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Syntheses and Structures of Alkaline Earth Metal Bis(diphenylamides)

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Various preparative procedures are employed in order to synthesize alkaline earth metal bis(diphenylamides) such as (i) metalation of $HNPh_2$ with the alkaline earth metal M, (ii) metalation of $HNPh_2$ with MPh_2, (iii) metathesis reaction of MI_2 with $KNPh_2$, (iv) metalation of $HNPh_2$ with PhMI in THF, and (v) metathesis reaction of PhMI with $KNPh_2$ followed by a dismutation reaction yielding MPh_2 and $M(NPh_2)_2$. The magnesium compounds $[(diox)MgPh_2]_\infty$ (**1**) and $(thf)_2Mg(NPh_2)_2$ (**2**) show tetracoordinate metal atoms, whereas in $(dme)_2Ca(NPh_2)_2$ (**3**), $(thf)_4Sr(NPh_2)_2$ (**4**), and $(thf)_4Ba(NPh_2)_2$ (**5**) the metals are 6-fold coordinated. Additional agostic interactions between an ipso-carbon of one of the phenyl groups of the amide ligand and the alkaline earth metal atom lead to unsymmetric coordination of the NPh_2 anions with two strongly different M–N–C angles in **3**–**5**.

Introduction

The amides of the alkaline earth metals are a substance class which was studied for a long time. Utke and Sanderson prepared diphenylamine complexes of calcium via the reaction of $HNPh_2$ with calcium metal in liquid ammonia.[1] However, characterization of this insoluble tan compound was limited to reactions with water and air. The preparation of magnesium bis(diphenylamide) from the metalation of $HNPh_2$ with $MgEt_2$ in diethylether was reported in the same year.[2] Also, the metathesis reaction of the alkaline earth metal halides with the 1,4-dioxane complex of $KNPh_2$ yielded the dioxane adducts of the diphenylamides of magnesium, calcium, strontium, and barium.[3]

In order to raise the solubility of the homoleptic amides of the heavy alkaline earth metals in common organic solvents, the alkaline earth metal bis[bis(trimethylsilyl)-amides] were prepared.[4] Several synthetic procedures were developed such as transmetallation of $Hg[N(SiMe_3)_2]_2$,[5] $Sn-[N(SiMe_3)_2]_2$,[6] and $Me_2Sn[N(SiMe_3)_2]_2$,[7] metalation of HN-

$(SiMe_3)_2$,[8] and metathesis reaction of halides,[9] alkoxides,[10] and triflates.[11] The substitution of one trimethylsilyl group by a bulky aryl substituent leads to soluble derivatives of the alkaline earth metals; however, a simple metalation of the amine was only possible for strontium and barium.[12,13] For the lighter alkaline earth metals, the metalation (magnesium derivative) or metathesis reactions (calcium compound) proved to be advantageous.[13] Also heterobimetallic complexes with the metals Li/Ca,[14,15] Li/Ba,[14] and Mg/Ca[16] are soluble in common organic solvents.

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The chemical behavior and molecular structures of organic compounds of the divalent lanthanoids are mainly determined by electrostatic and steric factors. This fact makes them rather similar to the corresponding alkaline earth metal derivatives. The metathesis reaction of potassium diphenylamide with the halides of divalent lanthanoids (salt elimination method) yielded the diphenylamides of ytterbium[17] and samarium,[18] and the molecular structures of [(18-crown-6)Yb(NPh$_2$)$_2$] and [(thf)$_4$Sm(NPh$_2$)$_2$] were determined.
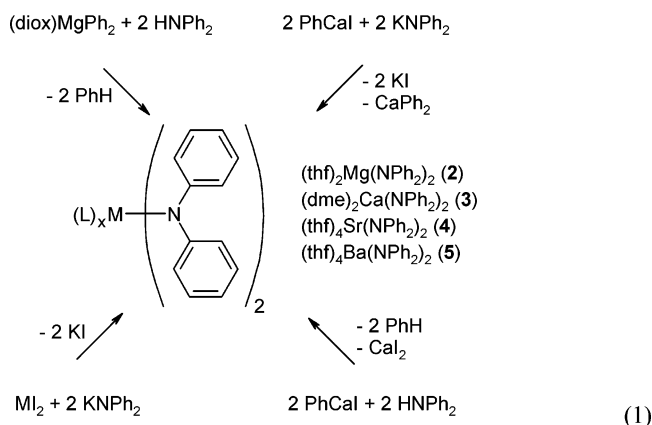
Up to now, solubility of the bis(amides) of the heavy alkaline earth metals was guaranteed by trialkylsilyl substituents alone or together with bulky aryl groups at the nitrogen atoms. Here we present the synthesis strategies and molecular structures of the alkaline earth metal bis(diphenylamides).

Results and Discussions

Synthesis. In order to avoid the formation of halide-containing products (which are structurally characterized, for example, for [(Et$_2$O)Mg(Cl){N(SiMe$_3$)$_2$}]$_2$[19] and [{(Et$_2$O)Mg}$_6$(NPh)$_4$Br$_4$]),[20] halogen-free diphenylmagnesium (diox)MgPh$_2$ (**1**) was prepared by adding 1,4-dioxane to a phenylmagnesium halide solution. However, the 1,4-dioxane complexes of magnesium dihalide and of diphenylmagnesium were only sparingly soluble and precipitated. Extraction of the organomagnesium compound from the precipitate succeeded with hot toluene. The preparation of diarylmagnesium derivatives was reported many decades ago, and since then, many aspects[21−30] regarding fluxionality, Schlenk equilibrium, molecular structure, solvation behavior, and reactivity have been investigated.

