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Article

Ligand Exchange Reaction Between an Alkylzinc Primary Amide and a Dialkylmagnesium Compound: Crystal Structures of [(thf)MeMg-μ-N(H)SiiPr3]2 and (tmeda)Mg[N(H)SiiPr3]2

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The reaction of alkylzinc triisopropylsilylamide with dialkylmagnesium leads to a ligand exchange. Besides the starting materials, heteroleptic alkylmagnesium triisopropylsilylamide and homoleptic magnesium bis(triisopropyl-silylamide) are detected by NMR spectroscopy. After the addition of 1,2-bis(dimethylamino)ethane (TMEDA) to the reaction mixture, (tmeda)Mg[N(H)SiiPr3]2 (**1**) precipitates as colorless cuboids ($C_{24}H_{60}MgN_4Si_2$, $a = 2269.6(2)$, $b = 1029.58(5)$, $c = 1593.2(1)$ pm, $\beta = 120.826(8)°$, monoclinic, $C2/c$, $Z = 4$). The amide nitrogen atoms are coordinated planarily with strongly widened Mg–N–Si bond angles of 139.2(1)°. The metalation of triisopropylsilylamine with dimethylmagnesium in THF yields quantitatively heteroleptic [(thf)MeMg–N(H)SiiPr3]2 (**2**) which crystallizes as colorless needles ($C_{28}H_{66}Mg_2N_2O_2Si_2$, $a = 1982.4(2)$, $b = 2034.1(1)$, $c = 907.22(6)$ pm, $\beta = 95.021(9)$, monoclinic, $P2_1/n$, $Z = 4$). Because of the bridging position of the triisopropylsilylamide anion, the tetracoordinate nitrogen atoms show rather long Mg–N bond lengths of 210.7 pm (average value).

Introduction

The zincation of primary amines with dialkylzinc yields quantitatively alkylzinc amides, the formation of zinc imides such as $[ZnNR']_n$ or $(RZn)_2NR'$ is not possible from this reaction.[1,2] The alkylzinc amides crystallize as dimers[1–3] or trimers[3,4] with quadruply coordinated nitrogen centers. Steri-cally demanding groups at the zinc and nitrogen atoms can enforce the formation of monomeric molecules.[5,6] In contrast to the zinc amide chemistry, very few examples of magne-sium imides are well-known since Power et al. succeeded in preparing hexameric phenylimide[7] and naphthylimide.[8] In contrast to the zinc primary amide chemistry, the more acidic P–H and As–H moieties in zincated primary phosphanes and arsanes reacted immediately with the zinc reagent, and the corresponding bis(alkylzinc) triisopropylsilylphosphane-diide and -arsanediide were formed according to eq 1a (E = P,[9] As[10]).
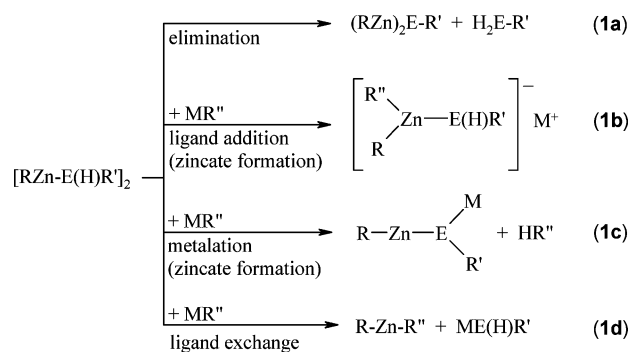
Stronger metalation reagents have to be employed to prepare imides of zinc. In principle, alkylzinc primary amides

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can react with metallating reagents in several ways as presented in eq 1. The addition of a lithium amide (E = N) to dialkylzinc yielded a zincate as shown in eq 1b which crystallized as a contact ion pair.[11] Solvent-dependent equilibria between the bis(trimethylsilyl)amides of calcium and zinc on one hand and calcium bis{tris[bis(trimethylsilyl)-amino]zincates} on the other have been observed;[12] the structure of the latter zincate anion showed extremely long Zn−N bond lengths.[13,14] The "ate" chemistry of main group metals and zinc was of interest for many decades,[15] and a recent and detailed overview is given in the literature.[16] Another possibility is represented in eq 1c, where geminally bismetalated compounds form after deprotonation. Here, we present another example of an interaction between organozinc and organomagnesium complexes, namely, the ligand exchange reaction (equation 1d).

