended in 30 mL of THF, and 3.73 g of aniline (40.05 mmol) was added dropwise at ambient temperature. This reaction mixture was heated under reflux for 5 h. During this time, strontium dissolved and hydrogen gas evolved. After filtration, the volume of the filtrate was reduced to half of its original volume, and the remaining solution was stored at 5 °C. After 2 days, crystalline $[(THF)_2Sr(NHPh)_2]_\infty$ (**3**) (6.19 g, 14.88 mmol, 74%) was obtained, isolated, and dried in vacuo. The solid decomposed above 40 °C.

^1H NMR (25 °C, 400 MHz): δ 1.73 (THF), 3.19 (2H, s, NH), 3.58 (THF), 6.01 (2H, t, $^3J_{H,H} = 7.2$ Hz, *p*-CH), 6.21 (4H, d, $^3J_{H,H} = 8.0$ Hz, *o*-CH), 6.73 (4H, t, $^3J_{H,H} = 7.2$ Hz, *m*-CH). ^{13}C NMR (25 °C, 100 MHz): δ 26.3 (THF), 68.1 (THF), 110.3 (2C, *p*-C), 116.3 (4C, *o*-C), 129.8 (4C, *m*-C), 161.7 (2C, *i*-C). MS (DEI, *m/z*, [%]): 41 [49], 42 [53], 93 ($PhNH_2$) [100], 105 (PhN_2) [3], 182

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(PhN═NPh) [6]. IR (Nujol, KBr, cm^{-1}): 1603 w, 1586 vs, 1557 w, 1498 w, 1344 vw, 1316 w, 1286 vs, 1172 m, 1063 vw, 1040 m, 982 m, 882 vw, 855 w, 816 w, 796 vw, 750 s, 695 m, 538 vw, 518 w.

Synthesis of [(THF)$_{1.5}$Ba(NHPh)$_2$·0.75THF]$_\infty$ (4). Activated barium (0.49 g, 3.57 mmol) and aniline (0.65 g, 6.98 mmol) were heated under reflux in 30 mL of THF for 1 h. During this time, barium dissolved and hydrogen gas evolved. After filtration, the filtrate was stored at ambient temperature. Crystallization began after 3 h and yielded colorless crystals of [(THF)$_{1.5}$Ba(NHPh)$_2$·0.75THF]$_\infty$ (1.39 g, 2.87 mmol, 82%) within 1 day. These crystals were isolated and dried in vacuo. The solid decomposed above 35 °C.

^{1}H NMR (25 °C, 400 MHz): δ 1.73 (THF), 3.58 (THF), 4.13 (2H, s, br, NH), 6.27 (2H, s, br, *p*-CH), 6.43 (4H, s, br, *o*-CH), 6.88 (4H, s, br, *m*-CH). ^{13}C NMR (25 °C, 100 MHz): δ 26.3 (THF), 68.1 (THF), 125.8, 135.7. MS (DEI, *m/z*, [%]): 41 [48], 43 [50], 77 (Ph) [100], 93 (PhNH$_2$) [72], 105 (PhN$_2$) [39], 169 (Ph$_2$NH) [10], 182 (PhN═NPh) [17]. IR (Nujol, KBr, cm^{-1}): 1583 vs, 1498 w, 1474 vs, 1291 vs, 1172 m, 1045 w, 980 m, 852 vw, 815 w, 748 m, 701 w, 623 vw, 519 vw.

X-ray Structure Determinations of 2, 3, and 4.[40] Intensity data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz polarization and for absorption effects.[41−43] Crystallographic data and structure solution and refinement details are summarized in Table 2.

The structures were solved by direct methods (*SHELXS*[44]) and refined by full-matrix least-squares techniques against F_o^2 (*SHELXL-97*[45]). For the amine-groups of **2** and for **3**, the hydrogen atoms were located by difference Fourier synthesis and refined isotropically. All of the other hydrogen atoms were included at calculated positions with fixed thermal parameters. All of the non-hydrogen atoms except for the solvent molecules and the disordered part were refined anisotropically. *XP* (Siemens Analytical X-ray Instruments, Inc.) and *POVRAY* were used for structure representations.

Table 2. Crystal Data and Refinement Details for the X-ray Structure Determinations

compound	**2**	**3**	**4**
formula	$C_{80}H_{112}Ca_4N_8O_8$	$C_{60}H_{84}N_6O_6Sr_3$	$C_{36}H_{48}Ba_2N_4O_3$ * 1.25 C_4H_8O
fw (g·mol^{-1})	1474.10	1248.20	949.59
T/°C	−90(2)	−90(2)	−90(2)
cryst syst	monoclinic	monoclinic	triclinic
space group	P2$_1$/n	P2$_1$/n	P$\bar{1}$
a/Å	12.3052(4)	10.935(2)	12.0064(7)
b/Å	21.7989(5)	23.084(5)	14.4655(7)
c/Å	14.8634(6)	25.096(5)	14.7707(9)
α/deg	90.00	90.00	99.935(3)
β/deg	92.150(2)	93.46(3)	103.939(3)
γ/deg	90.00	90.00	98.784(3)
V/Å^3	3984.1(2)	6323(2)	2401.3(2)
Z	2	4	2
ρ (g·cm^{-3})	1.229	1.311	1.313
μ (cm^{-1})	3.3	25.72	16.68
measured data	25 829	33 784	15 850
data with $I > 2\sigma(I)$	6097	9498	7254
unique data (R$_{int}$)	9075 (0.049)	13 641 (0.062)	10 604 (0.032)
wR2 (all data, on F^2)[a]	0.1481	0.1435	0.1643
R1 ($I > 2\sigma(I)$)[a]	0.0545	0.0518	0.0559
s[b]	1.010	1.030	1.039
Res. dens./e·Å^{-3}	0.506/−0.529	1.553/−0.561	1.476/−0.871
abs method	multiscan	multiscan	multiscan
abs corr *T* min/max	0.9406/0.9703	0.8594/0.9105	0.7594/0.8005
CCDC No.	646883	646884	646885

[a] Definition of the R indices: $R1 = (\sum||F_o| - |F_c||)/\sum|F_o|$ $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$. [b] $s = \{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

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Supporting Information Available: A listing of data collection and refinement procedures and positional coordinates of all of the atoms (CIF files). This material is available free of charge via the Internet at http://pubs.acs.org. In addition, the data deposited at the Cambridge Crystallographic Data Centre under CCDC-646883 (**2**), −646884 (**3**), and −646885 (**4**) and contains the supplementary crystallographic data excluding structure factors. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223−336-033; or deposit@ccdc.cam.ac.uk).

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(40) CCDC-646883 (**2**), -646884 (**3**), and -646885 (**4**) contain the supplementary crystallographic data excluding structure factors. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223−336-033; or deposit@ccdc.cam.ac.uk).

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