The reaction of diphenylmagnesium or commercially available dibutylmagnesium with diphenylamine in THF yielded colorless (thf)$_2$Mg(NPh$_2$)$_2$ (**2**). The reaction of (thf)$_4$Ca(Ph)I[31] with potassium diphenylamide gave phenyl-

calcium diphenylamide in accordance with the reaction already observed for the reaction with KN(SiMe$_3$)$_2$.[32] Change of solvent and dismutation of this heteroleptic compound yielded (dme)$_2$Ca(NPh$_2$)$_2$ with a hexacoordinate calcium atom (**3**). The homologous diphenylamides of strontium (**4**) and barium (**5**) were obtained as THF adducts via the metathesis reaction of KNPh$_2$ and MI$_2$ in THF. In eq 1 the possible

(diox)MgPh$_2$ + 2 HNPh$_2$ 2 PhCaI + 2 KNPh$_2$

− 2 PhH   − 2 KI, − CaPh$_2$

(L)$_x$M—N

(thf)$_2$Mg(NPh$_2$)$_2$ (**2**)
(dme)$_2$Ca(NPh$_2$)$_2$ (**3**)
(thf)$_4$Sr(NPh$_2$)$_2$ (**4**)
(thf)$_4$Ba(NPh$_2$)$_2$ (**5**)

− 2 KI   − 2 PhH, − CaI$_2$

MI$_2$ + 2 KNPh$_2$ 2 PhCaI + 2 HNPh$_2$ (1)

reaction pathways are summarized.

Molecular Structure of 1. The molecular structure of **1** is represented in Figure 1 and shows a one-dimensional polymer of [(diox)MgPh$_2$]$_\infty$ with tetracoordinate magnesium atoms. Comparable coordination spheres are found for bis-(THF) and TMEDA complexes of diphenylmagnesium with Mg−C values of 213 and 217 pm, respectively.[21−23] In **1**, a characteristic value of 213.5 pm is observed. Steric strain introduced by ortho-substitution of diarylmagnesium leads to an elongation of the Mg−C bonds[28] or to a reduction of the coordination number of the metal.[29]

The phenyl groups show very different Mg−C−C angles of 116.4° and 129.1° due to a steric repulsion with the bridging 1,4-dioxane molecules. Furthermore, a narrow C−C−C angle at the ipso-carbon atom supports the highly ionic character of the Mg−C bond. This observation can be explained by repulsive forces between the sp^2 lone pair (carrying the anionic charge) and the C(1)−C(2)/C(1)−C(6) bonds. This repulsion also leads to an elongation of the C−C bonds of the ipso-carbon atom by approximately 2 pm.

The bridging 1,4-dioxane molecules exhibit a chair conformation as found in other complexes such as, for example, [(μ_2-diox)MgEt$_2$]$_\infty$,[33] [(μ_2-diox)Mg(CH$_2$t-Bu)$_2$]$_\infty$,[34] [(μ_2-diox)$_5${Y(η^3-allyl)$_3$}$_2${Mg(CH$_2$CH=CH$_2$)$_2$}$_2$]$_\infty$,[35] [(μ_2-diox)$_5${Y(η^3-allyl)$_3$}$_2${Mg(CH$_2$CH=CH$_2$)$_2$}$_2$]$_\infty$,[35] and [(μ_2-diox){Mg(N(SiMe$_3$)$_2$)$_2$}$_2$].[36]

Molecular Structures of the Alkaline Earth Metal Bis-(diphenylamides). The molecular structures of the alkaline

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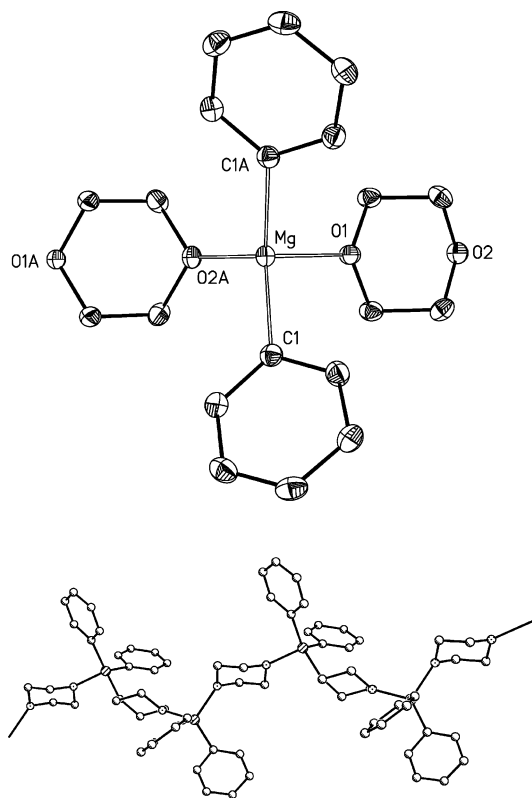
Figure 1. Part of the chain of [(diox)MgPh$_2$]$_\infty$ (**1**). The upper drawing displays the environment of the magnesium atom. The ellipsoids represent a probability of 40%, and hydrogen atoms are omitted for clarity reasons. The lower picture shows the chain structure with atoms represented with arbitrary radii. Selected bond lengths (pm): Mg−C(1) 213.5(2), Mg−O(1) 208.1(2), Mg−O(2A) 206.1(2), C(1)−C(2) 140.8(2), C(1)−C(6) 140.9(2), C(2)−C(3) 138.8(2), C(3)−C(4) 138.4(2), C(4)−C(5) 138.3(2), C(5)−C(6) 139.4(2). Selected bond angles (deg): C(1)−Mg−C(1A) 123.96(8), C(1)−Mg−O(1) 103.20(5), C(1)−Mg−O(2A) 110.22(5), O(1)−Mg−O(2A) 103.54(7), Mg−C(1)−C(2) 116.4(1), Mg−C(1)−C(6) 129.1(1), C(2)−C(1)-C(6) 113.9(1).
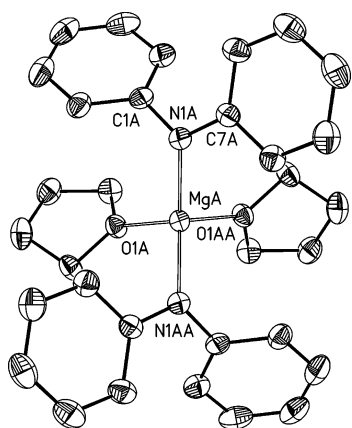