The research concerning magnesium amides is of vastly growing interest because of their wide variety of applications, such as the controlled polymerization of β-lactams[17] and lactides[18] or as superbases.[19] In addition to the extensive investigations regarding the synthetic potential, the molecular structure of coligand-free Mg[N(SiMe$_3$)$_2$]$_2$,[20] as well as its coordination behavior,[21] has been explored in detail. In addition, heteroleptic compounds of the type R−Mg−N(SiMe$_3$)$_2$ have been published.[22] In contrast to magnesium bis[bis(trimethylsilyl)amide], which has been well-known for more than 40 years,[23] magnesiated primary trialkylsilylamines have attracted a lot less attention. However, a few magnesiated primary alkyl- and arylamines have been published.[2,24]

Zhang and Eaton could also show that alkylmagnesium amides and magnesium bis(amides) express a different reactivity toward weakly CH acidic cyclopropane derivatives.[25]

Results and Discussion

Synthesis. The heteroleptic alkylzinc triisopropylsilyl-amides crystallize as dimers with tetracoordinate nitrogen and three-coordinate zinc atoms. The metalation power of the zinc-bonded alkyl groups is strongly reduced, and the isolation of the amine adducts of these compounds is favored compared to a second deprotonation reaction. Furthermore, no metalation reactions have occurred between the alkylzinc triisopropylsilylamides and the excess dimethylzinc;[1] bis-(alkylzinc)imides are not accessible by a 2-fold deprotonation of primary amines but by a rather complex reaction.[26] Therefore, more reactive metalation reagents such as dialkyl-magnesium were applied. The reaction sequence is shown in eq 2.
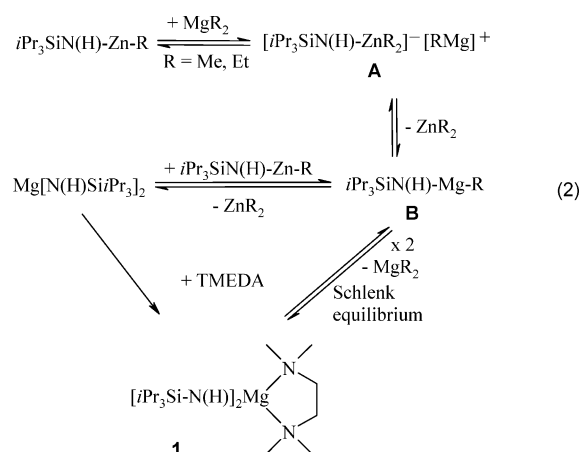
The first step was the addition reaction and the formation of intermediate alkylmagnesium dialkyl-triisopropylsilylami-nozincate; however, this compound, **A**, was not detected by NMR spectroscopy. The elimination of dialkylzinc yielded heteroleptic alkylmagnesium triisopropylsilylamide **B**. A similar reaction sequence could finally lead to magnesium bis(triisopropylsilylamide). Another possible pathway for the second reaction step is the Schlenk equilibrium, which interconnects the homoleptic magnesium bis(amide) and dialkylmagnesium with the heteroleptic alkylmagnesium amide, without a zincate intermediate. Yang et al.[27] already showed that strong Lewis bases, such as tris(dimethylamino)-phosphaneoxide (HMPA), are capable of causing a dismu-

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Table 1. NMR Data for (tmeda)Mg[N(H)Si*i*Pr$_3$]$_2$ (**1**) and [Me(thf)MgN(H)Si*i*Pr$_3$]$_2$ (**2**) and, for Comparison Reasons, NMR Data for [EtZnN(H)Si*i*Pr$_3$]$_2$[1] (solvent benzene-*d*$_6$, 30 °C)

	[EtZnN(H)Si*i*Pr$_3$]$_2$	**1**	**2**
		^{1}H NMR	
δ(M−R)	0.62, 1.52 (R = Et)	−	−0.93 (R = Me)
δ(SiCH)	1.02	1.18	1.25
δ(SiCHMe$_2$)	1.08	1.35	1.23
δ(NH)	−0.69	2.10	n.o.^{a}
δ(tmeda)	−	1.35, 1.53	−
δ(thf)	−	−	1.36, 3.68
		^{13}C{^{1}H} NMR	
δ(M−R)	4.6, 12.5 (R = Et)	−	−11.9 (R = Me)
δ(SiCH)	13.4	14.4	13.8, 14.3^b
δ(SiCHMe$_2$)	18.7	19.7	19.1, 19.4^b
δ(tmeda)	−	46.5, 55.9	−
δ(thf)	−	−	25.0, 68.8
		^{29}Si{^{1}H} NMR	
δ(Si)	11.9	3.9	9.5

