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Synthesis, properties, and reactivity of alkaline earth metal bis[bis(trialkylsilyl)amides]

Matthias Westerhausen*

Institut für Anorganische Chemie, Ludwig-Maximilians-Universität, Meiserstr. 1,
D-80333 München, Germany

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Contents

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* Tel.: +49 89 5902638; fax: +49 241 5902578; e-mail: maw@anorg.chemie.uni-muenchen.de

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Abstract

Due to their reactivity, the alkaline earth metal bis[bis(trimethylsilyl)amides] are valuable synthons to incorporate the metal atoms in numerous molecules. The easy access of these compounds by metathesis as well as transmetalation reactions led to a vast development of the molecular alkaline earth metal chemistry in the last decade. Due to a pK_a value of 25.8 for hexamethyldisilazane, metalation of more acidic molecules is a useful reaction to metallocenes, acetylides, phosphanides, arsanides, alcoholates, and others. Special interest is given to the dimeric alkaline earth metal bis[bis(trialkylsilyl)phosphanides] due to their unexpected structures in the solid state and in solution. These molecules crystallize with a central trigonal M_2P_3 bipyramide in the case of M = Ca, Sr and Ba. These are the minimum structures according to ab initio calculations for calcium and strontium for gaseous $[M(PH_2)_2]_2$, whereas for barium the structure of the type $M(\mu\text{-}PH_2)_4Ba$ has to be considered. Addition reactions of the homoleptic alkaline earth metal bis(amides) and bis(phosphanides) to benzonitrile yield the corresponding benzamidinates and 1-aza-3-phosphapropenides, respectively. Both ligands bind as bidentate ligands to the metal center. The nitrogen atoms show a trigonal planar surrounding in contrast to the phosphorus atoms. Reaction of the alkaline earth metal bis(amides) with 6,6-dialkylfulvenes gives the corresponding 1,1′-bis(alkenyl)alkaline earth metallocenes. Heterobimetallic molecules crystallize from the metalation of phosphanes with a mixture of alkaline earth metal and tin(II) bis(bistrimethylsilyl)amides. The wide preparative use of these compounds less than 10 years after the first synthesis of a bis(trimethylsilyl)amide of a heavier alkaline earth metal demonstrates the still growing importance of this compound class.

Keywords: Alkaline earth metal; Metal atoms; Molecules

1. Introduction: scope of the review

The chemistry of molecular compounds containing the heavier alkaline earth metals was summarized in the early 1970s [1–3] with the expectation that it would be a fast developing field [4].[1] For a variety of reasons, however, most of the derivatives remained poorly characterized. In contrast to the high reactivity of the alkaline earth metal organic compounds, the bulk metals themselves which are often used as starting materials, are fairly unreactive. Therefore not only do the

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[1] The derivatives of calcium, strontium, and barium have received only sporadic attention, but recently refined preparative methods may signal promising developments, especially for the potentially useful organocalcium reagents [4].

desired products form very slowly, but once formed, they are also reactive enough to attack the solvent or the remaining starting materials. Furthermore, the variety and limited commercial availability of organolithium compounds [5–14] as well as Grignard reagents [15–18] and dibutyl magnesium led to a decreasing interest in this substance class.

The realization of the two approaches, namely the enhancement of the reactivity of the metals and the lowering of the reactivity of the resulting alkaline earth metal derivatives, opened the fast developing field of molecular alkaline earth metal compounds. Several procedures and methods have been published for the activation of electropositive metals:

- Dissolving of the metals in liquid ammonia [19–21].
- Employment of an ammonia saturated solvent such as tetrahydrofuran or toluene [22–25].
- Vacuum distillation of the metals between 850 and 1000°C [26–31].
- Cocondensation of alkaline earth metals and substrates [32–37].
- Activation by ultra sound [38–43].
- Reduction of calcium diiodide with potassium (Rieke method) [44–46] or lithium biphenylide [47,48].
- Decomposition of alkaline earth metal anthracene complexes (Bogdanovic method) [49–55].
- Metal graphite method [56–59].
- Mechanical grinding of the metal [60].

The organo alkaline earth metal compounds and mainly the metallocenes were summarized lately by Hanusa [61–63] and others [64,65] and are not considered here. This review is mainly restricted to molecules with bonds between alkaline earth metals and main group elements such as a group 15 element (pentele, the IUPAC recommends the expression ‘pentele’ instead of ‘pnictogen’ due to the misleading meaning of ‘suffocate’, originating from Greek *πνικτός*) or chalcogen atom. The alkaline earth metal bis[bis(trialkylsilyl)amides] proved to be one of the easiest accessible synthons to the molecular alkaline earth metal chemistry, and consequently, this review begins with their synthesis and physical properties. Furthermore, a later section gives a perspective on the reactivity and application of the alkaline earth metal bis[bis(trialkylsilyl)amides]. In contrast to the growing knowledge of these compounds, the attention given to the structurally characterized bis(1,4-dioxane-*O*)calcium bis[bis(trimethylsilyl)methanide] [66, see also 67] is surprisingly insignificant as also pertains for tetrakis(tetrahydrofuran)calcium bis(trimethylstannanide) [68,69].

2. Amides of the alkaline earth metals

2.1. Homoleptic amides

The alkaline earth metal diamides $M(NH_2)_2$ are salt-like compounds [70] and insoluble in common organic solvents. The solid state structures of $Ca(NH_2)_2$ and $Sr(NH_2)_2$ are isotypic and show the metal atoms in an octahedral environment with Ca–N and Sr–N distances of 257 and 273 pm [71]. However, Juza and Schumacher were unable to locate the hydrogen atoms. In contrast to these derivatives, $Ba(NH_2)_2$ crystallizes with the barium atoms in somewhat irregular surroundings with Ba–N distances varying between 275 and 324 pm [72]. The hexakis(ammonia) complexes of the neutral metals calcium, strontium, and barium $M(NH_3)_6$ crystallize body centered cubic, however, M–N bond lengths were not given by the authors [73]. Alkyl as well as aryl substituted alkaline earth metal bis(amides) are isolated, but they are extremely sensitive towards moisture and air and insoluble in common organic solvents [74]. These properties restrict the characterization, and no NMR data was provided. In order to prevent aggregation, the trimethylsilyl substituted amides were synthesized by numerous research groups. Beryllium and magnesium bis[bis(trimethylsilyl)amide] are well-known for more than 2 decades, whereas the derivatives of the heavier alkaline earth metals have gained interest only in the last decade.

Beryllium bis[bis(trimethylsilyl)amide] which is liquid at room temperature is easily accessible by the metathesis reaction of $BeCl_2 \cdot OEt_2$ with sodium bis(trimethylsilyl)amide according to Eq. (1) [75]. This derivative is monomeric in solution [76] as well as in the gaseous phase [77,78].

The metalation of hexamethyldisilazane with magnesium dibutanide (Eq. (2)) yields quantitatively $Mg[N(SiMe_3)_2]_2$. The performance of this reaction in diethylether leads to an ether adduct, however, at 110°C in a vacuum the ether ligand is distilled off [79,80]. When hexane is chosen as a solvent, the homoleptic solvent-free derivative is isolated [81,82]. This compound is monomeric in the gaseous phase [79,80,83], but it crystallizes as a dimer [84]. In benzene or toluene solution, a monomer–dimer equilibrium is observed [85].

The only structurally characterized calcium amides are the heterobimetallic derivatives shown in Scheme 1 [86–90], which also contain aluminium. The synthesis succeeded by metalation of the amines with $Ca(AlH_4)_2$ or calcium metal.

2.1.1. Synthesis

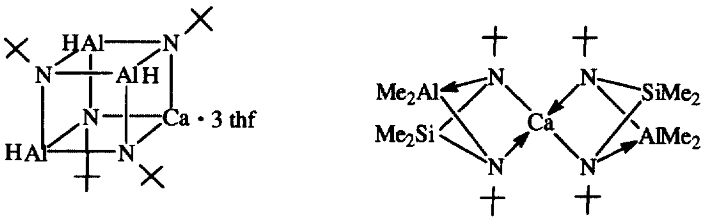
The reason why the bis(trimethylsilyl)amides of calcium, strontium, and barium remained unknown up to the beginning of this decade is the lack of well-characterized alkanides as well as the fact that calcium metal in liquid ammonia does not react with hexamethyldisilazane [85]. Even the addition of a small amount of mercuric chloride [91] or of fluorene, which yields metal difluorenide [92], does not catalyze the metalation reaction.

$$(Et_2O)BeCl_2 + 2\,NaN(SiMe_3)_2 \xrightarrow[\substack{-\,2\,NaCl \\ -\,Et_2O}]{} Be[N(SiMe_3)_2]_2 \qquad (1)$$

$$\mathrm{Mg^{s}Bu^{n}Bu} + 2\,\mathrm{HN(SiMe_3)_2} \xrightarrow[-2\,\mathrm{BuH}]{} \mathrm{Mg[N(SiMe_3)_2]_2} \tag{2}$$

The transmetalation of bis[bis(trimethylsilyl)amino]stannylene with distilled alkaline earth metals [85] according to Eq. (3) in toluene yields the homoleptic bis(trimethylsilyl)amides of calcium, strontium, and barium. These derivatives are dimeric in the solid state [93–95] as well as in benzene and toluene solution [85]. The use of Lewis bases such as tetrahydrofuran or 1,2-dimethoxyethane as a solvent leads to the corresponding adducts. In refluxing tetrahydrofuran, also mercury bis[bis(trimethylsilyl)amide] is transmetalated by the alkaline earth metals to give the bis(tetrahydrofuran)calcium, -strontium, and -barium bis[bis(trimethylsilyl)amides]. Even in the gaseous phase fragments of clearly dimeric species are found by mass spectroscopy and proven by a high resolved mass determination [85]. The mass of 488 m/z found for $\mathrm{(THF)_2Mg[N(SiMe_3)_2]_2}$ in the mass spectrum [91] could resemble the molecular ion or also a fragment of a dimer which would have formed during the evaporation of the compound.

It is very obvious that these transmetalation reactions have some disadvantages. The mercury–alkaline earth metal exchange has to be performed at elevated temperatures and thermally sensitive compounds are not accessible in this manner. Furthermore, the reduced reactivity of the group II metals compared to the alkali metals is apparent since the group I metals react with $\mathrm{Hg[N(SiMe_3)_2]_2}$ smoothly at room temperature [91]. The choice of a stannylene is limited to sterically demanding substituents. Due to rather long reaction periods, labile stannylenes are not suitable starting materials. Another fact has to be taken into account: If the stannylene contains other weakened bonds than the Sn–N bond, side reactions are to be expected [96]. If the isoelectronic $\mathrm{Sn[CH(SiMe_3)_2]_2}$ [97–99] is used, the consecutive insertion of still present stannylene into the formed metal–carbon bond is observed and a metal(II) bis{tris[bis(trimethylsilyl)methyl]stannanide} is isolated [100].



A B

Scheme 1.

$$\begin{array}{l} M + M'[N(SiMe_3)_2]_2 \longrightarrow M[N(SiMe_3)_2]_2 + M' \\ M = Ca, Sr, Ba \\ M' = Sn, Hg \end{array} \qquad (3)$$

$$\begin{array}{l} 16\,Ca + 15\ Me_2Sn(NR_2)_2 \xrightarrow{thf} \\ \quad 15\,(R_2N)_2Ca(thf)_2 + [(Me_3Sn)_3Sn]_2Ca(thf)_2 + 3\,SnMe_4 + 4\,Sn \\ R = SiMe_3 \end{array} \qquad (4)$$

The transmetalation of dimethyl-bis[bis(trimethylsilyl)amino]stannane by calcium metal in tetrahydrofuran yields $(THF)_2Ca[N(SiMe_3)_2]_2$ besides tetramethylstannane, tin metal and $(THF)_2Ca[Sn(SnMe_3)_3]_2$ [96] (Eq. (4)). The stoichiometry of this reaction is verified by NMR spectroscopy.

The metalation of hexamethyldisilazane by the alkaline earth metals succeeds neither in liquid ammonia nor in tetrahydrofuran or toluene, but in a mixture of ammonia and tetrahydrofuran [22–25] according to Eq. (5).

Lappert et al. [66,67,101] metalated $HN(SiMe_3)_2$ with calcium and strontium in refluxing tetrahydrofuran, however, the activation of the metals by cocondensation with toluene was necessary. The alkaline earth metal bis(amides) were isolated as a dimeric mono(THF) adduct (Eq. (6)).

Numerous research groups employed the metathesis reaction to prepare the alkaline earth metal bis[bis(trimethylsilyl)amides]. Boncella et al. [102] stirred sodium bis(trimethylsilyl)amide and anhydrous $BaCl_2$ in diethylether at room temperature for 24 h and isolated ether-free barium bis[bis(trimethylsilyl)amide]. Hanusa et al. [103] used the iodides of the alkaline earth metals and potassium bis(trimethylsilyl)amide. Suitable synthons for the metathesis reaction are also the alkaline earth metal alkoxides [101] and paratoluenesulfonates [104]. Eq. (7) summarizes these employed metathesis reactions.

$$M + 2\,HN(SiMe_3)_2 \xrightarrow[-\,H_2]{thf/\,NH_3} (thf)_2\,M[N(SiMe_3)_2]_2 \qquad (5)$$

$$Ca^* + 2\,HN(SiMe_3)_2 \xrightarrow[-\,H_2]{thf} \{(Me_3Si)_2N\text{–}Ca(thf)\,[\mu\text{–}N(SiMe_3)_2]\}_2 \qquad (6)$$

The conversion of the Lewis base-free dimeric alkaline earth metal bis[bis(trimethylsilyl)amides] into the base complexes is performed by adding the appropriate Lewis base such as tetrahydrofuran, 1,2-dimethoxyethane, or pyridine [102]. The ligand–ligand exchange reaction allows the synthesis of pyridine adducts from $(THF)_2M[N(SiMe_3)_2]_2$ [91].

2.1.2. *Solid state structures*

The homoleptic alkaline earth metal bis[bis(trimethylsilyl)amides] of magnesium, calcium, strontium, and barium crystallize as dimeric molecules with a central M_2N_2 cycle [84,93–95]. Fig. 1 shows the molecular structure of dimeric strontium bis[bis(trimethylsilyl)amide] representative for all these derivatives. In addition, selected structural parameters are listed in Table 1, together with the electron diffraction data of monomeric beryllium [77,78] and magnesium bis[bis(trimethylsilyl)amide] [83] determined in the gaseous phase. Due to the coordination number of two for monomeric $Be[N(SiMe_3)_2]_2$ and $Mg[N(SiMe_3)_2]_2$, very short $M-N^t$ bond lengths (t marks terminal ligands, b bridging ones) are found. The dimeric derivatives show a difference between the $M-N^t$ and $M-N^b$ distances of approx. 20 pm.

The N–Si bond lengths depend on the metal atom and on the fact whether the ligand is in a terminal or bridging position. In general, the N–Si distance decreases from the magnesium to the barium bis(amide) and is shorter for the terminal coordinated ligand due to the smaller coordination number of the nitrogen atom N^t. The increasing ionic character of the M–N bond towards the barium derivative leads to a diminishing difference of the N^t-Si and N^b-Si distances, which is 7 pm for $\{Mg[N(SiMe_3)_2]_2\}_2$ [84] and only 1 pm for the barium compound [95]. Another characteristic feature is the large Si–N–Si angle enforced by intraligand repulsion of the trimethylsilyl groups [113] and is often even further stretched due to agostic bonds between the low-coordinated metal center and the trimethylsilyl substituent. In this context even Si–N–Si values up to 133° are realized for example in $(THF)_2Ba[N(SiMe_3)_2]_2$ [95,101], however, even values up to 140° are found for the polymeric bis(dioxane) complex of sodium bis(trimethylsilyl)amide [114,115]. Due to the fact that the trimethylsilyl groups affect each other sterically, large Si–N–Si angles correspond to small N–Si bond lengths.