Figure 2. Molecular structure of (thf)$_2$Mg(NPh$_2$)$_2$ (**2**). The asymmetric unit contains two very similar molecules which are distinguished by "A" and "B". Only molecule A is shown here. The ellipsoids represent a probability of 40%, and H atoms are neglected for clarity reasons. Symmetry related atoms ($-x + 3$, y, $-z + 1.5$) are marked with a second "A". Selected bond lengths (pm): Mg(A)−N(1A) 201.3(3), Mg(A)−O(1A) 201.2(2), N(1A)−C(1A) 141.9(4), N(1A)−C(7A) 139.2(4). Selected bond angles (deg): N(1A)−Mg(A)−N(1AA) 126.9(2), N(1A)−Mg(A)−O(1A) 111.2-(1), N(1A)−Mg(A)−O(1AA) 103.8(1), O(1A)−Mg(A)−O(1AA) 95.5(2).

earth metal bis(diphenylamides) of magnesium (**2**), calcium (**3**), and strontium (**4**) are represented in Figures 2−4. A comparison of selected structural data with already well-
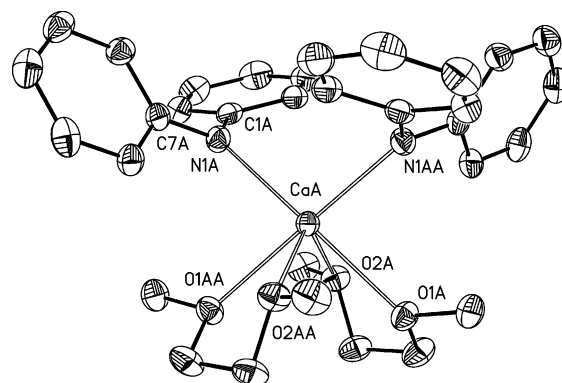
Figure 3. Molecular structure of (dme)$_2$Ca(NPh$_2$)$_2$ (**3**). The asymmetric unit contains two similar molecules which are distinguished by "A" and "B". Only molecule A is shown here. The ellipsoids represent a probability of 40%, and H atoms are neglected for clarity reasons. Symmetry related atoms ($-x + 1$, y, $-z + 1.5$) are marked with a second "A". Selected bond lengths (pm): Ca(A)−N(1A) 236.9(2), Ca(A)−O(1A) 247.7(1), N(1A)−C(1A) 140.0(2), N(1A)−C(7A) 137.5(2), Ca(A)···C(1A) 317.4(2). Selected bond angles (deg): N(1A)−Ca(A)−N(1AA) 98.44(8), Ca(A)−N(1A)−C(1A) 112.1(1), Ca(A)−N(1A)−C(7A) 128.4(1), C(1A)−N(1A)−C(7A) 119.5(2).
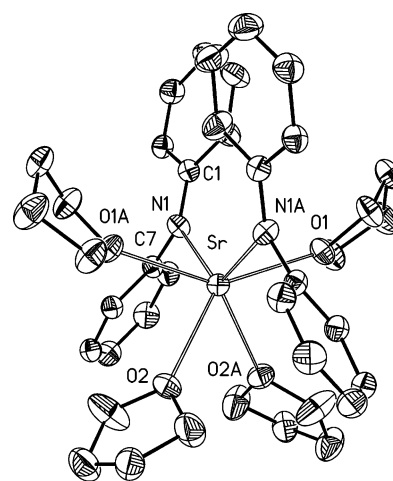

Figure 4. Molecular structure of (thf)$_4$Sr(NPh$_2$)$_2$ (**4**). The ellipsoids represent a probability of 40%, and H atoms are neglected for clarity reasons. Symmetry related atoms ($-x - 1$, y, $-z$) are marked with an "A". Selected bond lengths (pm): Sr−N(1) 255.2(2), Sr−O(1) 258.5(2), Sr−O(2) 260.6-(2), N(1)−C(1) 137.4(4), N(1)−C(7) 139.0(4), Sr···C(7) 323.6(2). Selected bond angles (deg): N(1)−Sr−N(1A) 123.9(1), Sr−N(1)−C(1) 131.7(2), Sr−N(1)−C(7) 106.6(2), C(1)−N(1)−C(7) 120.6(2).