^{a} Not observed (n.o.). ^{b} Two isomers were observed in solution (see text).

tation of heteroleptic EtMg−NPh$_2$ and hence the formation of the homoleptic compounds diethylmagnesium and magnesium bis(diphenylamide).

The reaction was followed up by NMR spectroscopy, and resonances were observed for several compounds; however, the isolation of the zincate species failed. The addition of TMEDA finally led to the formation of [(1,2-bis(dimethylamino)ethane-*N,N*′)magnesium bis(triisopropylsilylamide) (**1**) which crystallized slowly from this solution thus shifting the equilibrium toward this compound. The hard-chelating Lewis-base TMEDA preferably binds to the hard magnesium cation. Now, the four-coordinate alkaline earth metal center of this compound is coordinatively saturated and sterically shielded, and in this manner, the magnesium derivative **1** is removed from the equilibrium. The ^{29}Si{^{1}H} NMR spectrum, for example, showed singlets for the starting [RZnN(H)-Si*i*Pr$_3$]$_2$ at δ = 11.9[1] and for **1** at δ = 3.9, and it also showed two resonances at approximately δ = 9.5. Because these resonances could originate from zincate species **A** or from heteroleptic alkylmagnesium amide **B**, alkylmagnesium triisopropylsilylamide was prepared to interpret the NMR data (Table 1).

Dimeric [(thf)MeMg(*μ*-N(H)Si*i*Pr$_3$)]$_2$ (**2**) was prepared quantitatively in a reaction of dimethylmagnesium with H$_2$N−Si*i*Pr$_3$ in a THF solution according to eq 3; an equilibrium between this heteroleptic compound and the homoleptic compound has not been observed.

$$2\ i\text{Pr}_3\text{Si-NH}_2 + 2\ \text{MgMe}_2 \xrightarrow[-2\ \text{MeH}]{\text{THF}} \quad \textbf{2} \qquad (3)$$
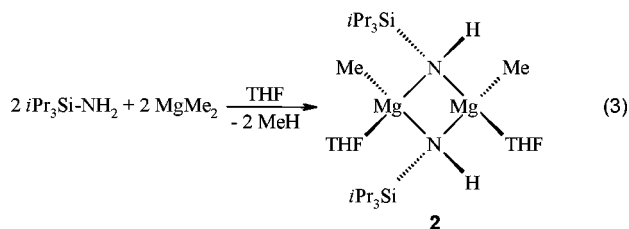
However, the isopropyl groups showed two sets of resonances in the ^{13}C{^{1}H} NMR experiments from the formation of two diastereomers, namely with the bulky triisopropylsilyl substituents on the same side of the Mg$_2$N$_2$
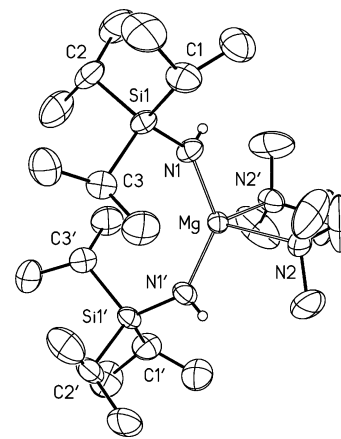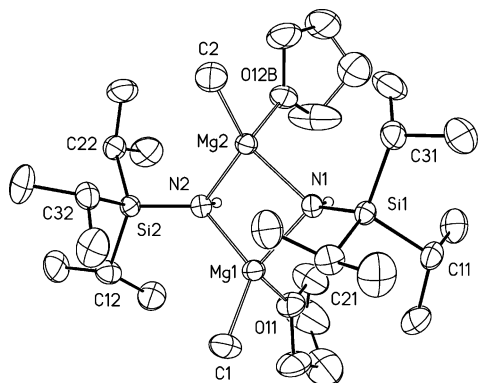