Table 2 summarizes selected structural data of the bis(tetrahydrofuran)alkaline earth metal bis[bis(trimethylsilyl)amides]. These compounds do not crystallize isotypically, however, the molecular structures are very similar. Fig. 2 shows the

$$M^{II}X_2 + 2\,M^{I}N(SiMe_3)_2 \longrightarrow M^{II}[N(SiMe_3)_2] + 2\,M^{I}X \qquad (7)$$

X = Cl, I, p-MeC_6H_4–SO_3, RO
M^I = Li, Na, K
M^{II} = Ca, Sr, Ba

Table 1
Selected bond lengths (pm) of homo- and heteroleptic alkaline earth metal bis(trialkylsilyl)amides

Compound	M–N^t	M–N^b	N^t–Si	N^b–Si	M–O	Ref.
$Be(NR_2)_2$	156		173			[77,78]
$Mg(NR_2)_2$	191		170			[83]
$Mg(NR'_2)_2$	197		171			[105]
$[Mg(NR_2)_2]_2$	198	215	171	177		[84]
$(THF)_2Mg(NR_2)_2$	202		171		209	[91]
$(DIOX)[Mg(NR_2)_2]_2$	195		170		205	[106]
$[Et_2O)Mg(Cl)NR_2)_2]_2$	197		170		200	[105]
$MeSi[N(^tBu)MgNR_2)_3]$	197		170			[107]
$[^sBuMgNR_2]_2$		212		174		[81]
$[R_2N{-}Mg(OCPh_2)O{-}CHPh_2]_2$	202				197/205	[82]
$[Ca(NR_2)_2]_2$	227	247	170	173		[93]
$(THF)_2Ca(NR_2)_2$	230		169		238	[108]
$(DME)Ca(NR_2)_2$	227		168		240	[93]
$(THF)_3Ca(NR''_2)_2$	234		170		240	[96]
$[Cp'CaNR''_2]_2$		241/248		173		[109]
$[Cp''Ca(THF)NR_2]_2$	229		168		235	[110]
$[Sr(NR_2)_2]_2$	244	264	169	171		[94]
$(THF)_2Sr(NR_2)_2$	246		167		253	[108,111]]
$[(DIOX)Sr(NR_2)_2]_n$	245		169		253	[66,67]
$(DME)_2Sr(NR_2)_2$	254		169		260,271	[94]
$[Ba(NR_2)_2]_2$	258	282	169	170		[95]
$[(THF)Ba(NR_2)_2]_2$	260	283/290	169	171	277	[95]
$(THF)Ba(NR_2)_2$	259		168		273	[96]
$R_2N{-}Ba(THF){-}OSi^tBu_2R'''$	258		168		260/278	[112]
$R_2N{-}Ba{-}OSi^tBu_2R'''$	263		167		262	[112]

Abbreviations: superscript t, terminal ligand; superscript b, bridging substituent; bond lengths (pm); NR_2, $N(SiMe_3)_2$; NR'_2, $N(SiMePh_2)_2$; NR''_2, $N(SiMe_2CH_2)_2$; Bu, butyl; Cp′, C_5Me_4Et; Cp″, $C_5H^iPr_4$; R‴, $(CH_2)_3NMe_2$; tetrahydrofuran, THF; 1,2-dimethoxyethane, DME; 1,4-dioxane, DIOX.

tetrahydrofuran complex of calcium bis[bis(trimethylsilyl)amide] as a representative example. The NMN angle decreases from the Mg derivative to the Ba compound due to the loss of steric strain with increasing M–N bond lengths. All the metal atoms are quadruply coordinated; which means that the barium atom cannot be coordinatively saturated and shielded as effectively as the magnesium compound. Indeed, the coordination number is enhanced by agostic interactions to the trimethylsilyl groups (shortest Ba ··· C contacts 333 and 336 pm) [95].

Special attention has to be drawn on the coordination geometry of the alkaline earth metal atom in $(Me_3Si)_2N{-}M[\mu{-}N(SiMe_3)_2]_2M{-}N(SiMe_3)_2$. Whereas the magnesium atom is surrounded trigonal planarily dictated by the crystallographic C_2 symmetry of the molecule [84], the angle sum ΣNMN of the heavier alkaline earth metals decreases from Ca (359° [93]), Sr (358° [94]) to Ba (352° [95]), thus leading to an increasing distance of the metal center to the plane deduced from the three neighboring nitrogen atoms (Ca 14 pm [93], Sr 21 pm [94], Ba 42 pm [95]).

Similar observations were made for the tris[bis(trimethylsilyl)amides] of the

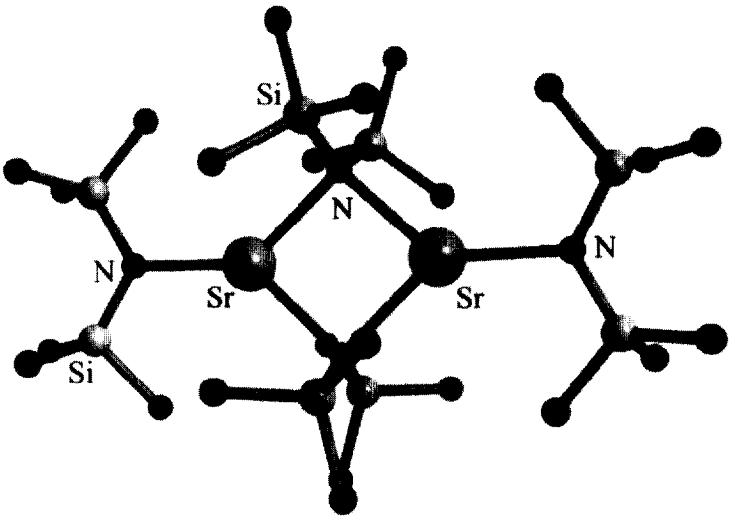


Fig. 1. Molecular structure of dimeric strontium bis[bis(trimethylsilyl)amide]. The hydrogen atoms are omitted for clarity.

group III metals scandium (angle sum ΣNScN: 347° [116]) and yttrium (ΣNYN: 344° [116]), whereas the derivatives of the group XIII metals aluminium to thallium contain trigonal planarily coordinated metal atoms [117–125]. The boron atom is too small to be bonded to three bulky $(Me_3Si)_2N$ ligands, therefore only bis[bis(trimethylsilyl)amido]boron chloride is isolated thus far [126,127].

Table 2
Comparison of selected structural data of the complexes of the alkaline earth metals of the type $(THF)_2M[N(SiMe_3)_2]_2$ (bond lengths (pm) and angles (°)

Metal M	Mg [91]	Ca [108,111]	Sr [111]	Ba [95]
Space group	$P2_1/c$	$P2_1/c$	Pbca	Pbca
a/pm	1404.3	841.6	1924.8	1795.2
b/pm	1209.9	1936.9	1747.8	2074.0
c/pm	1857.4	1938.0	1930.1	1765.2
β/°	97.5	100.8		
M-N1/M-N2	202/203	229/231	245/247	260/259
M-O	209/211	237/239	251/256	275/272
N1-Si	170/171	169/169	167/168	168/168
N2-Si		168/169	167/168	168/168
N1-M-N2	127.9	121.3	120.6	116.8
M-N1-Si		111/123	117/110	111.6/115
Si-N1-Si	120.2	126.5	132.5	133.0
M-N2-Si		110/124	117/111	114/116
Si-N2-Si	121.7	126.0	132.0	130.4

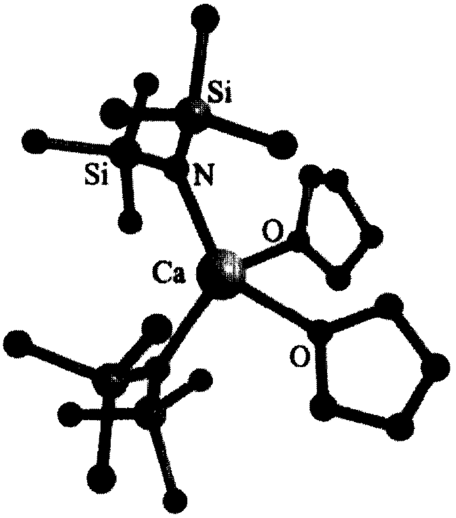


Fig. 2. Molecular structure of bis(tetrahydrofuran)calcium bis[bis(trimethylsilyl)amide]. Hydrogen atoms are omitted for clarity.

The synthesis of $M[N(SiMe_3)_2]_2$ in ether such as tetrahydrofuran or 1,2-dimethoxyethane leads to the isolation of monomeric bis(THF) (Fig. 2) or bis(DME) (Fig. 3) complexes. The preferred coordination numbers of the metals are four (THF adducts) and six (DME complexes). The metal oxygen distances vary in a rather narrow region and depend on the coordination number of the metal center. If the tetrahydrofuran adducts are exposed to a vacuum for a prolonged time period, dimeric mono(ether) complexes are formed with quadruple coordinated metal atoms [66,67,95,101], bis(tetrahydrofuran)barium bis[bis(trimethylsilyl)amide] even loses both the ether ligands [95].

Special attention has to be attributed to the dioxane complexes of magnesium [106] and strontium bis[bis(trimethylsilyl)amide] [66,67]. The dioxane molecule bridges two metal centers thus forming dimers in the case of the magnesium derivative with triply coordinated metal atoms. The strontium complex $(dioxane)Sr[N(SiMe_3)_2]_2$ crystallizes as a one-dimensional polymer (Fig. 4). The strontium atom is in a square planar environment consisting of two oxygen and two nitrogen atoms and is located on a crystallographic inversion center. However, the coordination number is enhanced due to agostic interactions with the trimethylsilyl groups ($Sr \cdots C1$ 316 pm, Sr–N–Si1 111.2°, Sr–N–Si2 122.4° [66,67]). If the steric bulk of the bis(trialkylsilyl)amide ligand is reduced, a tris(THF) complex as for example, tris(THF)calcium bis[2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentanide] [96], is isolated (Fig. 5). Following the VSEPR rule, the larger amide substituents are located in the equatorial plane of the trigonal bipyramidal coordination polyhedron of the metal center, whereas the axial positions are occupied by THF molecules.

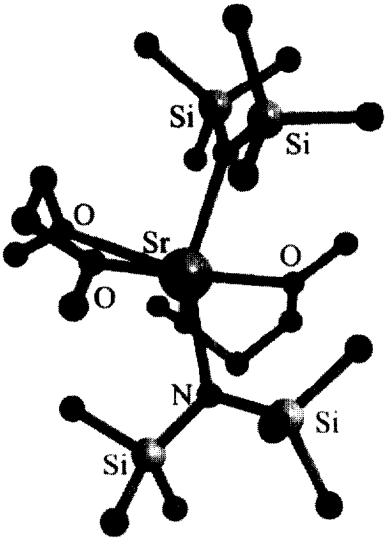


Fig. 3. Molecular structure of bis(1,2-dimethoxyethane-*O*,*O*′)-strontium bis[bis(trimethylsilyl)amide]. Hydrogen atoms are omitted for clarity.

Heterobimetallic species are isolable from the reaction of trimethylalane with magnesium bis[bis(trimethylsilyl)amide] in toluene (Eq. (8)). Here $AlMe_3$ works as a Lewis acid, coordinating to the nitrogen atom, as well as a methylating reagent [128]. The isolated compound is best described as a dimeric methylmagnesium bis(trimethylsilyl)amide, where the terminal methyl group shows agostic interactions to the magnesium center of magnesium bis[bis(trimethylsilyl)amide]. This molecule is shown in Scheme 2. Due to the small steric demand of the methyl substituent at the magnesium atom, the $Mg-N^b$ bond lengths are with values of approx. 208 pm rather small. The coordination of $AlMe_3$ to another terminal amino ligand leads to a lengthening of the Mg–N bond of approx. 19 pm.

2.1.3. *Structures in solution*

The ether adducts as well as the solvent-free dimeric molecules are soluble in benzene or toluene. The NMR data listed in Table 3 shows characteristic trends in dependency of the size of the alkaline earth metal. For the terminally bonded bis[bis(trimethylsilyl)amide] substituents the increasing size of the metal center leads to a low field shift of the $\delta(^{15}N)$-values and a high field shift of the ^{29}Si-nuclei. The coupling constant $^1J(Si,^{15}N)$ increases from 8.1 to 9.9 Hz from the magnesium to the barium derivative of $(THF)_2M[N(SiMe_3)_2]_2$. The high field shift of the $^{29}Si\{^1H\}$ resonances of the bridging amide ligands displays an even greater dependency on the size of the alkaline earth metal atom. The differences between the $\delta^b(SiMe_3)$ and $\delta^t(SiMe_3)$ decrease from the Mg to the Ba derivative of the compounds $(Me_3Si)_2N-M[\mu-N(SiMe_3)_2]_2M-N(SiMe_3)_2$.

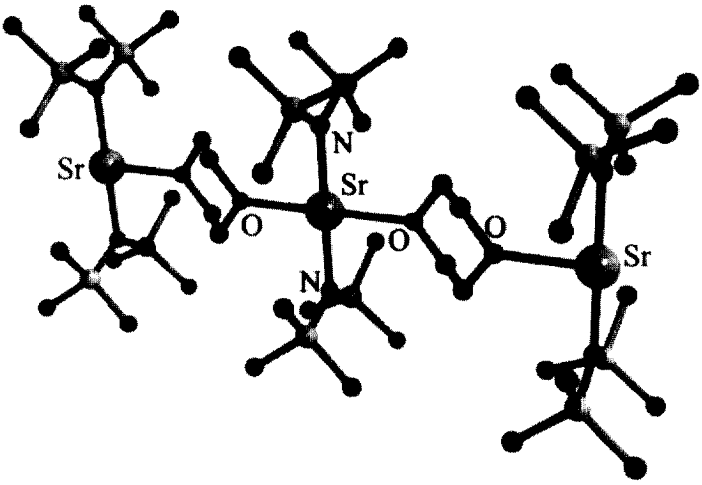


Fig. 4. Part of the polymer chain-like structure of (1,4-dioxane)strontium bis[bis(trimethylsilyl)amide]. Hydrogen atoms are omitted for clarity.

The solvent-free dimeric molecules of calcium, strontium, and barium do not dissociate in toluene or benzene as could be proven by cryoscopic determination of the molecular mass [85]. However, the calcium and strontium derivatives show a

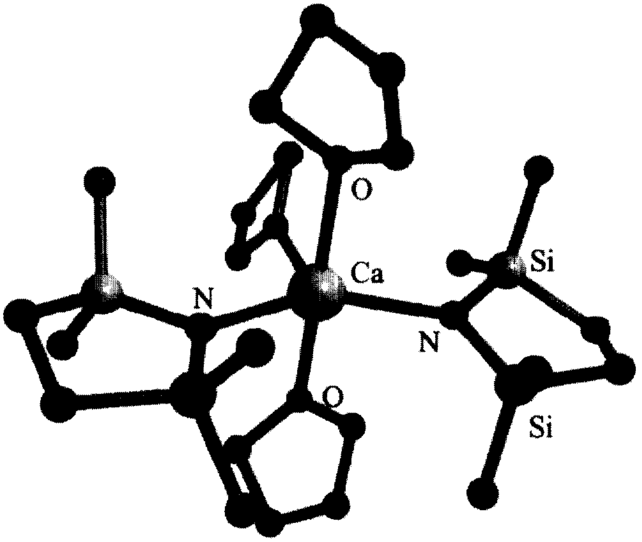


Fig. 5. Molecular structure of tris(tetrahydrofuran)calcium bis[2,2,5,5-tetramethyl-2,5-disilaazacyclopentanide]. Hydrogen atoms are omitted for clarity.

$$4\,AlMe_3 + 4\,Mg[N(SiMe_3)_2]_2 \longrightarrow \quad (8)$$
$$2\,[(Me_3Si)_2N\text{–}AlMe_2]_2 + [MeMgN(SiMe_3)_2]_2\cdot 2\,\{Mg[N(SiMe_3)_2]_2AlMe_3\}$$

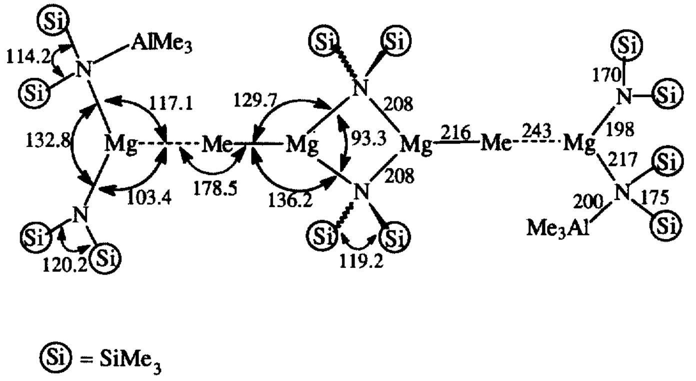
dynamic behaviour, thus leading to an exchange of the bridging and terminal bis(trimethylsilyl)amide substituents. $\{Ba[N(SiMe_3)_2]_2\}_2$ is mainly ionic, and therefore the NMR data of the bridging and terminal amide ligands are neither distinguishable in their chemical shifts, nor their coupling constants between ^{29}Si and ^{1}H as well as ^{13}C [85,95]. In contrast to the derivatives of the heavier alkaline earth metals, homologous $\{Mg[N(SiMe_3)_2]_2\}$ dissociates in benzene or toluene into monomeric molecules at elevated temperatures [85], weakly basic solvents such as chloroalkanes also lead to a monomerisation [79,80]. In the gaseous phase only monomeric magnesium bis[bis(trimethylsilyl)amide] is detected and its structure determined by electron diffraction methods [83]. The intramolecular exchange mechanism is shown in Eq. (9).