known trimethylsilyl-substituted amides is given in Table 1. Due to the low steric strain induced by diphenylamido groups, coordination numbers of 6 are observed for the derivatives **3**−**5** (see Figure 5 for molecular structure of **5**) of the heavy alkaline earth metals, whereas only two THF molecules coordinate to magnesium bis(diphenylamide). The larger coordination number of the metals leads to larger M−N distances than observed for (thf)$_2$M[N(SiMe$_3$)$_2$]$_2$ with tetracoordinate metal atoms.[8a,37] In general, the substitution of a trimethylsilyl group in (thf)$_2$M[N(SiMe$_3$)$_2$]$_2$ by an aryl

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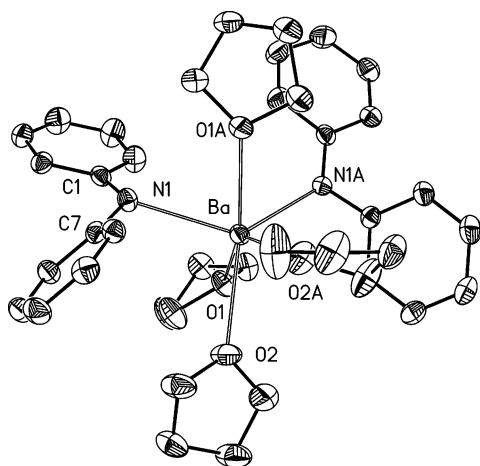
Figure 5. Molecular structure of (thf)$_4$Ba(NPh$_2$)$_2$ (**5**). The ellipsoids represent a probability of 40%, and H atoms are omitted for clarity reasons. Symmetry related atoms ($-x - 2$, y, $-z$) are marked with an "A". Selected bond lengths (pm): Ba−N(1) 269.8(4), Ba−O(1) 273.6(3), Ba−O(2) 275.2-(3), N(1)−C(1) 136.7(6), N(1)−C(7) 138.7(5), Ba···C(7) 329.3(4). Selected bond angles (deg): N(1)−Ba−N(1A) 120.8(2), Ba−N(1)−C(1) 132.7(3), Ba−N(1)−C(7) 102.7(2), C(1)−N(1)−C(7) 121.2(2).

Table 1. Comparison of Average Structural Data of Alkaline Earth Metal Bis(amides) of the Type L$_n$M(NRR′)$_2$ with M = Mg, Ca, Sr, and Ba

		bond distance/pm					
compound^a	CN^b	M−N	M−O	N−C	N−Si	bond angle N−M−N/deg	ref
(thf)$_2$Mg(NPh$_2$)$_2$ (**2**)	4	201.3	201.2	140.6		126.9	
(thf)$_2$Mg[N(SiMe$_3$)$_2$]$_2$	4	202.1	209.4		170.6	127.9	5
(thf)$_2$Mg[N(Ar)SiMe$_3$]$_2$	4	202.3	205.5	143.0	171.1	134.4	13
(dme)$_2$Ca(NPh$_2$)$_2$ (**3**)	6	236.9	246.1	138.8		98.4	
(thf)$_2$Ca[N(SiMe$_3$)$_2$]$_2$	4	230.1	237.7		168.6	121.3	37
(dme)Ca[N(SiMe$_3$)$_2$]$_2$	4	227.1	239.7		167.6	123.6	38
(thf)$_2$Ca[N(Ar)SiMe$_3$]$_2$	4	230.4	234.3	141.0	169.2	137.6	13
(thf)$_4$Sr(NPh$_2$)$_2$ (**4**)	6	255.2	259.6	138.2		123.9	
(thf)$_2$Sr[N(SiMe$_3$)$_2$]$_2$	4	245.8	253.4		167.4	120.6	37
(dme)$_2$Sr[N(SiMe$_3$)$_2$]$_2$	6	253.8	265.5		168.9	136.1	39
(thf)$_2$Sr[N(Ar′)SiMe$_3$]$_2$	4	248.0	251.1	140.2	169.2	123.6	12
(thf)$_4$Ba(NPh$_2$)$_2$ (**5**)	6	269.8	274.4	137.7		120.8	
(thf)$_2$Ba[N(SiMe$_3$)$_2$]$_2$	4	259.2	273.1		168.2	116.8	8a
(thf)$_2$Ba[N(Ar′)SiMe$_3$]$_2$	4	263.5	269.3	139.4	168.8	123.6	12

^{a} Aryl groups Ar = C$_6$H$_2$-2,4,6-Me$_3$ (mesityl), Ar′ = C$_6$H$_2$-2,6-iPr$_2$ (2,6-diisopropylphenyl). ^{b} Coordination number (CN).

group leads to smaller M−O distances (assuming that the coordination number is kept unchanged) due to decreasing steric strain because an aryl group is less bulky than a trimethylsilyl substituent. As a consequence of this shortening of the M−O bonds, the M−N bond lengths increase due to increasing electrostatic repulsion between the electronegative N and O atoms. An exchange of the trimethylsilyl group in (thf)$_2$M[N(Ar)SiMe$_3$]$_2$ leads to an even less hindered situation, and an enhancement of the coordination number of the alkaline earth metal atom was observed.