Figure 1. Molecular structure of **1**. The ellipsoids represent a probability of 30%. Symmetry-related atoms (−*x* + 1, *y*, −*z* + 1.5) are marked with primes. The H atoms are omitted for clarity reasons with the exception of the N-bound hydrogen atom. Selected bond lengths (pm): Mg−N1 196.1-(2), Mg−N2A 223.9(2), N1−Si1 169.1(2), N1−H1 73(3), Si1−C1 191.0-(3), Si1−C2 190.2(2), Si1−C3 189.3(2). Selected angles (deg): N1−Mg−N1′ 134.6(1), N1−Mg−N2A 109.80(7), N1−Mg−N2A′ 104.02(7), N2A-Mg−N2A′ 82.3(1), Mg−N1−Si1 139.2(1), Mg−N1−H1 110(2), Si1−N1−H1 111(2).

cycle (trans-annular cis) and a trans-annular trans arrangement of the Si*i*Pr$_3$ groups. The NMR data for **2** are in agreement with those which were detected during the formation of **1**. This fact supports the presence of the heteroleptic alkylmagnesium amide in the solution described above. Heteroleptic [(thf)MeMg−N(H)Si*i*Pr$_3$]$_2$ (**2**) crystallized as a dimer with tetracoordinate metal and nitrogen atoms. During the determination of the melting point, evolution of methane was observed above 169 °C and a melt was finally formed at 208 °C. The IR spectroscopic reinvestigation of this resolidified compound showed the absence of the N-bound hydrogen atoms; however, we could not obtain crystals of this nearly insoluble magnesium triisopropylsilylimide suitable for an X-ray structure determination. However, Power and co-workers[7,8] could already show that magnesium arylimides crystallize as hexamers with central hexagonal prismatic Mg$_6$N$_6$ cages.

Molecular Structure of 1. The molecular structure of **1** and its numbering scheme is represented in Figure 1. The symmetry-related atoms (−*x* + 1, *y*, −*z* + 1.5) are marked (i.e., N1′, N2′). The magnesium atom is in a distorted tetrahedral environment of four nitrogen atoms. The distortions originate from the small bite of the TMEDA ligand, which leads to the small bond angle of 82.3°, and from the steric demand of the triisopropylsilyl substituents giving a large N1−Mg−N1′ angle of 134.6°.

The value of the Mg−N1 bond length is approximately 28 pm smaller than the Mg−N2A distance. This large difference is caused by several synergetic factors: (i) the electrostatic attraction between the magnesium cation and the negatively charged amide nitrogen atom strengthens the Mg−N1 bond, (ii) the higher coordination number of N2A leads to larger steric hindrance at the TMEDA nitrogen atoms, and (iii) because of the planar coordination sphere of the N1 atom and its sp^2 hybridization, the s-orbital participation of the bond to the magnesium cation is increased. Similar reasons also account for the short N1−

Figure 2. Molecular structure and numbering scheme of **2**. The ellipsoids represent a probability of 30%. The hydrogen atoms are omitted for clarity reasons with the exception of the H1 at N1. Only one orientation of the disordered THF molecule (at O12B) is represented. Selected bond lengths (pm): Mg1−N1 210.4(2), Mg1−N2 211.0(2), Mg1−C1 212.6(3), Mg1−O11 209.4(2), Mg2−N1 210.7(3), Mg2−N2 210.6(2), Mg2−C2 212.6(3), Mg2−O12 209.1(2), Mg1···Mg2 294.8(1), N1−Si1 172.8(2), N1−H1 70-(3), N2−Si2 173.1(2), N2−H2 80(3). Selected angles (deg): O11−Mg1−N1 105.43(9), O11−Mg1−N2 105.06(9), N1−Mg1−N2 89.25(7), O11−Mg1−C1 103.4(1), N1−Mg1−C1 125.6(1), N2−Mg1−C1 125.7(1), O12−Mg2−N2 104.01(9), O12−Mg2−N1 101.05(9), N2−Mg2−N1 89.27(8), O12−Mg2−C2 103.2(1), N2−Mg2−C2 127.6(1), N1−Mg2−C2 127.7-(1), Si1−N1−Mg1 124.7(1), Si1−N1−Mg2 130.1(1), Mg1−N1−Mg2 88.87(8), Si2−N2−Mg2 125.4(1), Si2−N2−Mg1 130.0(1), Mg2−N2−Mg1 88.73(7).