The first reaction step is the breaking of a M–N^{b} bond thus allowing the free rotation around the remaining M–N^{b} bonds. The dynamic NMR experiments permit the estimation of the coalescence temperatures and also of the energy barriers $\Delta G^{\neq}$. The Gutowsky–Holm equation is valid only for the calcium ($\Delta G^{\neq} = 72$ kJ/mol [85]) and strontium derivatives ($\Delta G^{\neq} = 53$ kJ/mol [85]), whereas for the magnesium compound with an additional monomer–dimer equilibrium a rough approximation results in a $\Delta G^{\neq}$-value of approx. 80 kJ/mol [85].

2.2. Heteroleptic derivatives with an amide ligand

2.2.1. Synthesis

In this review heteroleptic derivatives are understood as molecules with one



Scheme 2.

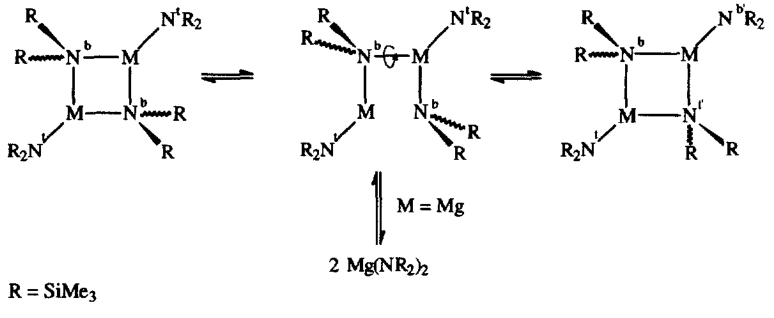
Table 3
NMR parameters of the alkaline earth metal bis[bis(trimethylsilyl)amides].

M	Be[a]	Mg	Mg	Ca	Ca	Sr	Sr	Ba	Ba
Solvent	C_6D_6	C_7D_8[b]	C_6D_6/THF[c]	C_7D_8[b]	THF[c]	C_7D_8[b]	THF[c]	C_7D_8[b]	C_7D_8/THF[c]
Temp (°C)	30	30	30	30	30	−60	30	−60	30
^1H									
$\delta^b(SiMe_3)$		0.45		0.21		0.12		0.14	
$\delta^t(SiMe_3)$	0.19	0.38	0.35	0.33	−0.01	0.33	−0.03	0.14	0.32
$^{13}C\{^1H\}$									
$\delta^b(SiMe_3)$		8.12		6.94		6.31		5.42	
$^1J(Si,C)$		53		51.4		51.8		52.1	
$\delta^t(SiMe_3)$	3.98	7.14	6.60	6.48	5.69	6.14	5.93	5.39	5.73
$^1J(Si,C)$		53	52.8	52.2	51.5	52.0	51.8	52.1	51.9
$^2J(N,C)$			2.3		2.5		2.4		2.3
$^{15}N\{^1H\}$									
$\delta(N)$	−323[d]		−345.5		−304.5		−301.9		−275.9
$^{29}Si\{^1H\}$									
$\delta^b(SiMe_3)$		−3.29		−6.54		−10.58		−18.32	
$\delta^t(SiMe_3)$		−11.57	−8.60	−13.25	−15.00	−14.95	−16.70	−18.32	−18.44
$^1J(Si,N)$			8.1		9.0		9.1		9.9

[a] Monomeric.
[b] Dimeric, $(Me_3Si)_2N^t{-}M[\mu{-}N^b(SiMe_3)_2]_2M{-}N^t(SiMe_3)_2$.
[c] Monomeric bis(tetrahydrofuran) complex.
[d] $\delta(^{14}N)$-value.
Superscript t marks terminally bonded groups; b, bridging ligands.

amide and one different anionic ligand at the alkaline earth metal center neglecting all neutral coligands such as THF or DME. Two basic synthetic routes are applicable to prepare such compounds:

1. After the synthesis of the alkaline earth metal bis[bis(trialkylsilyl)amide] one



(9)

$$2\,M[N(SiMe_3)_2]_2 + 2\,HX \longrightarrow [(Me_3Si)_2NM(\mu\text{-}X)]_2 + 2\,HN(SiMe_3)_2 \tag{10}$$

$M = Ca, Ba;\ X = P(SiMe_3)_2$
$M = Ba;\ X = OSi(^tBu)_2(CH_2)_3NMe_2$

$$[RO\text{-}M(thf)\text{-}N(SiMe_3)_2]_2 \xrightarrow{thf} (thf)_2M[N(SiMe_3)_2]_2 + M[OR]_2 \tag{11}$$

of the amide groups is substituted by a reaction with a H-acidic molecule such as a phosphane [129,130] or an alcohol [112] (Eq. (10)).

These heteroleptic compounds crystallize as dimers. The bis(trimethylsilyl)amide ligand is bound terminally in all these derivatives with bridging phosphanide and alcoholate ligands, respectively. In THF solution, barium amide alcoholate shows ligand redistribution reactions as displayed in Eq. (11) [112], however, no redistribution reactions occur in benzene or toluene.

2. The bis(trialkylsilyl)amide ligand is incorporated in a second reaction step to yield the heteroleptic alkaline earth metal derivative. Examples for this pathway are the metathesis reactions according to Eq. (12) [110] and Eq. (13) [109].

In dimeric calcium ethyltetramethylcyclopentadienide 2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentanide the nitrogen atom bridges both the calcium centers and is quadruply-coordinated.

2.2.2. Structures

Table 1 contains selected structural data of heteroleptic alkaline earth metal derivatives with one bis(trialkylsilyl)amide substituent. The bond lengths are similar to those of the homoleptic alkaline earth metal bis(amides). Distortions of the ligand geometries, particularly strongly differing M–N–Si angles, result from agostic interactions between the alkaline earth metal and one of the trimethylsilyl groups of the amide ligand. One clearly presented example is shown by Hanusa et

$$(C_5Me_5)_2Ca(thf)_2 + LiN(SiMe_3)_2 \xrightarrow{thf} (C_5Me_5)Ca(thf)_3N(SiMe_3)_2 + LiC_5Me_5 \tag{12}$$

$$2\,(C_5Me_4Et)CaI(thf)_2 + 2\,KN(SiMe_2CH_2)_2 \longrightarrow$$
$$[(C_5Me_4Et)CaN(SiMe_2CH_2)_2]_2 + 2\,KI + 4\,thf \tag{13}$$

al. [110] for ($^{i}Pr_4HC_5$)Ca(THF)N($SiMe_3$)$_2$, where the distal and proximal Ca–N–Si angles differ by 23°. The shortest Ca ··· C contact to one group comes to 295 pm, whereas the shortest Ca ··· C distance to the other trimethylsilyl group of the same ligand amounts to 390 pm.

In general, the alkaline earth metal dications tend to maximize their coordination numbers. The three basic possibilities for accomplishing this, namely the coordination of neutral coligands such as tetrahydrofuran or pyridine, oligomerization and the operation of intramolecular interactions such as agostic bonding, all serve to enhance the steric saturation of the metal centers. The drive to increase the coordination number was ignored at the beginning of the work in heavier alkaline earth metal chemistry, and therefore mostly insoluble and poorly characterized materials were published (see for example the amides prepared by Utke and Sanderson [74]).

The question whether the amide ligand or the other substituent is located on the bridging position in dimeric derivatives seems to be directed by the steric demand and probably by the hardness and softness of the base as stated by Pearson [131–136]. The sterically smaller ligand bridges the two metal centers, whereas the bulky substituent is bonded terminally. The position of the ligand is not directed by the pK_a value of the corresponding hydrogen compound as is clearly seen from the comparison HOR ($pK_a = 15.5$ for methanol [137]), cyclopentadiene ($pK_a \approx 15.5$ [138,139]), and hexamethyldisilazane ($pK_a = 25.8$ [140]), where the alcoholate group always appears as a bridging and cyclopentadienide as a terminal ligand.

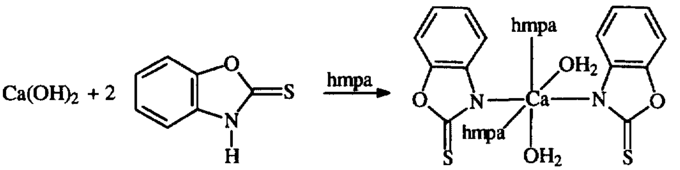
2.3. *Miscellaneous amides*

This short section is only added to complete the picture of the heavier alkaline earth metal bis(amides). Whereas numerous magnesium bis(amides) [15–18] as well as imides [141–143] exist, very few calcium, strontium, and barium derivatives are thus far known.

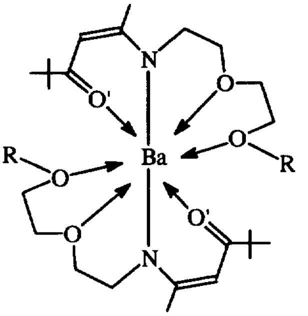
Interesting derivatives are isolated by the metalation reaction of 2-mercaptobenzoxazol with barium in the presence of tris(dimethylamino)phosphane oxide (HMPA). The barium center displays a coordination number of 7, with two bonds to nitrogen (Ba–N 291 pm), two to sulfur (Ba–S 331 m) and three to oxygen atoms (of HMPA, Ba–O 260 pm) [144,145]. Even the use of $Ca(OH)_2$ and the formation of water, which remains in the coordination sphere of the metal center, yields the desired product according to Eq. (14). The calcium atom is surrounded by two water molecules (Ca–O 239 pm), two HMPA ligands (Ca–O 227 pm), and two N-bonded mercaptobenzoxazolide substituents (Ca–N 255 pm) [146,147].

Investigating MOCVD reactions with barium derivatives a β-ketoiminate complex found the interest of Marks et al. [148]. The barium center is eightfold coordinated as shown in Scheme 3 with Ba–N distances of approx. 285 pm. Although these complexes are volatile, they are not sublimeable without decomposition.

The carbazolides of the heavier alkaline earth metals are prepared by the



(14)



R = Me:
Ba-N 283 pm
Ba-O' 256 pm
Ba-O 282-291 pm

R=CH_2CH_2OEt:
Ba-N 286 pm
Ba-O' 258 pm
Ba-O 280-284 pm

Scheme 3.

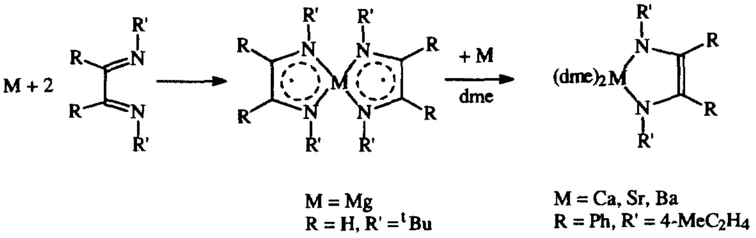
metalation of carbazole with the metal dissolved in liquid ammonia [149]. In order to obtain crystalline compounds, the ammonia ligands can be substituted by DME or pyridine; selected structural data is given in Table 4.

The electron transfer from the alkaline earth metal to a substituted 1,4-diazabutadiene yields metallacycles. A one-electron reduction of the diazabutadiene leads to the formation of radical anions and deep-red paramagnetic magnesium bis[1,4-di-tert.-butyl-1,4-diazabutadienide] [150]. If the ligands react as a two-electron acceptor, diamagnetic magnesium (1,4-di-tert.butyl-1,4-diazaabutandiide) is isolated according to Eq. (15) [151]. For the heavier alkaline earth metals calcium, strontium and barium, only the two-electron transfer reaction is observed in DME. The X-ray structure of the bis(DME) complex of calcium shows a distorted octahedral

Table 4
Selected bond lengths (pm) and angles (°) of the bis(carbazolyl)alkaline earth metal compounds [149]

	M–N[a]	NMN
$(Carbazolyl)_2Ca(py)_4$	244	172.7
$(Carbazolyl)_2Sr(DME)_2(NH_3)$	257/262	171.3
$(Carbazolyl)_2Ba(DME)_3$	275	98.1

[a] Distance between the metal and the carbazolyl substituent.



(15)

coordinated metal center with mean Ca–N and Ca–O distances of 233 and 242 pm, respectively [152], whereas the barium derivative is dimeric.

3. Ab-initio SCF calculations

The growing interest in alkaline earth metal chemistry also led to an enhancement of theoretical knowledge such as charge distribution and geometrical parameters derived from ab-initio SCF calculations. A well-known feature already incorporated into some student textbooks is the non-linearity of some alkaline earth metal dihalides [153–156]. The expansion of these investigations to the hydroxides, amides and methanides shows decreasing angles XMX from the linear magnesium to the bent barium derivatives (Table 5). The smallest angle is predicted for monomeric barium dimethanide with a CBaC value of 116° [157], the corresponding angle for $Ba(NH_2)_2$ amounts to 118° [157]. The neglect of neutral complex ligands, such as THF or DME, is a simplification, solvent-free monomeric molecules would precipitate as oligomers or polymers. Nevertheless, the bending of the molecules emphasizes the unique bonding characteristics for alkaline earth metal derivatives. Already in 1966, Hayes [158] explained these deviations from linearity by d orbital participation and concluded a favored sd hybridization against an sp hybridization [153,154,158]. Guido and Gigli [159] also offered the model of the 'reverse polarisation' of the soft dications by the relatively hard anions. For soft (for example cyclopentadiienide) anions the intramolecular van der Waals attraction of the ligands has to be considered [160].

The calculated geometries of calcium, strontium and barium dications coordinated by two or three ammonia or water molecules also show the preference of a bent or pyramidal coordination sphere, respectively [161,162]. The Hartee–Fock results give smaller X–M–X angles than the NP2 calculations, however, the trend is similar. The calcium derivative displays angles XCaX between 132 and 143°, depending on the method as well as on the fact whether the dihydrate or the bis(ammonia) complex is considered. Furthermore, the energy potential is very shallow, that means, $Ca(H_2O)_2^{2+}$ is a quasi-linear dication. On the other hand, BaX_2^{2+} with X as water or ammonia, a XBaX angle between 110 and 117° is

Table 5
Selected bond lengths (pm) and angles (°) of monomeric alkaline earth metal compounds of the type MX_2

MX_2		Mg	Ca	Sr	Ba	Ref.
MF_2	M–F		205	219	233	[155,156]
	FMF		180	144	126	
$M(OH)_2$	M–O	176	206	220	235	[157]
	OMO	180	180	151	131	
$M(NH_2)_2$	M–N		222	236	250	[157]
	NMN		180	132	118	
$M(CH_3)_2$	M–C		249	262	276	[157]
	CMC		180	131	116	

estimated with a deeper energy minimum. Similar results were obtained for ScX_2^{3+}, YX_2^{3+} and LaX_2^{3+} with X as H_2O or NH_3 [161,162].