In **2**, the tetracoordinate magnesium atom is in a distorted tetrahedral environment. In complexes **3**−**5** with hexacoordinate metal atoms, N−M−N angles of 98.4° (M = Ca), 123.9° (M = Sr), and 120.8° (M = Ba) are observed. Unusual structures of d^0-metal compounds were investigated earlier, and d-orbital participation was suggested in order to explain the bent MX$_2$ of the alkaline earth metals and the

Table 2. Comparison of the NMR Data of the Diphenylamides of Mg (**2**), Ca (**3**), Sr (**4**), and Ba (**5**) (Ambient Temperature, [D$_8$]THF)

	HNPh$_2$^{38}	**2**	**3**	**4**	**5**
	^{1}H NMR Chemical Shift (ppm)				
ortho-H	7.05	6.79	6.73	6.83	6.83
meta-H	7.26	6.93	6.89	6.96	6.97
para-H	6.93	6.45	6.33	6.33	6.32
	^{13}C{^{1}H} NMR Chemical Shift (ppm)				
ipso-C	143.6	157.0	157.7	158.0	156.8
ortho-C	118.3	121.4	119.6	119.1	118.3
meta-C	129.8	129.6	129.8	129.8	130.0
para-C	121.4	117.0	115.3	114.4	114.2

pyramidal MX$_3$ of the scandium group.^{40} Furthermore, the M−N−C angles to the ipso-carbon atoms differ significantly (112.1(1)/128.4(1)° for **3**, 106.6(2)/131.7(2)° for **4**, and 102.7(2)/132.7(3)° for **5**). Related to these strongly different angles are also differing N−C bond lengths: The N−C value related to the proximal angle is significantly smaller than the N−C distance of the distal angle (140.0(2)/137.5(2) pm for **3**, 139.0(4)/137.4(4) pm for **4**, 138.7(5)/136.7(5) pm for **5**). These distortions are caused by strong attractive forces between the metal atoms and the π-system of the phenyl group, leading to short M−C bonds to the ipso-carbon atoms which are related to the proximal angles (Ca···C 317.4(2) pm, Sr···C 323.6(2) pm, Ba···C 329.3(4) pm).

The N−C bond lengths of the alkaline earth metal bis-(diphenylamides) **2**−**5** are smaller than observed for M[N(aryl)SiMe$_3$]$_2$ (see Table 1). The bulkiness of the trimethylsilyl group leads to steric strain, and furthermore, silyl groups lower the basicity of the nitrogen atom due to hyperconjugative effects (backdonation of charge from the p$_z$(N) lone pair of the nitrogen atom into σ*(Si−C) antibonds of the silyl group). In **2**−**5**, the nitrogen atoms show only small deviations from planarity and a delocalization of the anionic charge into the phenyl rings leads to shortened N−C bonds.

Diphenylamine shows an average N−C bond length of 140.0 pm in the solid state and an average C−N−C angle of 129.1°, with a nitrogen atom in a nearly planar environment.^{41} The metalation leads to a significantly reduced C−N−C angle of 119.3(3)° for **2**, 119.5(2)° for **3**, 120.6-(2)° for **4**, and 121.2(4)° for **5**.

NMR Spectroscopy. The NMR spectroscopic parameters of the alkaline earth metal bis(diphenylamides) are listed in Table 2. For comparison reasons, the data of HNPh$_2$^{42} are included as well.

The chemical shifts of the ^{1}H and ^{13}C atoms show a very weak dependency on the alkaline earth metal atom. However, the ipso-carbon atoms show a low field shift of approximately 14 ppm in comparison to diphenylamine. In the ^{1}H NMR spectrum, the phenyl groups of HNPh$_2$ show resonances at a lower field than observed for the amides.

Summary and Conclusion

In principle, five synthetic procedures are possible in order to prepare alkaline earth metal bis(diphenylamides). (i)

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Calcium, strontium, and barium can easily be activated by dissolving in liquid ammonia. Subsequent complete removal of NH_3 leaves a reactive metal powder in the flask. In boiling THF, the barium powder reacts quantitatively within 30 min with diphenylamine, whereas the metalation of $HNPh_2$ with Sr powder is slower by a factor of 10. Calcium and magnesium show no reactivity under similar conditions. (ii) The metalation of $HNPh_2$ with diarylmetal offers an easy access to the magnesium derivative; however, the diaryl derivatives of Ca, Sr, and Ba are not accessible as easily.[43] (iii) The metathesis reaction of the alkaline earth metal diiodides and $KNPh_2$ leads to good yields for the Sr and Ba derivatives. The iodides $(thf)_5SrI_2$ and $(thf)_5BaI_2$ are very soluble in THF at room temperature (121 mmol L^{-1} for SrI_2, 133 mmol L^{-1} for BaI_2), whereas the iodides of Ca and Mg are far less soluble and therefore, no complete turnover is observed. (iv) The metalation of $HNPh_2$ with $PhCa(thf)_4I$ and the subsequent dismutation reaction yield homoleptic calcium bis(diphenylamide), calcium diiodide, and benzene. Purification difficulties arise from a similar solubility of Ca-$(NPh_2)_2$ and CaI_2 in THF. (v) The metathesis reaction of $PhCa(thf)_4I$ with $KNPh_2$ leads to the formation of the THF adduct of $PhCaNPh_2$ which dismutates immediately to homoleptic $Ca(NPh_2)_2$ and $CaPh_2$. Because of the high solubility of diarylcalcium in THF,[43,44] sparingly soluble Ca-$(NPh_2)_2$ can be crystallized from these reaction solutions. In solution, remaining $CaPh_2$ can be used to deprotonate $HNPh_2$ in order to maximize the yield. This reaction can also be performed for the strontium and barium compounds.