Si1 bond. Furthermore, in this case, hyperconjugative effects (back-bonding from the p(N) lone pair into the σ^*(Si−C) bond) cause an additional shortening of the N1−Si1 bond and simultaneously lead to a lengthening of the Si1−C3 bond which is nearly in a coplanar alignment with the p orbital of N1. Less ionic amides and compounds with bridging triisopropylsilylamide substituents (sp³-hybridized nitrogen atom), such as in the dimeric alkylzinc triisopropylsilyl-amides, expectedly, reveal longer N−Si distances of approximately 174 pm.[1]

Comparable findings have been published for (tmeda)-Mg[N(CH₂Ph)₂]₂.[28] Although the bond lengths are very similar (Mg−N$_{tmeda}$ 223.6(2) pm, Mg−N$_{amide}$ 197.8(2) pm), the N$_{amide}$−Mg−N$_{amide}$ angle shows a value of only 124.8-(1)°. This is a consequence of the higher flexibility of the benzyl groups compared to that of the spherical triisopropylsilyl substituent; therefore, because of a favorable orientation of the benzyl groups the intramolecular steric strain can be reduced and a 10° smaller bond angle is realized.

Molecular Structure of 2. The molecular structure of the dimer **2** and its numbering scheme are displayed in Figure 2. The dimerization leads to tetracoordinate magnesium and nitrogen atoms. The molecule shows a trans-annular cis arrangement of the THF-ligands on one hand and of the bulky triisopropylsilyl substituents on the other. Because of this configuration, the demanding THF bases and the bulky trialkylsilyl groups have the favorable all-trans arrangement.

The Mg−N and Si−N bond lengths (average values of 210.7 and 173.0 pm, respectively) are more than 10 and ~4 pm, respectively, larger than those observed for compound **1**. The nitrogen atoms show a strongly distorted tetrahedral

Table 2. Comparison of Selected Structural Data (average values) of Alkylmagnesium Amides of Type [R″-Mg(L) (μ-NRR′)]₂ with Quadruply Coordinated Magnesium Atoms

R	R′	R″	L	Mg−C	Mg−N$_{NRR'}$	ref
SiiPr₃	H	Me	THF	212.6(3)	210.7(3)	
(CH₂)₂NMe₂	Me	Me	−^{a}	210.0(4)	210.5(3)	31
CH₂Py	SiMe₂tBu	Me	−^{b}	213.2(5)	213.7(4)	32
CH₂Py	SiMe₂tBu	Me^c	−^{b}	211.9(4)	212.6(3)	32
CMe₂CH₂−	CMe₂CH₂−	nBu	−	212.8(4)	212.3(4)	33
(CH₂)₂NMe₂	CH₂Ph	nBu	−^{a}	213.5(2)	211.5(2)	34
CH(Ph)CH₂NC₅H₁₀	Me	nBu	−^{a}	215.6(1)	212.9(1)	35
SiMe₃	SiMe₃	sBu	−^{d}	208(1)^e	211.8(4)	36
tBu	H	tBu	THF	219.4(4)	209.8(3)	2

^{a} Lewis-acid/base interaction between Mg and the pyridyl moiety. ^{b} Lewis acid/base interaction between Mg and the dialkylamino group. ^{c} Cocrystallization with [(thf)MgN(SiMe₂tBu)CH−C₅NH₄]₂. ^{d} Three-coordinate magnesium atom because of the steric shielding by the bulky trimethylsilyl groups. ^{e} Large esd because of the disordering of the sBu substituent.

coordination sphere. The Mg₂NSi moiety is flattened (angle sum of N1 in this fragment is 343.7°), and the nitrogen atom lies only 44 pm above the Mg₂Si plane; therefore, it can roughly be regarded as being sp² hybridized with the hydrogen atom bound to the p(N) orbital. This flattened fragment is caused mainly by the steric repulsion between the bulky triisopropylsilyl groups and the magnesium-bound methyl substituents.

The Mg−C bond lengths of 212.6 pm compare well with those of already known alkylmagnesium compounds with terminally bound alkyl groups.[29] Bridging alkyl substituents show larger Mg−C distances.[30] The Mg−N distances also lie in an expected range, as already observed for other magnesium amides.[2,20,21] Within the field of organomagnesium chemistry, the bridging amide and bridging alkyl groups are well-known. The more electron-rich nitrogen atom accounts for the preference of the amide ligands in a bridging position in compound **2**, thus avoiding an endocyclic MgCMg three-center two-electron bond.