Monomeric [163] and dimeric structures [164] were optimized by ab-initio SCF methods for the hydrides and show transferable trends. The tris(ammonia)barium dication is built pyramidically [161,162]. Comparable coordination geometries are found in $HBa(\mu\text{-}H)_2BaH$ [164], however, the minimum structure is not the monocyclic but the bicyclic structure, and even the quadruply bridged tricyclic species has to be considered (Scheme 4). For the dimer Mg_2H_4 the planar molecule of D_{2h} symmetry of the type $HMg(\mu\text{-}H)_2MgH$ is the lowest in energy, whereas the triply bridged bicyclic species $HMg(\mu\text{-}H)_3Mg$ with a C_{3v} symmetry is disfavored by 28 kcal/mol (Table 6). For Ca_2H_4 the C_{3v} symmetric triply bridged molecule is higher in energy by only 4 kcal/mol, this isomer even turns out to be the most favorable for strontium and barium.

Similar Hartree–Fock calculations for the dimeric phosphanides $M_2(PH_2)_4$ favor the magnesium derivative, the monocyclic C_{2h} symmetric isomer of the type $H_2P\text{–}Mg(\mu\text{-}PH_2)_2Mg\text{–}PH_2$. For dimeric calcium and strontium bis(phosphanide) the bicyclic C_1 symmetric congeners are the lowest in energy, whereas for the heaviest alkaline earth metal the quadruply bridged $Ba(\mu\text{-}PH_2)_4Ba$ is the favored isomer [165]. With the pyramidical coordination geometry of the metal centers of the dimeric alkaline earth metal bis[bis(trimethylsilyl)amides] in mind, the exocyclic $M\text{–}M\text{–}P^t$ angle of $H_2P^t\text{–}M(\mu\text{-}PbH_2)_2M\text{–}P^tH_2$ gives similar results. The magnesium and calcium atoms are in a planar surrounding, whereas the pyramidalization of the coordination sphere of strontium ($Sr\text{–}Sr\text{–}P^t$ 163.5°) and barium ($Ba\text{–}Ba\text{–}P^t$ 127.3°) leads to an energetic favoring.

A closer view of the bond lengths of the bicyclic C_1 symmetric dimers suggests a formulation as $[H_2P\text{–}M]^+[(H_2P)_3M]^-$. The intraionic distances are clearly shorter than the interionic contacts, where the differences in percentages decrease from

Table 6
Relative energies obtained by ab-initio SCF calculations of dimeric alkaline earth metal dihydrides and bis(phosphanides) (kJ/mol); see also Scheme 4

Symmetry	Mg	Ca	Sr	Ba
M_2H_4 [164]				
D_{2h}[a]	0.0	0.0	8.4	41.0
C_{2h}[b]			8.4	22.2
C_{3v}[c]	118.9	17.2	0.0	0.0
D_{4h}[d]	513.7	159.5	103.0	52.8
$M_2(PH_2)_4$ [165,166]				
C_{2h}[b]	0.0	51.6	41.3	60.0
C_i[c]	27.9	0.0	0.0	8.0
D_{4h}[d]	212.3	44.2	17.9	0.0

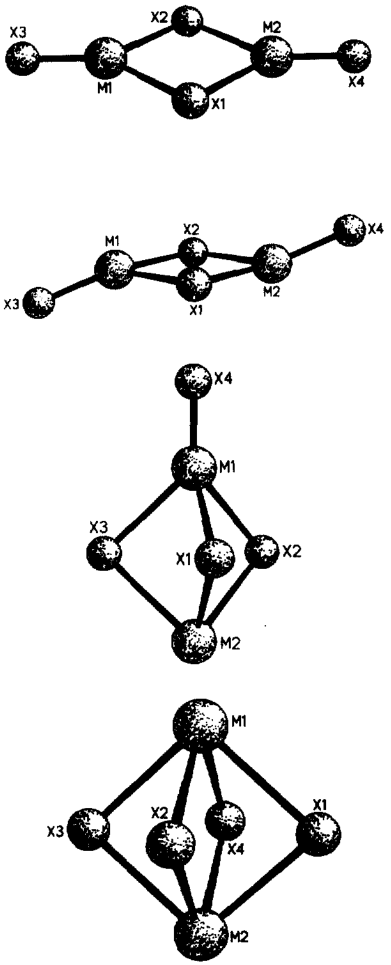
[a] Monocyclic, planar.
[b] Monocyclic, pyramidalization of the coordination sphere of the metal center allowed.
[c] Bicyclic.
[d] Tricyclic.

magnesium to barium: Mg–P/Mg ··· P 250/275 pm, Ca–P/Ca ··· P 286/307 pm, Sr–P/Sr ··· P 304/325 pm, and Ba–P/Ba ··· P 324/344 pm. For the D_{4h} symmetric isomers the bond lengths lie between the values mentioned above: Mg–P 267.4 pm, Ca–P 296.3 pm, Sr–P 313.1 pm, and Ba–P 331.9 pm [166,167].

The reason for these somewhat unexpected structures is a combination of the polarization of the heavier metal dications by the small anions ('reverse polarization') and small but significant d-orbital participation at the metal atoms for the σ-bond contributions. The influence of neutral coligands such as THF or TMEDA were not taken into account, however, Schleyer et al. [149] concluded that 'the preferred anion orientation in unsolvated species will dominate the coordination geometries of the solvated complexes as well', if the neutral coligands are not too bulky thus enforcing another coordination geometry at the alkaline earth metal center. In contrast to the orientation, the bond lengths are affected by additional coordination of Lewis bases to the metal centers.

4. Reactions of the alkaline earth metal bis(amides)

Since the first report of the heavier alkaline earth metal bis[tri(methylsilyl)amides] a vast development of the alkaline earth metal chemistry has occurred. The importance of the alkoxides and siloxides as precursors for MOCVD processes led to a parallel elaboration of this branch of molecular alkaline earth metal chemistry [168–176]. A point of contact is the synthesis of a siloxide [177] and of alkoxides [178–180] by the reaction of the alkaline earth metal [bis(trimethylsilyl)amides] with the corresponding alcohols. Further possible reaction pathways to the alcoholates are only mentioned in this review:



D_{2h} symmetry (X = H),
reduced to C_{2h} for phosphanide (X = PH_2)
monocyclic
M1, M2 trigonal planar

C_{2h} symmetry (X = H, PH_2)
monocyclic
M1, M2 trigonal pyramidal

C_{3v} symmetry (X = H),
reduced to C_1 for phosphanide (X = PH_2)
bicyclic
M1 distorted tetrahedral,
M2 trigonal pyramidal

D_{4h} symmetry (X = H, PH_2)
tricyclic
M1, M2 square pyramidal

Scheme 4.

- The metalation of alcohols with alkaline earth metals, which are often activated, is the most common access to alcoholates [66,67,101,178,179,181–190].
- The use of alkaline earth metal dihydrides avoids the need of metal activation [186,191] as well as separation procedures due to the evolution of dihydrogen.
- The metathesis reaction of alkaline earth metal dihalogenides and potassium alcoholate [178,179,192], thiolate, and selenolate [193] adds a separation step from the precipitating potassium halogenide.
- The alcoholate/alcohol exchange reaction is only suitable, if the starting alcoholate leads to a volatile alcohol, which is easily removed in order to direct the equilibrium towards the product [194].

$$MO + SiO_2 + 3\,HOCH_2CH_2OH \xrightarrow[-3\,H_2O]{} M[(OCH_2CH_2O)_3Si] \qquad (16)$$

M = Mg, Ca, Ba

- The reaction of the oxides MO (M = Mg, Ca, Ba) with SiO_2 and glycol yields an alcoholate (Eq. (16)), where the central moiety $[Si(OCH_2CH_2O)_3]$ consists of a hexa-coordinated silicon atom; these dianions are connected via M–O contacts. The crystal structure of the barium derivative reveals Ba–O bond lengths of 268–296 pm [195–197].

The structures of the alcoholates show similar features as the ones of the phosphanides discussed in a later section. Solvent-poor dimeric derivatives crystallize with a bicyclic trigonal bipyramidal M_2O_3 core, where the metal atoms occupy the apical positions, and the oxygen atoms are located on the equatorial positions. The alcoholates are not discussed more deeply since most of them were not prepared via the alkaline earth metal bis[bis(trimethylsilyl)amide] route. This review is limited to those products, where the bis(trialkylsilyl)amides are essential synthons for the formation of bonds between an alkaline earth metal and another main group element such as a pentele or chalcogen.

4.1. Selenolates and tellurolates

The presence of bulky ligands guarantees soluble alkaline earth metal derivatives, however, the incorporation of weak or reactive bonds limits quite often the synthetic routes. Examples are tris(trimethylsilyl)silylselenol and -tellurol, since the reaction with alkaline earth metal in liquid ammonia leads to a fragmentation of these compounds. The use of $M[N(SiMe_3)_2]_2$ in tetrahydrofuran yields quantitatively the desired selenolates and tellurolates according to Eq. (17) [198–200].

The magnesium derivatives are easily accessible by metalation of the H–Se and H–Te moiety with magnesium dibutanide, a commercially available chemical. Table 7 summarizes selected structural features of the alkaline earth metal bis[tris(trimethylsilyl)silylselenolates] and -tellurolates]. All these molecules are isolated as crystalline Lewis base adducts. The angles M–E–Si increase with the size of the alkaline earth metal and the coordination number (C.N.) of the metal atom. The raised ionicity of the M–E bond for the heavier metals and the

$$M[N(SiMe_3)_2]_2 + 2\,HESi(SiMe_3)_3 \xrightarrow{thf} (thf)_4M[ESi(SiMe_3)_3]_2 + 2\,HN(SiMe_3)_2 \qquad (17)$$

M = Ca, Sr, Ba
E = Se, Te

Table 7
Selected bond lengths (pm) and angles (°) of the complexes $(L)M[ESi(SiMe_3)_3]_2$ with E as a selenium or tellurium atom

M/C.N.[a]	E	L	M–E	EME	MESi	Ref.
Mg/4	Se	$^{t}BuC(CH_2PMe_2)_3$[b]	248.3 250.0	132.7	115.5 113.5	[200]
Sr/6	Se	2 TMEDA	294.6	180.0	167.0	[200]
Mg/4	Te	2 THF	272.0 271.4	135.5	113.4 115.3	[199,200]
Ca/6	Te	4 THF	319.7	180.0	128.5	[199,200]
Ca/6	Te	4 THF	319.4	180.0	128.6	[198]
Ba/7	Te	5 Py	338.2	171.9	144.4	[200]

[a] Coordination number, C.N. of the alkaline earth metal atoms.
[b] Molecule operates as a bidentate ligand.

enhanced interligand strain due to the higher coordination numbers are the main reasons for this observation. However, the formal substitution of the tris(trimethylsilyl)silyl substituent by a 2,4,6-tri(tert.-butyl)phenyl group gives different crystallographic results. In tetrakis(tetrahydrofuran)strontium bis[2,4,6-tri(tert.-butyl)phenylthiolate] and -selenolate] rather small Sr–E–C angles of 120.9 and 117.6°, respectively, are found, the Sr–Se bond lengths amount to 306.6 pm and are strongly widened by more than 10 pm due to the steric strain between the ligands [193]. In contrast to these derivatives, dimeric bis(DME)barium bis[2,4,6-tri(isopropyl)phenylthiolate] displays a value for the angle Ba–S–C of the terminal ligand of 163.2°. The floppyness of the angles M–E–C and M–E–Si is a consequence of the mainly ionic bonding situation, where the anion–cation attraction and the anion–anion repulsion dominate the bonding parameters, however, the orientation of the ligand is enforced by steric arguments.

4.2. Phosphanides and arsanides

4.2.1. Synthesis

Already in 1942 calcium bis(phosphanide) was described as a hexakis- as well as a bis(ammonia) adduct. The metalation of phosphane PH_3 with calcium, dissolved in liquid ammonia, yields quantitatively the desired phosphanide $(H_3N)_6Ca(PH_2)_2$, which loses ammonia above 0°C and even phosphane above 55°C (Eq. (18)) [201].

More than a decade later, Stone and Burg [202] isolated methyl substituted arsane via the metalation of arsane by calcium in liquid ammonia according to Eq. (19), however, no further details on the properties of $Ca(AsH_2)_2$ and $Ca(AsHMe)_2$ were provided.

The metalation of bis(trialkylsilyl)phosphane and -arsane with the alkaline earth

$$\mathrm{Ca/NH_3} + 2\,\mathrm{PH_3} \xrightarrow[-\mathrm{H_2}]{\mathrm{NH_3/\text{-}70^\circ C}} \mathrm{(H_3N)_6Ca(PH_2)_2} \xrightarrow[-4\,\mathrm{NH_3}]{0^\circ\mathrm{C}} \mathrm{(H_3N)_2Ca(PH_2)_2}$$

$$\xrightarrow[-2\,\mathrm{NH_3}]{55\text{-}70^\circ\mathrm{C}} \mathrm{CaPH} + \mathrm{PH_3} \qquad (18)$$

$$\mathrm{Ca} + 2\,\mathrm{AsH_3} \xrightarrow[-\mathrm{H_2}]{\mathrm{NH_3}} \mathrm{Ca(AsH_2)_2} \xrightarrow[-\mathrm{CaI_2}]{+2\,\mathrm{MeI}} 2\,\mathrm{MeAsH_2}$$

$$\xrightarrow[-\mathrm{H_2}]{\mathrm{Ca/NH_3}} \mathrm{Ca(AsHMe)_2} \xrightarrow[-\mathrm{CaI_2}]{+2\,\mathrm{MeI}} 2\,\mathrm{Me_2AsH} \qquad (19)$$

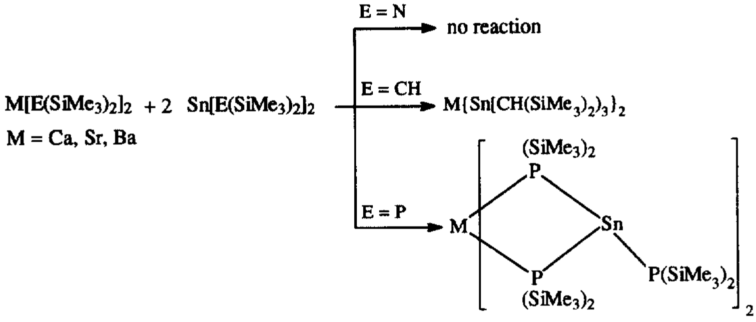
metal bis[bis(trimethylsilyl)amides] in tetrahydrofuran yields the corresponding phosphanides and arsanides (Eq. (20)) [108,203]. This preparative access to the alkaline earth metal bis(phosphanides) is in contrast to the heavier alkali metal chemistry. The reaction of potassium bis(trimethylsilyl)amide with bis(trimethylsilyl)phosphane leads to a redistribution of the trimethylsilyl groups, and all possible derivatives of $PH_x(SiMe_3)_{3-x}$ are detectable, and no potassium phosphanides have formed. However, the metalation of bis(trimethylsilyl)phosphane with KH or KO^tBu succeeds nearly quantitatively [204–207]. The metalation of bis(trialkylsilyl)phosphane by the commercially available magnesium dibutanide offers an easier access to the phosphanides of this alkaline earth metal [208].

In THF solution the alkaline earth metal bis[bis(trialkylsilyl)phosphanides] and -arsanides] are monomeric, colorless and sensitive towards air and moisture.

The synthesis of these derivatives from alkaline earth metals, dissolved in a toluene/ammonia mixture, and bis(trimethylsilyl)phosphane as described by Drake et al. [209] is irreproducible. The spectroscopic data are erroneous and incompatible with an alkaline earth metal bis[bis(trimethylsilyl)phosphanide] (see also Westerhausen et al. [129]; even the NMR data for $HP(SiMe_3)_2$) and $P(SiMe_3)_3$ given by Drake et al. [209] are incorrect). The transmetalation reaction with bis[bis(trimeth-

$$\mathrm{(thf)_2M[N(SiMe_3)_2]_2} + 2\,\mathrm{HE(SiR_3)_2} \xrightarrow{\mathrm{thf}} \mathrm{(thf)_nM[E(SiR_3)_2]_2} + 2\,\mathrm{HN(SiMe_3)_2}$$

M/n = Mg/2, Ca/4, Sr/4, Ba/4 (20)
E = P, As; R = alkyl



(21)

ylsilyl)phosphanyl]stannylene employed so successfully for the synthesis of the alkaline earth metal bis[bis(trimethylsilyl)amides] does not yield the desired phosphanides. Whereas the bis(amino)stannylene does not react with the already formed alkaline earth metal bis(amides), an insertion reaction is observed for the isoelectronic $Sn[CH(SiMe_3)_2]_2$ [100] and the homologous dimeric $\{Sn[P(SiMe_3)_2]_2\}_2$ [96] as summarized in Eq. (21).