Perspective

Magnesium bis(amides) already proved to be valuable precursors in organic and macromolecular chemistry.[45] The reaction of these molecules with MgH_2 yielded heteroleptic $HMgNR_2$ which were used for the reduction of ketones.[46] These magnesium bis(amides) react readily with CO_2 and its fixation leads to the formation of N,N'-diorganocarbamoxymagnesium compounds.[47] The major application, however, is the use as an initiator in anionic polymerization reactions.[48] The reactivity of the heavier homologous compounds is much higher than observed for **2**. On the one hand, however, the solubility of the more ionic diphenylamides of the heavy alkaline earth metals is strongly reduced compared to $Mg(NPh_2)_2$. On the other hand, usually large concentrations of the polymerization catalysts are not necessary.

Experimental Section

All manipulations were carried out in an argon atmosphere under anaerobic conditions. These compounds are extremely moisture sensitive and lose coordinated THF 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.

^{1}H NMR and ^{13}C NMR spectra were recorded at [D$_8$]THF solutions at ambient temperature on a Bruker AC 400 MHz spectrometer. All 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), and IR measurements were carried out on a Perkin-Elmer System 2000 FTIR. Decomposition points were measured with a Reichert– Jung apparatus type 302102 and are uncorrected.

Prior to use, all solvents were thoroughly dried and distilled in an argon atmosphere. Diphenylamine was purchased from Alfa Aesar and used without further purification. Barium (99.7%) was purchased from ABCR GmbH & Co. KG and strontium (99+ %) were purchased from Aldrich. Both metals were activated prior to use.[31b] Phenylcalcium iodide was prepared according to literature procedure.[31b] A solution of potassium diphenylamide in THF was prepared from potassium and diphenylamine in THF.[3] $(thf)_5SrI_2$ and $(thf)_5BaI_2$ were prepared via the oxidation of the alkaline earth metals by iodine in THF.[49]

Synthesis of (Diox)MgPh$_2$ (1). 1,4-Dioxane (13.6 mL) was dropped into a stirred solution (100 mL) of phenylmagnesium bromide (1.0 M) in diethylether. A white precipitate formed gradually while the solution became warm. The ether was removed in vacuo, and the residue was extracted with a hot solvent mixture of 100 mL of toluene and 20 mL of 1,4-dioxane. From the extract, colorless $(diox)MgPh_2$ (**1**) crystallized at -40 °C. The product was collected on a Schlenk frit, washed with diethylether, and dried in vacuo. Yield: 7.8 g (58.5%) of colorless, moisture and air-sensitive crystals. Elemental analysis (calcd for $C_{16}H_{18}MgO_2$, 266.6 g mol^{-1}): Mg, 9.36 (9.12). ^{1}H NMR (25 °C, [D$_8$]THF): δ 3.54 (8H, s, CH$_2$), 6.45–7.03 (6H, m, p-CH, m-CH), 7.67–7.72 (4H, m, o-CH). ^{13}C-{^{1}H} NMR (25 °C, [D$_8$]THF): δ 67.8 (CH$_2$), 124.4 (p-CH), 126.2 (m-CH), 141.2 (o-CH), 170.1 (i-C).

Synthesis of (thf)$_2$Mg(NPh$_2$)$_2$ (2). A solution of 1.47 g of (diox)-MgPh$_2$ (5.51 mmol) in 30 mL of THF was stirred at room temperature. Solid $HNPh_2$ (1.87 g, 11.05 mmol) was added in small portions. After complete addition, the reaction mixture was stirred for another hour. Thereafter the solution was stored at -25 °C, and 2.80 g of colorless crystals of $(thf)_2Mg(NPh_2)_2$ (**2**) (5.18 mmol, 94%) precipitated and was collected on a precooled frit. Recrystallization from THF (room temperature/-40 °C) is possible. Crystalline **2** decomposes above 50 °C. ^{1}H NMR (25 °C, [D$_8$]THF): δ 1.70 (thf), 3.54 (thf), 6.45 (2H, dt, $^4J_{H,H}$ = 1.0 Hz, $^3J_{H,H}$ = 7.0 Hz, p-CH), 6.79 (4H, dd, $^4J_{H,H}$ = 0.8 Hz, $^3J_{H,H}$ = 8.4 Hz, o-CH), 6.93 (4H, dt, $^4J_{H,H}$ = 1.6 Hz, $^3J_{H,H}$ = 7.8 Hz, m-CH). ^{13}C NMR (25 °C, [D$_8$]THF, HSQC): δ 26.3 (thf), 68.2 (thf), 117.0 (2C, p-C), 121.4 (4C, o-C), 129.6 (4C, m-C), 157.0 (2C, i-C). MS (DEI, m/z, [%]): 42 [13], 71 [11], 168 (Ph$_2$NH − H) [9], 170 (Ph$_2$NH + H) [100], 336 (Ph$_2$NNPh$_2$) [2]. IR (Nujol) ν: 3407, w; 3384, m; 1595,

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Table 3. Crystal Data and Refinement Details for the X-ray Structure Determinations