The trialkylstannanide bonds via the tin atom to the alkaline earth metal, whereas the tris (phosphanyl)stannanide shows an inverse coordination behaviour as shown in Eq. (21). Subsequent loss of tris(trimethylsilyl)phosphane yields heterobimetallic derivatives of tin(II) and the alkaline earth metals with trimethylsilylphosphandiide besides bis(trimethylsilyl)phosphanide ligands. The synthesis and properties of the heterobimetallic compounds are consolidated in Section 4.6, here we limit the discussions to the homometallic alkaline earth metal compounds.

4.2.2. Structures

Table 8 summarizes selected data of monomeric bis(trialkylsilyl)phosphanides and -arsanides of the alkaline earth metals, all of them being Lewis base adducts. The dependency of the P-bonded substituents on the Mg–P distances is remarkably large. Whereas in $(TMEDA)Mg(PHPh)_2$ a Mg–P bond length of 259 pm [211,212] is observed, the corresponding distances of the ether adducts of magnesium bis[bis(trimethylsilyl)phosphanides] are approx. 10 pm smaller [208,210]. All known phosphanides of the heavier alkaline earth metals are trialkylsilyl substituted as can be seen from Table 8. The coordination number of the metal atoms rises from four for the magnesium compounds to eight for tris(DME)barium bis(2,2,5,5-tetramethyl-2,5-disilaphospholanide) as shown in Fig. 6. The angle sum ΣXEX of the pentele atom varies between 309° for $(THF)_2Mg[As(SiMe_3)_2]_2$ (Fig. 7) [208] and a planar coordinated pentele atom as for example in $(THF)_4Ba[P(SiMe_2{}^iPr)_2]_2$ [165]. If both the phosphanide or arsanide ligands of one molecule are not related by crystallographic symmetry, the angle sums of the pentele atoms differ quite often drastically as for example in tetrakis(tetrahydrofuran)strontium bis[bis(trimethylsilyl)arsanide] [216,217] with values of 337.8 and

Table 8
Selected bond lengths (pm) and angles (°) of the complexes $(L)_nM[E(SiR_3)_2]_2$ as well as chemical $^{31}P[^1H]$ shifts of the bis(phosphanides)

Compound	$\delta(^{31}P\{^1H\})$	M–E	EME	SiPSi	ΣXEX	Ref.
$(THF)_2Mg[P(SiMe_3)_2]_2$	−295	250.3	143.6	104.8	328.7	[208]
$(DME)Mg[P(SiMe_3)_2]_2$	−296	248.7	122.5	106.6	325.3	[210]
$(TMEDA)Mg(PHPh)_2$	−124	259.2 258.7	122.5			[211,212]
$(THF)_4Ca[P(SiMe_3)_2]_2$	−282	291.1 292.4	175.2	103.9 103.9	356.2 356.2	[130]
$(TMTA)_2Ca[P(SiMe_3)_2]_2$	−277	299.4	110.2	101.2	357.3	[203]
$(THF)_4Ca[PHSi^iPr_3]_2$	−313	294.7	180.0	97[a)]	332	[166,167]
$(THF)_4Sr[P(SiMe_3)_2]_2$	−274	303.5 300.6	174.2	106.0 106.5	356.0 359.9	[213]
$(THF)_4Sr[P(SiMe_2{}^iPr)_2]_2$	−290	308.9	168.5	104.5	344.2	[214]
$(THF)_4Ba[P(SiMe_3)_2]_2$	−251	315.8 319.0	174.9	104.9 103.7	347.3 342.6	[203]
$(THF)_4Ba[P(SiMe_2{}^iPr)_2]_2$	−274	320.0 318.4	139.9	109.0 105.7	341.8 360.0	[165]
$(DME)_3Ba[P(SiMe_2CH_2)_2]_2$	−289	333.3	178.9	89.7	340.3	[215]
$(THF)_2Mg[As(SiMe_3)_2]_2$		258.9 259.7	147.4	101.6 102.9	309.1 325.7	[208]
$(THF)_4Ca[As(SiMe_3)_2]_2$		301.7 297.2	175.1	102.3 102.8	348.0 355.5	[216]
$(THF)_4Sr[As(SiMe_3)_2]_2$		310.2 314.6	171.1	102.8 101.4	359.6 337.8	[216]
$(THF)_4Ba[As(SiMe_2{}^tBu)_2]_2$		330.2	140.8	109.6/ 111.9	331.1/ 350.5[b)]	[217]

[a] Si–P–H angle.
[b] Disorder of the trialkylsilyl groups.

359.6°. These findings enforce a closer view on the conformations of the tetrakis(tetrahydrofuran) complexes of calcium, strontium, and barium. The PSi_2 planes of the calcium [130] and strontium bis[bis(trimethylsilyl)phosphanides [213] are nearly perpendicular to each other and staggered to the metal–oxygen bonds. Another possibility is realized for crystalline $(THF)_4Sr[As(SiMe_3)_2]_2$, where two As–Si bonds are eclipsed to one M–O bond, whereas the other As–Si bonds are arranged in a staggered manner (Scheme 5).

The barium atom is large enough to coordinate five THF molecules in the equatorial plane of a pentagonal bipyramide. One of these THF molecules is

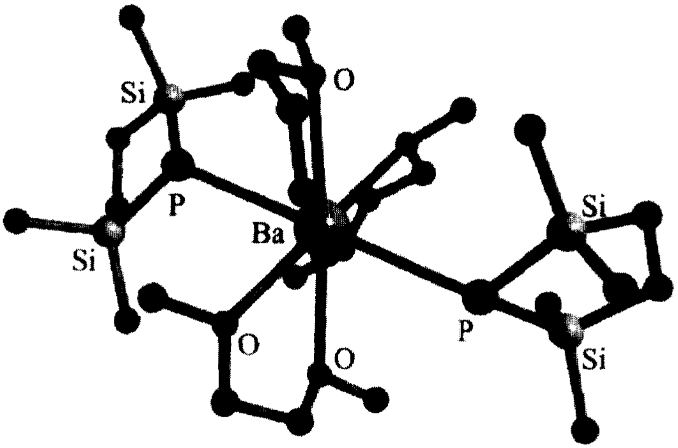


Fig. 6. Molecular structure of tris(1,2-dimethoxyethane-*O*,*O*′)barium bis[2,2,5,5-tetramethyl-2,5-disilaphospha-cyclo-pentanide]. Hydrogen atoms are omitted for clarity.

released to give a coordination gap shielded by trialkylsilyl groups. The other two E–Si bonds are more or less eclipsed to two M–O bonds. Due to the coordination gap the E–Ba–E moiety is bent towards this gap with a value of approx. 140°.

The degree of planarization of the coordination sphere of the pentele atom has no influence on any kind of back bonding from the anion to the metal dication. Due to the ionicity of these compounds the distance between cation and anion plays the key role, not the orientation of the ligand. The orientation is a conse-

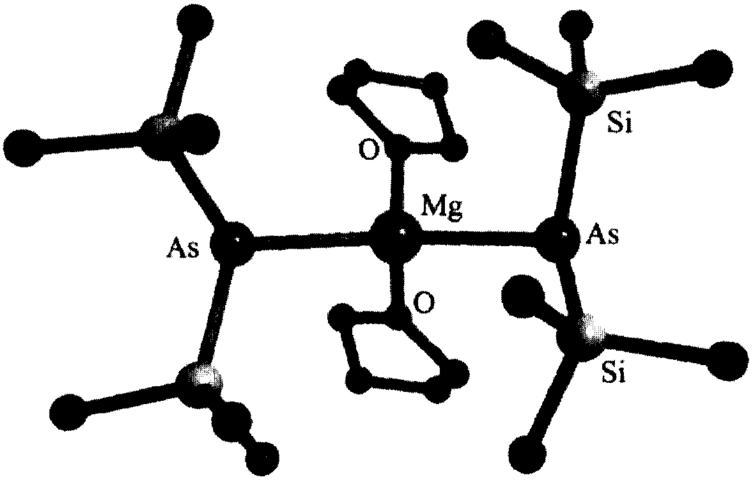
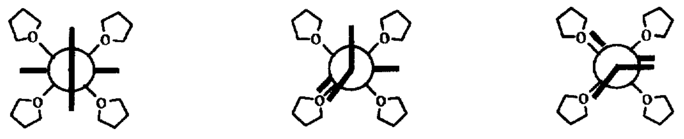


Fig. 7. Molecular structure of bis(tetrahydrofuran)magnesium bis[bis(trimethylsilyl)arsanide]. Hydrogen atoms are omitted for clarity.



$(thf)_4Sr[P(SiMe_3)_2]_2$
$(thf)_4Ca[As(SiMe_3)_2]_2$
$(thf)_4Ca[P(SiMe_3)_2]_2$

E planar

$(thf)_4Sr[As(SiMe_3)_2]_2$

E pyramidal

$(thf)_4Ba[P(SiMe_3)_2]_2$
$(thf)_4Ba[As(SiMe_3)_2]$

E pyramidal

Scheme 5.

quence of intramolecular ligand–ligand repulsion. The longest Ca–P bonds of 299 pm are observed for $(TMTA)_2Ca[P(SiMe_3)_2]_2$, where the tridentate amino bases enforce a planar surrounding at the phosphorus atoms; furthermore, the enhanced coordination number of eight at the calcium atom explains the long Ca–P bonds [203].

The crystallization of the bis(trialkylsilyl)phosphanides of the alkaline earth metals from a toluene solution, saturated at elevated temperatures, yields dimeric molecules. In contrast to the amides discussed in Section 2.1 and to the lithium bis(trimethylsilyl)phosphanides, which form four-membered ring systems [218,219], often annulated to ladder structures [220], the alkaline earth metal bis[bis(trialkylsilyl)phosphanides] crystallize with bicyclic trigonal bipyramidal structures. The metal atoms are located in the apical positions, and the pentele atoms are arranged in the equatorial plane. The fourth phosphanide ligand is bonded terminally to one of the metal centers. The coordination spheres are completed by Lewis bases (neutral coligands) such as THF or DME (Fig. 8). In Table 9 characteristic structural parameters are listed, the superscript numbers of the metal atoms give the number of the coordinated anionic ligands, the superscripts b and t at the pentele atoms symbolize bridging and terminal ligands, respectively. The distances between M^4 and the terminal bonded phosphorus atom P^t lie in the range for characteristic M–P bond lengths as shown in Table 8.

Enhanced steric repulsion of the bis(trialkylsilyl)phosphanide ligands prevents the bicyclic constitution of the type $R{-}M(\mu{-}R)_3M$, and monocyclic dimers of the type $RM(\mu{-}R)_2MR$ crystallize. An example is the centrosymmetric dimeric bis(tetrahydrofuran)barium bis[bis(dimethyl-isopropylsilyl)phosphanide] [165] with five-fold coordinated metal centers. The Ba–P bond lengths to the bridging and to the terminal phosphanide ligands lie with values of 332 and 316 pm, respectively, in the expected range.

The reaction of strontium bis[bis(dimethyl-isopropylsilyl)phosphanide] with water in tetrahydropyran (THP, oxacyclohexane) yields a tetranuclear, oxygen-centered phosphanide of strontium as displayed in Eq. (22) and Fig. 9. This polycyclic derivative can be described as a heteroatom Sr_4P_6 adamantane structure with an

Table 9
Comparison of the bicyclic structures of the type $X^t\text{–}M^4(L)_n[\mu\text{-}P^bRR']_3M^3(L)_m$ with the geometries obtained from ab-initio SCF calculations for $H_2P^t\text{–}M^4(\mu\text{-}P^bH_2)_3M^3$

M	Ca[a]	Ca[b]	Sr[a]	Sr[b]	Ba[a]	Ba[b]
X^t	$N(SiMe_3)_2$	PH_2	$P(SiMe_3)_2$	PH_2	$P(SiMe_2CH_2)_2$	PH_2
L	THP	–	THF	–	DME	–
n	0	–	0	–	1	–
m	3	–	3	–	2	–
R	H	H	$SiMe_3$	H	$SiMe_2CH_2$	H
R′	Si^iPr_3	H	$SiMe_3$	H	$SiMe_2CH_2$	H
$M^3\text{–}P^b$	297.8 298.3 297.1	285.8 285.7 285.7	312.8 320.2 320.4	303.5 303.5 303.5	325.4 326.8 328.7	323.1 323.1 323.1
$M^4\text{–}P^b$	290.9 294.7 288.2	307.9 307.4 307.4	308.2 304.0 305.0	325.1 324.7 324.7	338.1 327.2 332.7	344.7 344.3 344.3
$M^4\text{–}X^t$	228.1	286.5	304.3	304.8	317.8	325.1
Ref.	[221]	[166,167]	[213]	[166,167]	[215]	[166,167]

[a] X-ray structures.
[b] Ab-initio SCF calculations.
Superscripts 3 and 4 give the number of anionic ligands bonded to the metal center; b and t characterize bridging and terminal ligands.

oxygen atom in the center of the polyhedron. Another alternative to look at this molecule is the Sr_4O tetrahedron, where all edges are bridged by bis(dimethyl-isopropylsilyl)phosphanide substituents. The mean Sr–O (236 pm) and Sr–P bonds (309 pm) lie in the already well-known range. The strontium atoms are only quadruply coordinated, therefore agostic bonds to the trialkylsilyl groups enhance the coordination number of the metal centers (Sr ⋯ C 312 and 328 pm [214]).

Solvent-free magnesium bis[bis(triorganylsilyl)phosphanides] are only accessible, if the steric shielding of the Lewis acid metal center is effective enough to prevent polymerisation. The use of diisopropylsilyl groups leads to the formation of a dimer (Eq. (23)), whereas the trimethylsilyl substituted phosphanides crystallize as trimers (Eq. (24)) [222], Fig. 10 shows the molecular structure.

Dimeric magnesium bis[diisopropylsilyl)phosphanide] shows a $^2J(P,P)$ coupling constant of 22 Hz with $\delta(P)$ values of -301 and -347 ppm for the bridging and

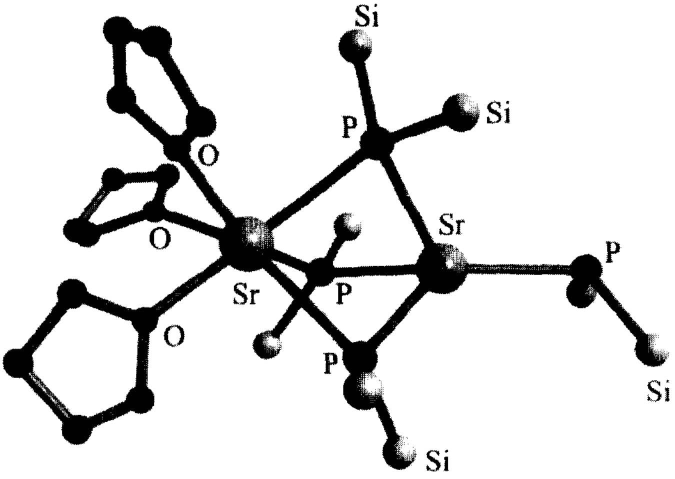


Fig. 8. Molecular structure of the dimeric tris(tetrahydrofuran) complex of strontium bis[bis(trimethylsilyl)phosphanide]. The methyl groups as well as the hydrogen atoms are omitted for clarity.

terminal phosphanide ligands. The ligand exchange reaction between terminal and bridging positions is very slow on the NMR time scale.

4.2.3. Solution equilibria

In ethers such as THF or DME the alkaline earth metal bis[bis(trialkylsilyl)phosphanides] are monomeric. However, in aromatic hydrocarbons such as toluene or benzene a monomer–dimer equilibrium is observed by NMR spectroscopy (Eq. (25)). At low temperatures the monomeric molecule dominates, and with increasing temperature the concentration of the dimeric complexes increases. The $^{31}P\{^1H\}$-NMR spectroscopy allows an unambiguous distinction of the two chemically and magnetically different phosphanide ligands of the dimer and the $(R_3Si)_2P$ substituents of the monomer (Fig. 11). If the trialkylsilyl groups are small, the bicyclic monomer is favored. In the case of $(DME)_3Ba_2[P(SiMe_2CH_2)_2]_4$ the coupling pattern of the phosphorus nuclei proves the bicyclic structure in toluene solution. The quartet of the terminal phosphorus atom and the dublet of the three bridging ones show a very small $^2J(P^t,P^b)$ coupling constant of 6.7 Hz [215]. Due to an additional intramolecular ligand exchange reaction, which can be fast on the NMR time scale, the bridging and the terminal phosphanide substituents often cause only one broad resonance [215,223].

The species observed in toluene or benzene solution interact according to Eq. (25). The monocyclic dimer is stabilized by sterically demanding trialkylsilyl groups. The ligand exchange occurs after breaking of a M–P^b bond and rotation about the remaining M–P bonds. The ligand exchange mechanism of the bicyclic derivatives only needs the breaking of one M–P^b bond in that way that the monocyclic

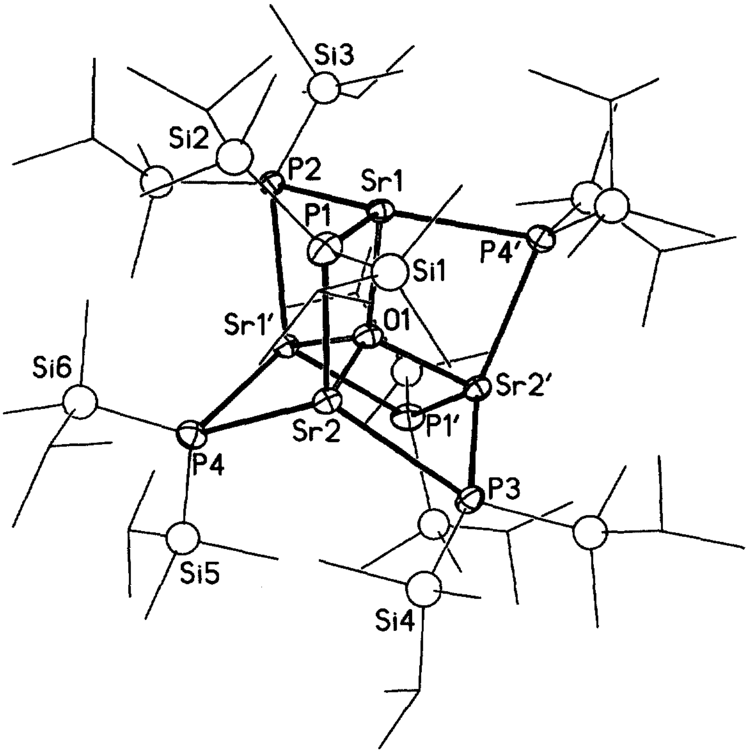
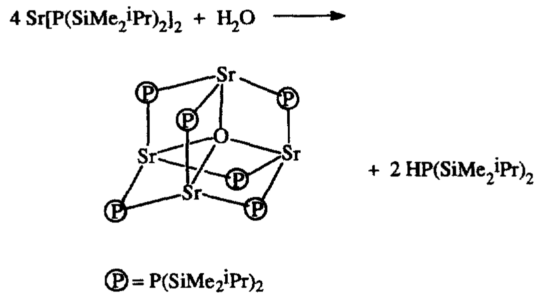


Fig. 9. Molecular structure of $Sr_4(\mu_4\text{-}O)[\mu\text{-}P(SiMe_3)_2]_6$. The oxygen, strontium and phosphorus atoms are drawn as ellipsoids and the Si atoms as circles. The carbon atoms are only shown schematically by the Si–C and C–C bonds. Hydrogen atoms are omitted for clarity.

molecule forms. Now the other terminal phosphanide ligand can form the bridge between the two alkaline earth metal centers.

In Eq. (25) the coligands such as THF, DME, or THP are omitted for clarity,



$$4\,Sr[P(SiMe_2{}^iPr)_2]_2 + H_2O \longrightarrow \quad + 2\,HP(SiMe_2{}^iPr)_2 \qquad (22)$$

Ⓟ = $P(SiMe_2{}^iPr)_2$

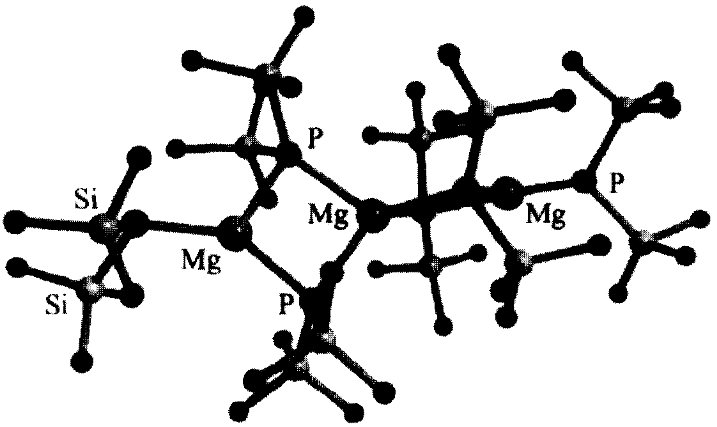
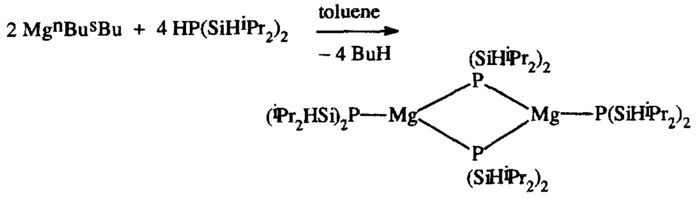
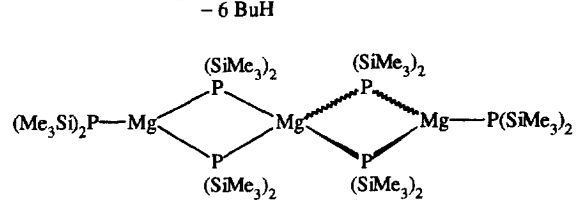


Fig. 10. Molecular structure of trimeric magnesium bis[bis(trimethylsilyl)phosphanide]. Hydrogen atoms are omitted for clarity.



(23)

however, they play a key role for the monomerization process. The coordination sphere of the monomeric complex is saturated by neutral ether coligands. For the dimerization some of these coligands are released and the phosphorus lone pair bonds into the resulting coordination gap of a second alkaline earth metal center. The driving force of this process is mainly the entropy of the reaction as demonstrated for example in Eq. (26) [213].



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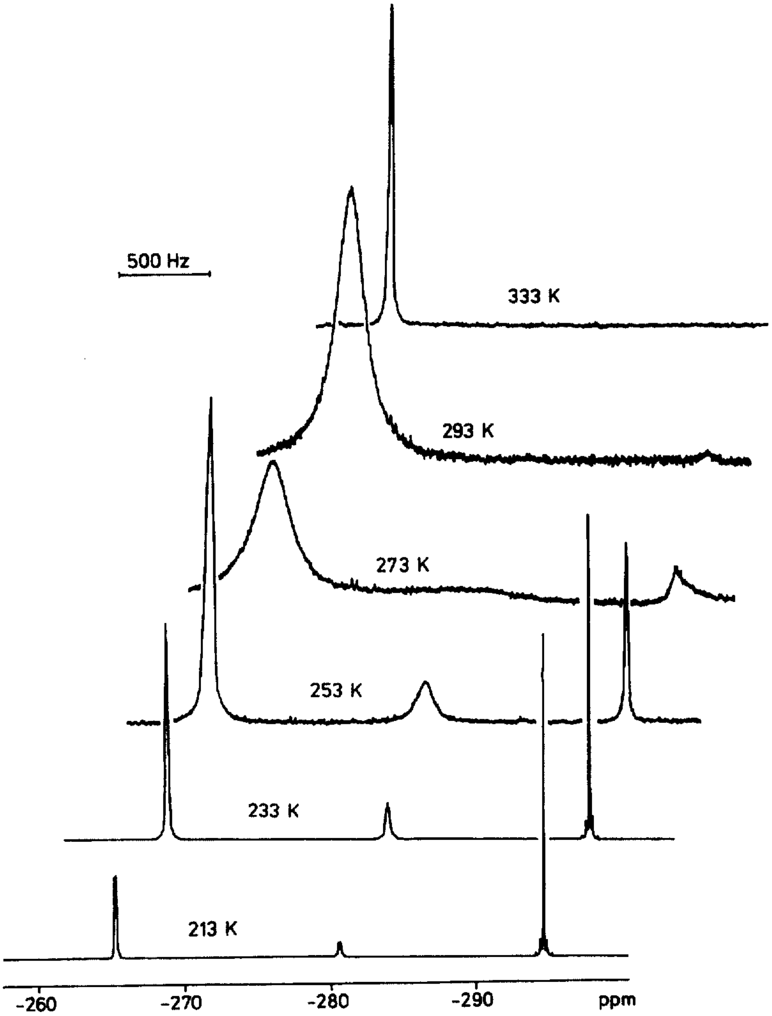
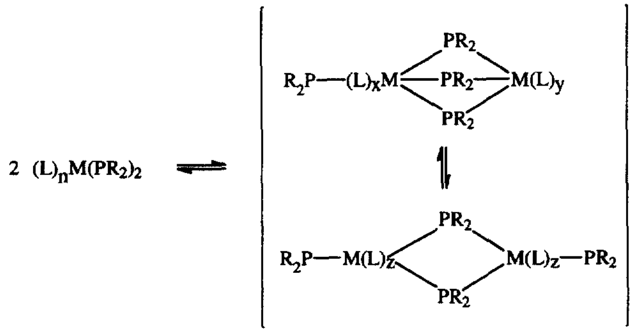


Fig. 11. Dynamic $^{31}P[^{1}H]$-NMR spectra of tris(1,2-dimethoxyethane-*O*,*O*′)barium bis[2,2,5,5-tetramethyl-2,5-disilaphospha-cyclo-pentanide] in toluene-d_8. Temperatures are given on each spectrum.

4.3. Bidentate ligands

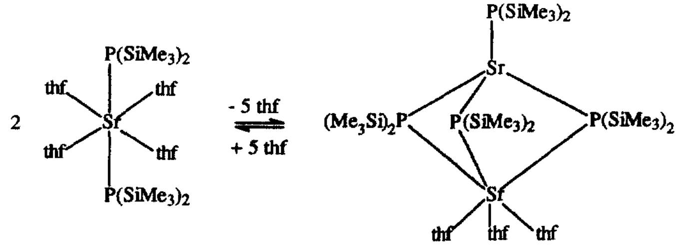
4.3.1. Bidentate diaza substituted ligands

The alkaline earth metal bis[bis(trimethylsilyl)amides] are less reactive than the corresponding lithium derivative. The presence of pivalonitrile leads to a complex formation with a nitrile ligand, whereas the more reactive benzonitrile can be inserted into the M^{II}–N bond, followed by a 1,3-trimethylsilyl shift according to Eq. (27) to yield the alkaline earth metal bis[*N*,*N*′-bis(trimethylsilyl)benz-



(25)

amidinates] [224]. The importance of this substance class is shown in review articles written by Dehnicke [225] and Edelmann [226] who also included the synthesis and properties of the benzamidinates of the group II metals. Therefore here only the key results are briefly described (Table 10). The *N*,*N'*-bis(trimethylsilyl)benzamidinate anion bonds to the group II dications in the bidentate manner with a NCN heteroallyl fragment. Both the CN bond lengths of approx. 132 pm lie in the expected range for a CN multiple bond. Due to the steric repulsion between the phenyl group and the trimethylsilyl substituents the CNSi angles are widened to values between 131 and 135°. The M–N distances are larger than the metal nitrogen bonds of the bis(tetrahydrofuran)alkaline earth metal bis[bis(trimethylsilyl)amides]. The benzonitrile adduct of magnesium bis[*N*,*N'*-bis(trimethylsilyl)benzamidinate] shows two slightly different Mg–N distances of 211 and 214 pm [227], explainable by the Gillespie–Nyholm concept. The metal center is coordinated trigonal bipyramidically with the shorter Mg–N bonds located in the equatorial plane. The calcium and strontium derivatives display M–N values of 243 [224] and 259 pm [228], respectively. In (DME)(THF)Ba[$(Me_3SiN)_2CPh]_2$ the benzamidinate ligands are bonded unsymmetrically with Ba–N bond lengths of 274 and 281 pm [229]. This unsymmetric coordination does not influence the delocalization of the anionic charge within the 1,3-diazaallyl fragment. Fig. 12 shows the calcium



(26)

Table 10
Selected average structural parameters of the alkaline earth metal complexes of the type $(L)_nM[(Me_3SiN)_2E]_2$ and chemical shifts of the ^{29}Si nuclei of the trimethylsilyl substituents (for references see text)

$M(L)_m$	C.N.(M)	$\delta(^{29}Si[^1H])$	M–N	N–E	M–O	NEN
E = C–Ph (benzamidinates)						
Be	4		272.7	133.0	–	112.5
Mg(NC–Ph)	5	−5.58	212.4	132.2	220.8	118.8
$Ca(THF)_2$	6	−9.22	243.1	132.0	237.9	120.7
$Sr(THF)_2$	6	−10.03	258.3	133	252.0	122.6
Sr(diglyme)	7	−10.48	259.6	132.2	261.2 268.1 284.8	120.9
Ba(DME)(THF)	7	−11.40	273.4/282.4	132.6	283.1	121.9
E = PPh_2 (phosphoranates)						
Be	4	−3.23	176.5	159.4	–	99.1
Mg	4	−7.71	207.5	159.4	–	104.4
Ca(THF)	5	−11.40	239.5/254.9	165.5/159.0	235.3	108.8
$Sr(THF)_2$	6	−13.14	260.8/266.4	158.6	262.3	109.3
$Ba(THF)_2$	6	−14.44	274.3/282.3	158.2	279.4	109.9
E = S–Ph (sulfinates)						
$Ca(THF)_2$	6	−3.84	243.5	160.6	246.3	102.6
$Sr(THF)_2$	6	−4.04	257.3	160.4	259.4	103.1
$Ba(THF)_2$	6	−4.46	272.4	160.1	276.4	103.3
E = $S–N(SiMe_3)_2$ (sulfites)						
Mg	4		205.9	161.1	–	98.5
Sr(THF)	5		254.8	159.5	257.1	102.0
E = $N[P(NMe_2)_2]_2$ (phosphazenide)						
Ba	6	+7.1	285	155	276[a]	158 PNP 108 NPN

[a] Ba–N distance to the central nitrogen atom.

complex. In contrast to these benzamidinates, the beryllium bis[*N*,*N'*-bis(trimethylsilyl)benzamidinate] crystallizes coligand-free [230]. Due to the small radius of the beryllium atom, the NCN angle is drastically smaller than in the derivatives of the heavier alkaline earth metals.