	1	2	3	4	5
formula	$C_{16}H_{18}MgO_2$	$C_{32}H_{36}MgN_2O_2 \cdot C_4H_8O$	$C_{32}H_{40}CaN_2O_4$	$C_{40}H_{52}N_2O_4Sr \cdot C_4H_8O$	$C_{40}H_{52}BaN_2O_4 \cdot C_4H_8O$
fw/(g·mol^{-1})	266.61	577.04	556.74	784.56	834.28
T/°C	−90(2)	−90(2)	−90(2)	−90(2)	−90(2)
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
space group	*Pnma* (No. 62)	*P2/n* (No. 13)	*C2/c* (No. 15)	*C2* (No. 5)	*C2* (No. 5)
a/Å	11.5579(5)	13.1143(4)	24.9375(8)	19.0176(8)	19.5613(11)
b/Å	18.6002(6)	14.4644(5)	17.2162(5)	11.9452(6)	11.9298(4)
c/Å	6.7094(3)	19.8690(4)	18.4757(6)	9.2214(4)	9.1896(5)
α/deg	90.00	90.00	90.00	90.00	90.00
β/deg	90.00	106.111(2)	129.216(2)	93.354(3)	93.622(2)
γ/deg	90.00	90.00	90.00	90.00	90.00
V/Å^3	1442.38(10)	3620.94(18)	6145.6(3)	2091.23(16)	2140.22(18)
Z	4	4	8	2	2
ρ/(g·cm^{-3})	1.228	1.059	1.203	1.246	1.295
μ/cm^{-1}	1.18	0.82	2.41	13.34	9.71
measured data	9727	24242	20544	6891	6472
data with $I > 2\sigma(I)$	1293	5307	4811	4112	4242
unique data	1702	8274	7029	4371	4371
wR2 (all data, on F^2)^a	0.1015	0.3199	0.1144	0.0864	0.0922
R_1 ($I > 2\sigma(I)$)^a	0.0382	0.0952	0.0441	0.0410	0.0426
s^b	1.024	1.030	1.012	1.034	1.032
res density/(e·Å^{-3})	0.244/−0.274	1.423/−0.363	0.227/−0.248	0.342/−0.332	0.733/−0.715
Flack-parameter				0.006(6)	0.02(2)
abs method	multiscan	multiscan	multiscan	multiscan	multiscan
abs corr $T_{min/max}$	0.7581/0.7895	0.9573/1.0119	0.9403/0.9702	0.7765/0.8028	0.8224/0.8584
CCDC no.	637914	637915	637916	637917	637918

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

vs; 1494, vs; 1418, w; 1308, s; 1173, w; 1023, wv; 986, vw; 876, vw; 745, vs; 690, m; 504, vw.

Synthesis of (dme)₂Ca(NPh₂)₂ (3). Method A. A 0.75 M solution of KNPh₂ in THF (8.59 mL, 6.44 mmol) was added at room temperature to 35.0 mL of a 0.184 M solution of phenylcalcium iodide in THF. A colorless precipitate of KI formed immediately and was removed after 1 h. The volume of the filtrate was reduced to approximately 5 mL, and 40 mL of DME was added. The major part of **3** precipitated as colorless crystals. In order to enhance the yield, the solution was cooled to −25 °C and then all solid materials were collected on a cooled frit. The colorless and very moisture sensitive crystals of (dme)₂Ca(NPh₂)₂ (**3**) (1.42 g, 2.55 mmol, 79%) were dried in vacuum.

Synthesis of (dme)₂Ca(NPh₂)₂ (3). Method B. Solid diphenylamine (0.45 g, 2.66 mmol) was added in small portions at room temperature to 15.0 mL of a 0.175 M solution of phenylcalcium iodide in THF (2.63 mmol). After complete addition, a very small amount of (thf)₄CaI₂ slowly precipitated. Reduction of the volume of the reaction mixture to a few milliliters led to precipitation of (thf)₄CaI₂. After filtration, 20 mL of DME was added and 0.57 g of **3** (1.02 mmol, 78%) precipitated immediately.

Physical Data for 3. Decomposition above 65 °C. ¹H NMR (25 °C, [D₈]THF): δ 3.23 (dme), 3.39 (dme), 6.33 (2H, t, $^3J_{H,H}$ = 7.2 Hz, *p*-CH), 6.73 (4H, d, $^3J_{H,H}$ = 7.6 Hz, *o*-CH), 6.89 (4H, t, $^3J_{H,H}$ = 7.2 Hz, *m*-CH). ¹³C NMR (25 °C, [D₈]THF): δ 58.9 (dme), 72.6 (dme), 115.3 (2C, *p*-C), 119.6 (4C, *o*-C), 129.8 (4C, *m*-C), 157.7 (2C, *i*-C). MS (DEI, *m/z*, [%]): 29 [11], 45 (DME/2) [100] 60 [20], 77 (Ph) [6], 90 (DME) [19], 167 (Ph₂NH − 2H) [44] 168 (Ph₂NH − H) [18], 169 (Ph₂NH) [28]. IR (Nujol) *ν:* 3407, vw; 3384, w; 3049, w; 1595, vs; 1575, vs; 1519, m; 1418, vw; 1318, vs; 1243, vw; 1211, w; 1172, w; 1107, w; 1060, vs; 1023, w; 982, w; 901, vw; 865, w; 822, w; 746, s; 696, s; 519, vw; 498, w.

Synthesis of (thf)₄Sr(NPh₂)₂ (4). Method A. A solution of KNPh₂ (0.75 M, 11.25 mL, 8.44 mmol) was dropped into a solution of 2.96 g of (thf)₅SrI₂ (4.22 mmol) in 50 mL of THF. Precipitated KI was removed, and the volume of the filtrate was reduced to

half of the original volume. Storage at −25 °C led to crystallization of 2.62 g of colorless (thf)₄Sr(NPh₂)₂ (**4**) (3.34 mmol, 79%).