The NMR parameters of the ^1H and ^{13}C nuclei are essentially unaffected by the

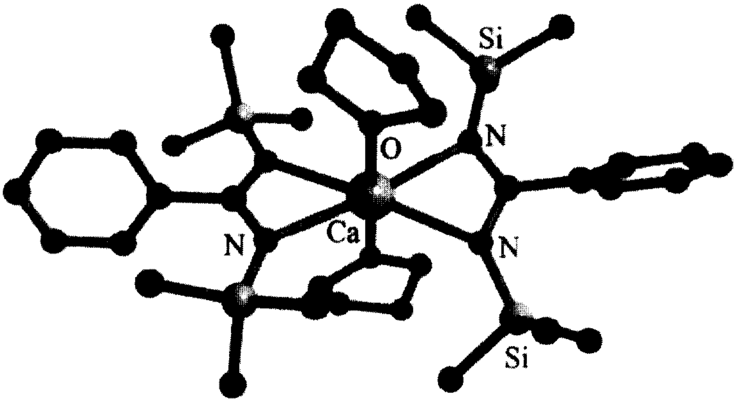
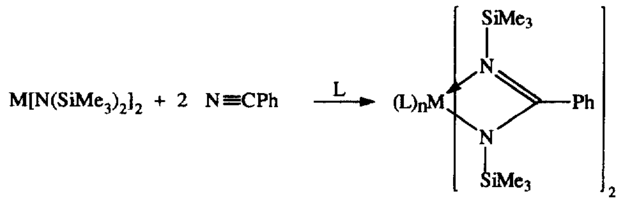


Fig. 12. Molecular structure of bis(tetrahydrofuran)calcium bis[*N*,*N*′-bis(trimethylsilyl)benzamidinate]. Hydrogen atoms are omitted for clarity.

size of the alkaline earth metal atom. The chemical shift of the heteroallyl carbon atom amounts 180.3 ± 1.3 ppm. Solely the $\delta(^{28}Si)$ values show a characteristic trend from 5.5 for $[(Me_3SiN)_2{-}CPh]_2Mg(NCPh)$ [227] to 11.6 ppm for $[(Me_3SiN)_2{-}CPh]_2Ba\,(NCPh)(THF)_2$ [229].

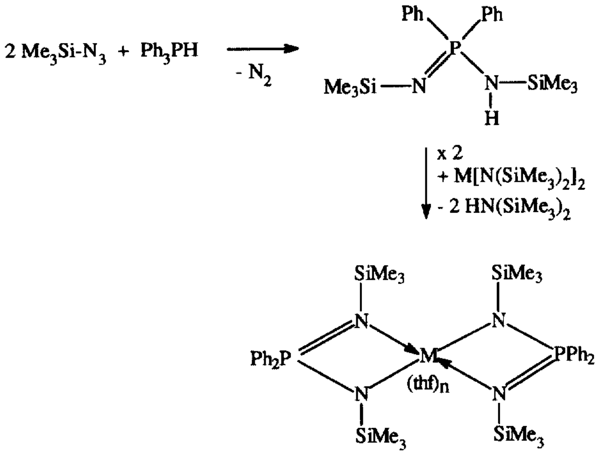
The formal substitution of the carbon atom of the 1,3-diazaallyl fragment of the benzamidinates by a $P{-}C_6H_5$ moiety leads to derivatives of the type $(THF)_nM[(Me_3SiN)_2PPh_2]_2$. Trimethylsilylamino-trimethylsilylimino-diphenylphosphorane [231] is prepared by the reaction of diphenylphosphane with trimethylsilylazide under loss of dinitrogen. The subsequent metalation of this phosphorane by alkaline earth metal bis[bis(trimethylsilyl)amides] yields the corresponding phosphoranates according to Eq. (28) [232].

The reaction of *N*,*N*′-bis(trimethylsilyl)aminoiminophenylsulphine with alkaline earth metal bis[bis(trimethylsilyl)amides] yields compounds of the type $(THF)_nM[(Me_3SiN)_2S{-}Ph]_2$ as shown in Eq. (29) [233]. The addition of an alkaline earth metal–nitrogen bond to the double bond of bis(trimethylsilyl)sulfurdiimide



(27)

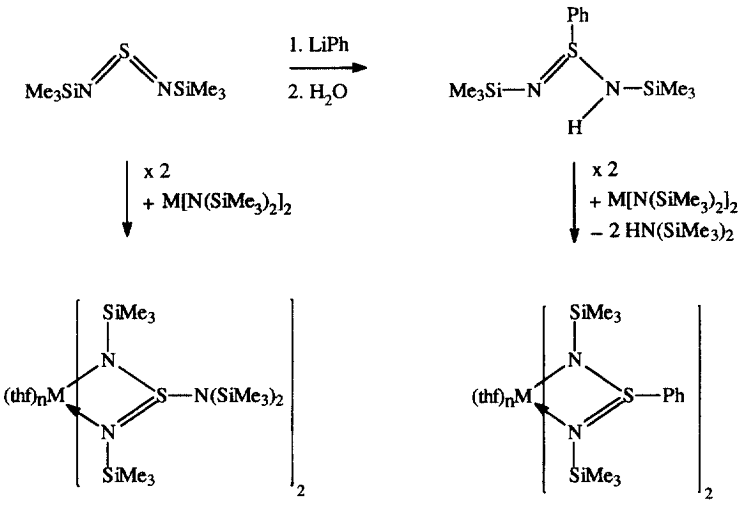
M = Mg, Ca, Sr, Ba
L = NCPh, thf, dme



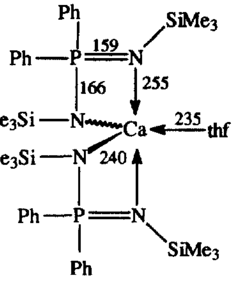
(28)

leads to the formation of the alkaline earth metal bis[*N,N,N'N''*-tetrakis(trimethylsilyl)triazasulfites]. All these compounds are colorless, moisture- and air sensitive. The magnesium derivatives even crystallize solvent-free from tetrahydrofuran solutions.

In Table 10 selected structural parameters as well as the $\delta(^{29}Si\{^1H\})$ values are listed. The ^{29}Si resonances are shifted to higher field with increasing size of the metal center. With increasing size of the alkaline earth metal atom the bidentate ligands tend to coordinate in a unsymmetric fashion with undisturbed delocaliza-



(29)



Scheme 6.

tion of the anionic charge between the two coordination sites. The only exception is the (tetrahydrofuran)calcium bis[*N*,*N*′-bis(trimethylsilyl)aminoiminodiphenylphosphoranate], where the P–N bonds differ by 6.5 pm. The calcium atom is surrounded trigonal bipyramidically with the long Ca–N distances of 255 pm to the apical nitrogen atoms, whereas the equatorial Ca–N-bond lengths amount to 240 pm [233]. Scheme 6 shows schematically the bonding situation with mainly localized P–N double and single bonds.

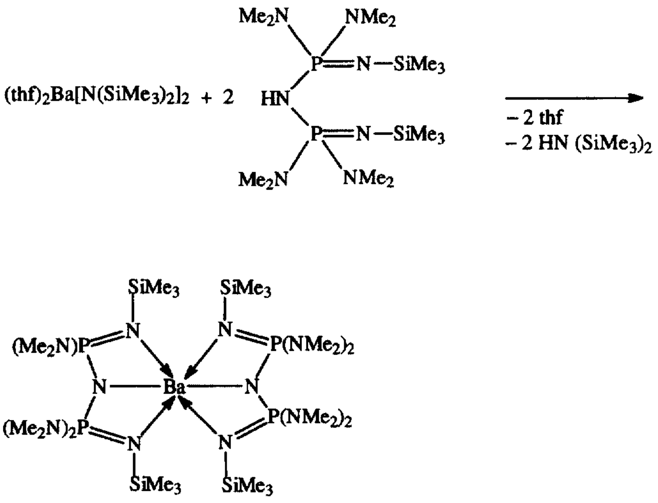
With increasing size the distance of the alkaline earth metal atom from the NEN plane increases for one of the phosporanate ligands, whereas the metal atom remains in the plane of the other ligand. Explanations for this behavior range from steric repulsion between the ligands to an increasing attraction between the heavier metals and the delocalized anionic charge of the π(NEN)-system.

The reaction according to Eq. (30) yields a complex with tridentate phosphazene ligands [234–236]. The N_3P_2 backbone of the ligands are nearly planar and oriented perpendicular to each other. The Ba–N bond lengths to the central nitrogen atoms amount to 276 pm, whereas the four other ones are approx. 9 pm longer. This compound is moisture-sensitive and decomposes above 110°C in a vacuum.

4.3.2. Bidentate azaphospha substituted ligands

Regarding the *N*,*N*′-bis(trimethylsilyl)benzamidinates of the alkaline earth metals, not only the central atom of the 1,3-diazaallylic fragment can be formally substituted but also one of the nitrogen atoms. The insertion of the CN-triple bond of benzonitrile into a metal–phosphorus-bond of an alkaline earth metal bis[bis(trimethylsilyl)phosphanide] according to Eq. (31) [237] followed by a 1,3-trimethylsilyl shift yields alkaline earth metal bis[1,3-bis(trimethylsilyl)-2-phenyl-1,3-azaphosphapropenide] (Fig. 13).

These derivatives allow the comparison of the nitrogen and phosphorus surroundings of an 1-aza-3-phosphaallylic system as summarized in Table 11, where only the 1,2-dimethoxyethane complex of the barium derivative [238] is taken into account due to the higher quality of the crystal structure determination. The most



(30)

striking difference is the pyramidal coordination sphere of the heavier pentele atom. Due to the ionicity of these compounds small intra- (electrostatic and steric repulsion of the ligands) and intermolecular forces (packing of the molecules in the crystalline state, ligand–ligand-repulsion) are able to tip the ligand, and enforces the metal center to lie outside of the allylic plane.

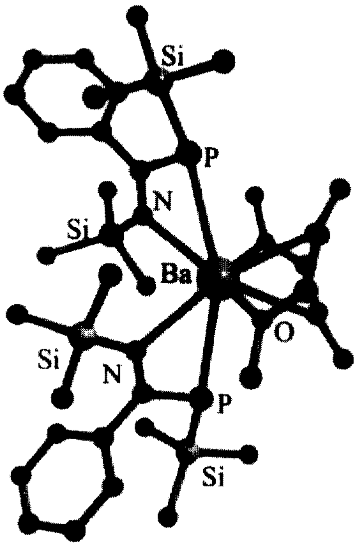
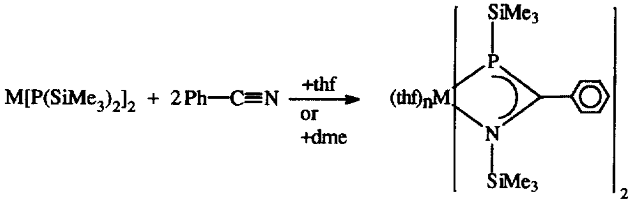


Fig. 13. Molecular structure of bis(1,2-dimethoxyethane-*O*,*O′*)barium bis[1,3-bis(trimethylsilyl)-2-phenyl-1,3-azaphosphapropenide]. Hydrogen atoms are omitted for clarity.



(31)

The most informative NMR information is gained from the ^{29}Si nuclei bonded to the nitrogen atoms. With increasing size of the alkaline earth metal the $\delta(^{29}\mathrm{Si_N})$ value is shifted to a higher field. The metal atom has nearly no dependency on the chemical shift of the allylic carbon atom, and the influence of the metal atom on the shift of the $^{29}\mathrm{Si_P}$ nuclei is rather small. For the $\delta(^{31}\mathrm{P})$ values a low field shift from the calcium to the barium compound is detected, however, the magnesium derivative shows a chemical ^{31}P shift located between those of the strontium and barium compounds.

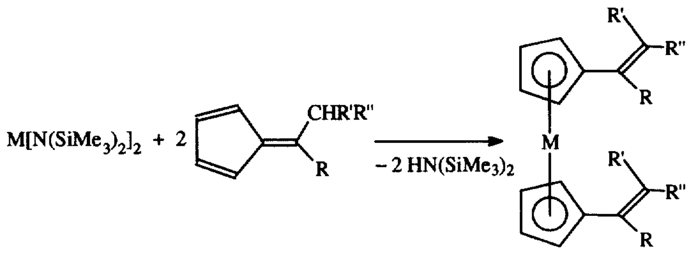
4.4. Alkenyl substituted alkaline earth metallocenes

Whereas benzonitrile inserts into a metal nitrogen bond of the alkaline earth metal bis[bis(trimethylsilyl)amides] no reactions with alkenes and alkynes are

Table 11
Selected structural and NMR spectroscopic data of the alkaline earth metal bis[1,3-bis(trimethylsilyl)-2-phenyl-1-aza-3-phosphapropenides] of the type $(\mathrm{L})_n\mathrm{M[Me_3SiN{-}C(Ph){=}PSiMe_3]_2}$

$\mathrm{M(L)}_n$	$\mathrm{Mg(THF)_2}$	$\mathrm{M(NC{-}Ph)_2}$	$\mathrm{Ca(THF)_2}$	$\mathrm{Sr(THF)_2}$	$\mathrm{Ba(DME)_2}$
C.N.(M)	6	6	6	7	8
M–N	219	215	246	265	285
M–P	273	271	289	308	326
M–O	213	222[c]	234	261	285
ΣXNX[a]	359.9	359.2	359.0	359.7	360.0
ΣXPX[b]	334.9	312.5	331.2	334.3/346.1	342.2
$\delta(^{29}\mathrm{Si_N})$	−2.3	−0.5	−5.4	−8.1	−9.4
$\delta(^{29}\mathrm{Si_P})$	−3.1	−0.2	−3.6	−4.2	−4.5
$\delta(^{13}\mathrm{C_{NCP}})$	223.1	[d]	223.3	222.3	221.7
$\delta(^{31}\mathrm{P})$	−7.8	−21.6	−13.1	−9.1	−1.6
Ref.	[237]	[221]	[237]	[237]	[238]

[a] Angle sum of the nitrogen atom.
[b] Angle sum of the phosphorus atom.
[c] Distance between Mg and the N atoms of the benzonitrile ligands.
[d] Signal not found in the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectrum.



(32)

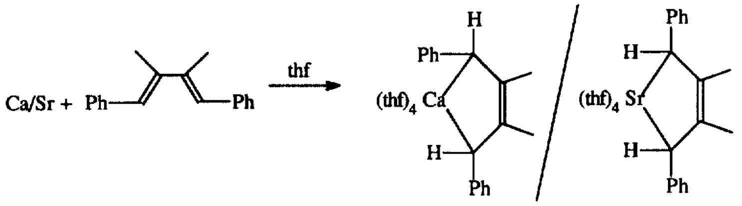
M = Ca, Sr, Ba
R', R'' = H, R = Me, Ph, CH_2CHMe_2
R', R'' = CH_2, R = cyclo-propyl

described so far. Alkaline earth metal carbon σ-bonds are not preparable by an insertion reaction of this kind. If alkaline earth metal bis[bis(trimethylsilyl)amide] is reacted with fulvenes, the formation of the aromatic system is the driving force of this reaction (Eq. (32)). The metalation of the fulvenes yields alkenyl substituted metallocenes [239].

Even the reaction of calcium bis[bis(trimethylsilyl)amide] with bis(cyclopropyl)fulvene [240] yields the alkenyl substituted metallocene, however, the ring strain enforces elevated reaction temperatures and an extended reaction period. This slow reaction allows the detection of the heteroleptic intermediate. The equimolar reaction of calcium bis[bis(trimethylsilyl)amide] and calcium bis[cyclopropyl-cyclopropylidenmethylcyclopentadienide] shows an equilibrium between these homoleptic and the heteroleptic species.

4.5. Miscellaneous reactions of the alkaline earth metal bis[bis(trimethylsilyl)amides]

The bond between a carbon atom and a heavier alkaline earth metal is well investigated for metallocenes [61–63]. Possible pathways to this compound class are the metalation of cyclopentadienes by the metals or metal bis(amides) [103,241,242], the metalation of fulvenes by the metal bis(amides), and the metathesis reaction of substituted potassium cyclopentadienide and alkaline earth metal diiodides. A Grignard-type reaction by cocondensation of calcium metal and brom-bis(trimethylsilyl)methane in THF and the subsequent addition of 1,4-dioxane yields the dioxane complex of calcium bis[bis(trimethylsilyl)methanide] [66], the carbanionic character of the alkyl substituent is proven by the methyne high field shift of $\delta(^1H) = -1.7$. By a metathesis reaction Hanusa et al. [243,244] isolated an ‘open’ calcocene. The oxidative addition of 2,3-dimethyl-1,4-diphenylbutadiene to calcium or strontium metal in tetrahydrofuran yields the tetrakis(tetrahydrofuran) complexes of calcium and strontium 2,3-dimethyl-1,4-diphenylbut-2-en-1,4-diide as shown in Eq. (33) [245]. Both the compounds contain distorted octahedral surrounded metal centers, however, the conformation of the carbanionic ligand differs for the calcium and strontium derivative.