Synthesis of (thf)₄Sr(NPh₂)₂ (4). Method B. Activated strontium (0.69 g, 7.87 mmol) was suspended in 30 mL of THF, and 2.67 g of diphenylamine (15.8 mmol) was added at once. This reaction mixture was heated under reflux for 5 h. During this time, the strontium dissolved and hydrogen gas escaped. After filtration, storage of the filtrate at −40 °C yielded 4.28 g of (thf)₄Sr-(NPh₂)₂ (**4**) (5.46 mmol, 69%). Crystalline **4** decomposed above 70 °C.

Physical Data for 4. ¹H NMR (25 °C, [D₈]THF): δ 1.73 (thf), 3.59 (thf), 6.33 (2H, t, $^3J_{H,H}$ = 6.8 Hz, *p*-CH), 6.83 (4H, d, $^3J_{H,H}$ = 8.0 Hz, *o*-CH), 6.96 (4H, t, $^3J_{H,H}$ = 7.2 Hz, *m*-CH). ¹³C NMR (25 °C, [D₈]THF): δ 26.3 (thf), 68.2 (thf), 114.4 (2C, *p*-C), 119.1 (4C, *o*-C), 129.8 (4C, *m*-C), 158.0 (2C, *i*-C). MS (DEI, *m/z*, [%]): 41 [10], 166 (Ph₂NH − 3H) [22], 168 (Ph₂NH − H),¹⁰⁰ 336 (Ph₂-NNPh₂).⁸ IR (Nujol) *ν:* 3407, vw; 3384, vw; 3052, w; 1581, vs; 1555, w; 1418, vw; 1332, vs; 1244, vw; 1210, w; 1197, w; 1173, s; 1147, w; 1075, w; 1029, s; 984, w; 897, w; 877, w; 857, vw; 809, w; 744, vs; 698, vs; 518, w; 499, w.

Synthesis of (thf)₄Ba(NPh₂)₂ (5). Method A. A 0.665 M solution of KNPh₂ (15.64 mL, 10.4 mmol) was added to a solution of 3.91 g of (thf)₅BaI₂ (5.20 mmol) in 40 mL of THF. After stirring for 1 h at room temperature, precipitated KI was removed. The volume of the filtrate was reduced to half of the original volume. Storage at −25 °C yielded 3.56 g of colorless crystals of (thf)₄Ba-(NPh₂)₂ (**5**) (4.27 mmol, 82%).

Synthesis of (thf)₄Ba(NPh₂)₂ (5). Method B. Activated barium (0.50 g, 3.64 mmol) and 1.23 g of HNPh₂ (7.28 mmol) were heated under reflux in 30 mL of THF for 30 min. During this time, barium dissolved and hydrogen gas evolved. After filtration, the filtrate was stored at −25 °C and 2.22 g of (thf)₄Ba(NPh₂)₂ (**5**) (2.66 mmol, 73%) precipitated. Crystalline **5** decomposed above 50 °C.

Physical Data for 5. ¹H NMR (25 °C, [D₈]THF): δ 1.71 (thf), 3.58 (thf), 6.32 (2H, t, $^3J_{H,H}$ = 7.1 Hz, *p*-CH), 6.83 (4H, d, $^3J_{H,H}$ = 7.6 Hz, *o*-CH), 6.97 (4H, t, $^3J_{H,H}$ = 8.0 Hz, *m*-CH). ¹³C NMR

(25 °C, [D$_8$]THF): δ 26.3 (thf), 68.1 (thf), 114.2 (2C, *p*-C), 118.3 (4C, *o*-C), 130.0 (4C, *m*-C), 156.8 (2C, *i*-C). MS (DEI, *m/z*, [%]): 39 [16], 51 [28], 84 [46], 115 [13], 167 (Ph$_2$NH − 2H) [100], 169 (Ph$_2$NH) [42], 336 (Ph$_2$NNPh$_2$).[3] IR (Nujol) *ν:* 3407, vw; 3384, vw; 3039, vw; 1587, s; 1560, vw; 1552, w; 1418, vw; 1306, vs; 1243, vw; 1198, m; 1170, s; 1149, vw; 1079, vw; 1037, w; 990, vw; 880, w; 804, w; 751, vs; 712, m; 701, s; 690, w; 530, w; 522, vw; 503, w.

X-ray Structure Determination of 1−5. 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.[50−52] Crystallographic data as well as structure solution and refinement details are summarized in Table 3.

The structures were solved by direct methods (SHELXS)[53] and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97).[53] Compounds **2** and **3** crystallized with two crystallographically independent molecules A and B, but only molecule A is represented in Figure 2. Furthermore, two additional THF molecules are located between the calcium complexes. The hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms except for the solvent molecules were refined anisotropically.[54] The structure determination of **2** was of rather poor quality due to a disordering of the THF molecules which lie between the (thf)$_2$Mg(NPh$_2$)$_2$ molecules. XP (Siemens Analytical X-ray Instruments, Inc.) and POVRAY were used for structure representations.

Supporting Information Available: A listing of data collection and refinement procedures as well as positional coordinates of all atoms (in CIF format). 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-637914 (**1**), CCDC-637915 (**2**), CCDC-637916 (**3**), CCDC-637917 (**4**), and CCDC-637918 (**5**) 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, U.K.; fax, (+44) 1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

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