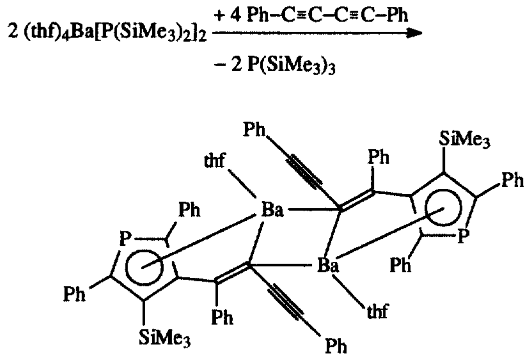


(33)

Up to now, there is no reaction between a bis(trimethylsilyl)amide of calcium, strontium and barium with an alkyne known. However, the homologous phosphanides have proven to be more reactive towards C ≡ C triple bonds. The reaction of $(THF)_4Ba[P(SiMe_3)_2]_2$ [221] with diphenylbutadiyne according to Eq. (34) yields a dimeric complex with a η^5-bonded phosphacyclopentadienide ligand. The dimerization occurs via a planar Ba_2C_2 four-membered cycle with Ba–C bond lengths of 288 and 307 pm.

The metalation of a para-methyl substituted benzyl-benzylidene-diphenylphosphorane with barium bis[bis(trimethylsilyl)amide] in tetrahydrofuran yields solvent-free barium bis[diphenylphosphoniumdibenzylide] [246]. The barium atom bonds 'side-on' mainly to the ortho- and ipso-phenyl carbon atoms as well as to the methyne groups with Ba–C distances in the wide range between 298 and 345 pm (Eq. (35)).

In solution the rigid solid state structure is verified at very low temperatures by NMR spectroscopy, however, at elevated temperatures fluxional processes occur. The rotation around the C–C-bond of the benzylide group leads to a magnetic equivalence of both of the ortho- and of the meta-hydrogen atoms, respectively. However, not only the contact between the barium atom and the phenyl group of the benzylide substituent can be broken, also the bond between the benzylic carbon atom and the metal center. The latter case presupposses a barium atom



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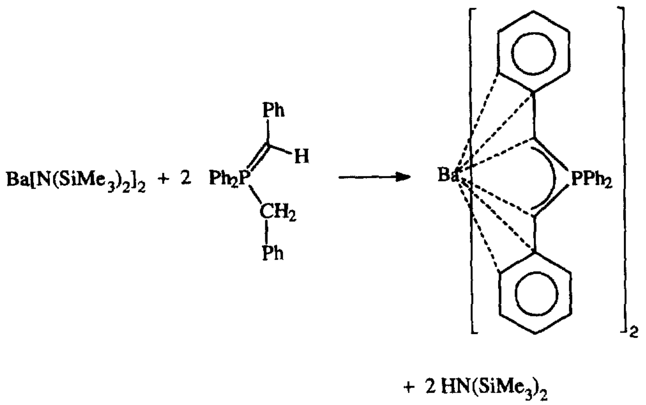


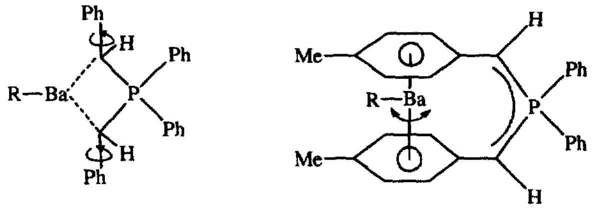
(35)

encapsulated between the two phenyl groups, which now allows a wobbling movement around the phenyl ··· Ba contact. This dynamic process interchanges a δ-symmetric into a λ-symmetric ligand and vice versa [246] as shown in Scheme 7.

4.6. Heterobimetallic derivatives

Heterobimetallic derivatives are prepared by the addition reaction of two different metal organic compounds. Depending on the electronegativity of the metals two principal reaction pathways have to be considered. If the metal is more electropositive than the alkaline earth metal, the ligand is transferred to the group II metal, and alkaline earth metalates are formed. In the opposite case the substituent at the group II metal is transferred to the other metal atom. Eq. (36) summarizes these pathways together with the possibilities of contact ion pairs for the case of calcium derivatives.

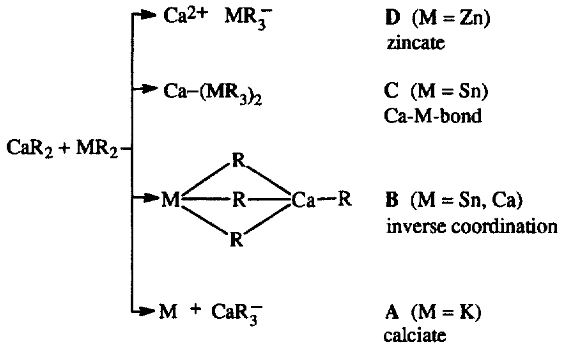
Lappert et al. [104] reacted the threefold molar amount of potassium bis(tri-



Rotation around
C-Ph bond

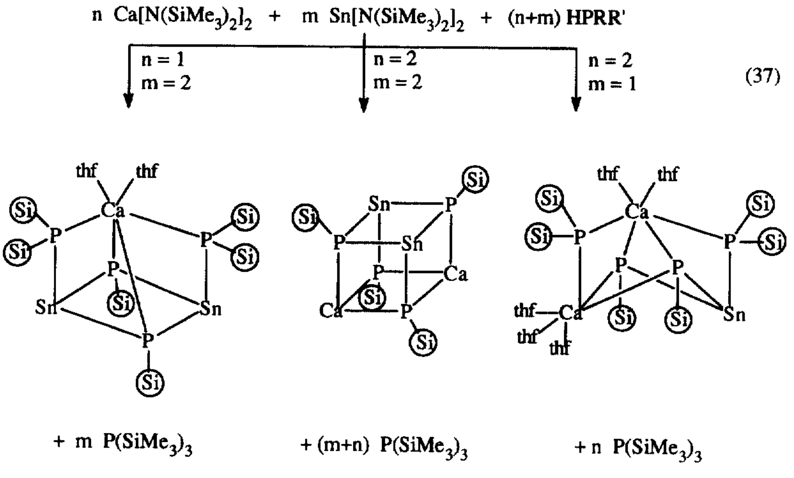
Wobbling around the
Ba ···Ph contact

Scheme 7.



(36)

methylsilyl)methanide with calcium diiodide to yield the corresponding calciate *A* with R as $CH(SiMe_3)_2$. In the absence of Lewis bases calcium bis[bis(trimethylsilyl)amide] does not react with zinc bis[bis(trimethylsilyl)amide], however, the addition of 1,2-dimethoxyethane leads to the formation of the solvent-separated calcium bis{tris[bis(trimethylsilyl)amino]zincate} [247], a compound of type **D**. Recently the zincate anion is structurally described by Dehnicke et al. [248]. A bimetallic derivative of type **C** has been isolated via the insertion of a calcium atom into the Sn–Sn bond of hexamethyldistannane [68,69]. Whereas bis[bis(trimethylsilyl)amino]stannylene does not react with alkaline earth metal bis[bis(trimethylsilyl)amides], the homologous bimetallic bis(trimethylsilyl)phosphanides show a variety of novel structures, depending upon the ratio of tin to calcium, however, molecules of complex type **B** crystallize from toluene solutions

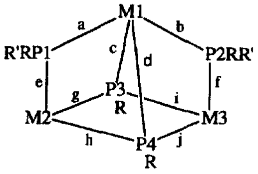


(37)

[129,130]. The performance of the reaction in tetrahydrofuran leads to the elimination of tris(trimethylsilyl)phosphane. Eq. (37) shows the products of these reactions. The dicalciadistanna tetraphosphacubane molecule forms besides the other products with a ratio of tin to calcium of 2:1 and 1:2 [130].

Both the 1:2 and the 2:1 reactions yield polycyclic molecules, which can be understood as two trigonal bipyramids with the metal atoms in apical positions, connected via a common CaP_2 face (Fig. 14). Table 12 gives all bond lengths within these polyhedra. The substitution of calcium in **I** by a barium atom leads to a slight contraction of the Sn_2P_4 backbone together with an enhancement of the P1 ··· P2 contact. A comparison of the tris(tetrahydrofuran) (**II**) and tetrakis(tetrahydrofuran) (**III**) complexes of the barium derivative shows the flexibility of the $Sn_2[P(SiMe_3)_2]_2(\mu\text{-}PSiMe_3)_2$ dianion (Table 12). Due to intramolecular strain, incorporated by the fourth THF molecule, the Ba–P bond length are elongated, and, moreover, the Ba–P1 and Ba–P2 distances differ by approx. 10 pm. The same reasons account for the difference in the Ba–P3 and Ba–P4 bond lengths. Fig. 14 shows the bis(THF) calcium complex.

Table 12
Structural parameters of heterobimetallic compounds, consisting of two trigonal bipyramids with a common M1/P3/P4-face



Compound	I	II	III	IV
M1	Ca(thf)$_2$	Ba(thf)$_3$	Ba(thf)$_4$	Ca(thf)$_2$[a]
M2	Sn	Sn	Sn	Ca(thf)$_3$
M3	Sn	Sn	Sn	Sn
R	SiMe$_3$	SiMe$_3$	SiMe$_3$	Si^{i}Pr$_3$
R'	SiMe$_3$	SiMe$_3$	SiMe$_3$	H
a	290.3	328.1	335.1	299.5/296.4
b	291.0	332.2	345.2	302.0/298.9
c	291.8	320.9	326.8	291.0/290.7
d	291.8	326.8	335.3	294.2/295.2
e	268.0	268.4	268.4	302.6/300.4
f	268.7	268.9	268.9	275.8/273.7
g	264.3	262.2	262.2	288.5/288.3
h	264.3	261.5	261.5	392.3/293.0
i	264.1	263.5	263.5	259.5/262.0
j	264.1	263.3	263.3	275.8/273.7

[a] Two crystallographically independent molecules.

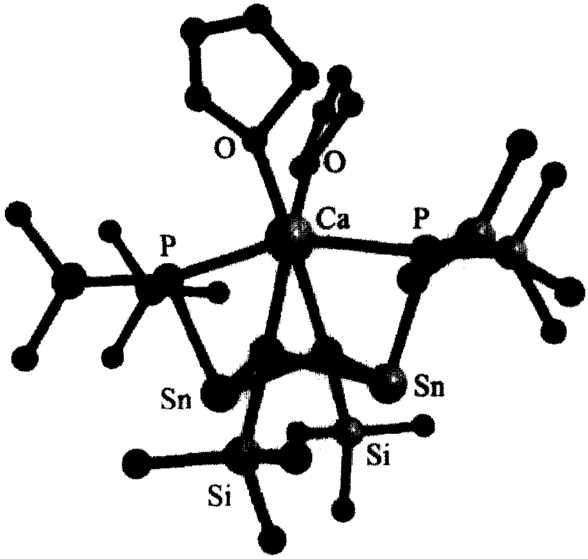


Fig. 14. Molecular structure of the heterobimetallic complex $(THF)_2CaSn_2[\mu_2\text{-}P(SiMe_3)_2]_2[\mu_3PSiMe_3]_2$. Hydrogen atoms are omitted for clarity.

If the reaction is performed in the absence of solvents with Lewis basicity, the elimination of tris(trimethylsilyl)phosphane can be avoided. Eq. (38) shows the reaction of barium bis[bis(trimethylsilyl)amide] and bis[bis(trimethylsilyl)amino]stannylene with $HP(SiMe_3)_2$ in toluene. Whereas in the crystalline state the tris[bis(trimethylsilyl)phosphanyl]stannanide ligand coordinates in the bidentate fashion, the phosphanyl substitutents are magnetically equivalent in toluene or benzene solution. In contrast to this molecule with a ratio of barium to tin of 1:2, the reversed molar ratio leads in the case of a calcium derivative to a molecule, where the $[(Me_3Si)_2P]_3Sn$ anion caps one calcium atom of the cation $Ca[\mu\text{-}P(SiMe_3)_2]_2Ca\text{–}N(SiMe_3)_2$. The latter moiety is already known from the heteroleptic alkaline earth metal amide phosphanides (Section 2.2.1).

Divalent tin and alkaline earth metal containing heterobimetallic bis(trimethylsilyl)amides are unknown thus far. This is the reason why the transmetalation of distilled $Sn[N(SiMe_3)_2]_2$ yields nearly quantitatively halogen-free alkaline earth metal bis[bis(trimethylsilyl)amides] (Section 2.1.1). The presence of aluminium allows the isolation of heterobimetallic substances as mentioned in the introductory part of Section 2.

5. Conclusion

The enormous success of the molecular lithium and magnesium alkanide and amide chemistry led to high expectations in the chemistry of the heavier alkali and alkaline earth metal chemistry. More than 15 years ago the expectation in this chemistry was expressed by Eisch and King [4], however, numerous preparative difficulties such as insolubility, tendency to Wurtz coupling reactions, air- and moisture-sensitivity, lack of easily available starting materials prevented a fast development of the chemistry of calcium, strontium, and barium.

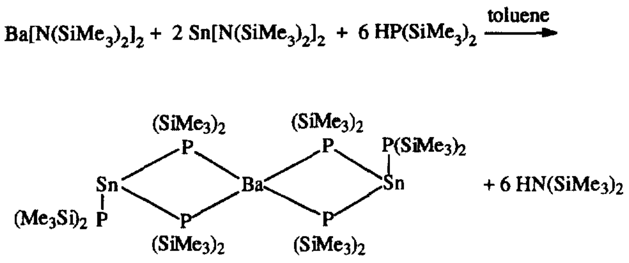
The expectations in this solution chemistry of the heavier alkaline earth metals led to the progress in preparing the bis(trimethylsilyl)amides, which are soluble in common organic solvents. Now a variety of derivatives are accessible by a subsequent performed metalation of H-acidic molecules, addition to reactive triple and double bonds, metathesis reaction with metal halides, or addition to other metal amides and phosphanides. The results summarized in this review give an insight of the synthetic potential of the alkaline earth metal bis[bis(trimethylsilyl)amides]. Polydentate N-heteroaromatic ligands bonded to heavier alkaline earth metal atoms are summarized elsewhere [249].

An even more reactive synthon, the alkaline earth metal bis[trialkylsilyl)phosphanides], could accelerate the development of the fruitful chemistry of the heavier group II metals. Different reaction behavior than the corresponding lithium and magnesium derivatives may be evoked by easier polarization of the larger dications by the anions (‘reverse polarization’) as well as the participation of d-orbitals at the metal center. Renouncing steric shielding, a tuning of the reactivity by the choice of the metal is possible as can be seen for example in Eq. (39).

The molecular chemistry of the heavier alkaline earth metals is still booming with the main accents on the synthesis of new molecules with for example metal–silicon or metal–germanium bonds, on the development of an easy high-yield approach to molecules with metal–carbon σ-bonds and thirdly on the reactivity compared to corresponding lithium and magnesium compounds.

6. List of symbols and abbreviations

b	Bridging (superscript)
bpy	Bipyridine, bipyridyl
Bu	Butyl
C.N.	Coordination number
diglyme	Diethyleneglycoldimethylether
DIOX	1,4-Dioxane
DME	1,2-Dimethoxyethane
Et	Ethyl
HMPA	Tris(dimethylamino)phosphane oxide
Me	Methyl
Ph	Phenyl
Pr	Propyl
Py	Pyridine
t	Terminal (superscript)
THF	Tetrahydrofuran
THP	Tetrahydropyran
TMEDA	1,2-Bis(dimethylamino)ethane
TMTA	1,3,5-Trimethyl-1,3,5-triazinane



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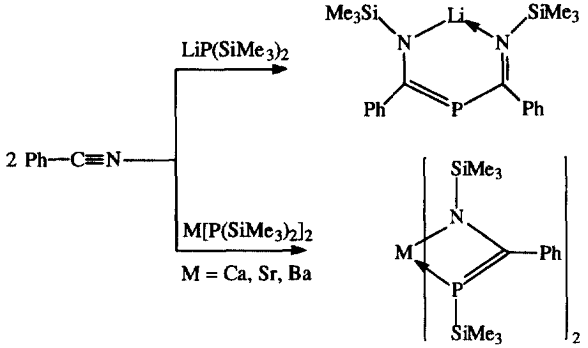

(39)

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