In dimeric alkylmagnesium amides, which are listed in Table 2, the Mg atoms show the coordination number of four with the exception of the crowded [sBu-Mg(μ-N(SiMe₃)₂)]₂.[36] This can be achieved by intramolecularly pendent Lewis bases or by coordination of a neutral coligand such as THF. In these molecules, the Mg−C and Mg−N

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distances lie in the same region. For [sBu-Mg(μ-N(SiMe$_3$)$_2$)]$_2$, similar Mg−N values have been observed, but the Mg−C bond is shorter than that found for the derivatives with four-coordinate magnesium atoms. However, the uncertainty is large because of the thermal motion and disordering of the sBu group. Compared to monomeric (tmeda)Mg(NRR′)$_2$, the Mg−N bonds are elongated because of the bridging position of the amide ligand and hence have a larger coordination number at the nitrogen atom. Solely [tBuMg(thf)(μ-N(H)-tBu)]$_2$ exhibits a larger Mg−C distance because of enhanced steric strain.[2]

Conclusion

The reaction of dialkylmagnesium with alkylzinc triisopropylsilylamide leads to a ligand exchange reaction and the formation of magnesium bis(triisopropylsilylamide) which can be crystallized after TMEDA addition. Neither a deprotonation of the amide (formation of an imide) nor the formation of a solvent-separated magnesium dialkyl-triisopropylsilylaminozincate have been observed. However, the NMR spectroscopic follow-up of the reaction showed that heteroleptic alkylmagnesium triisopropylsilylamide is an intermediate which speaks for a stepwise ligand exchange. The formation of a zincate has neither been observed in solution nor been obtained after the addition of chelating bases and common workup procedures. However, solution equilibria of magnesium amides showed that free amide anions are unlikely to exist in solution, and therefore, the intermediate zincate species works as amide transfer reagent. Comparable complex anions have already been studied for zincates of lithium[11] and calcium[12] with very long Zn−N bonds, which could explain the short lifetime of these species in the presence of these magnesium derivatives.

Because there is an alkylmagnesium amide, two possible pathways could lead to the homoleptic magnesium bis-(amide): one pathway proceeds via the zincate intermediate and the other pathway proceeds via a dismutation reaction of the alkylmagnesium amide. The second pathway has already been observed for several alkylmagnesium amides in the presence of a polar solvent;[27,34,37] however, alkylmagnesium triisopropylamide **2** showed no ligand redistribution reactions in the absence of zinc compounds. Dialkylmagnesium, which would also originate from the Schlenk equilibrium, is identical to the starting compound and, again, would react with the starting alkylzinc primary amide.

Whereas the reference compounds (L)$_2$Mg(NRR′)$_2$ and [R″-Mg(L)(μ-NRR′)]$_2$ have been prepared by magnesiation of an amine with dialkylmagnesium, the ligand exchange reaction, according to eq 1, starting from an alkylzinc amide was unexpected. Magnesium and zinc have similar cation radii ($r(Mg^{2+}) = 71$ pm and $r(Zn^{2+}) = 74$ pm for tetracoordinate metal cations); however, the Pauling electronegativities differ for these metals (Mg is 1.3 and Zn is 1.7) which corresponds to a larger Lewis acidity of the Mg cations. Therefore, the soft carbanions bind to the zinc atom thus

forming mainly covalent Zn−C bonds, whereas the harder amino (TMEDA) and amido bases prefer the more electropositive metal thus forming electrovalent Mg−N bonds with a strong electrostatic attraction. The dismutation of alkylmagnesium amides can be interpreted as a Schlenk equilibrium with the amido substituents regarded as pseudo-halides. Very recent investigations show that the solvation enthalpies favor a (L)$_2$MgX$_2$ complex compared with (L)$_2$MgMeX and (L)$_2$MgMe$_2$.[38] Therefore, the addition a of Lewis base, such as THF, can shift the Schlenk equilibrium toward the homoleptic compounds.

In contrast to the amide chemistry of magnesium and zinc, the heavier homologous phosphanides are soft anions, and a differing chemistry has been observed. They are easily deprotonated twice, even by weak metallating reagents. Thus, oligomeric trialkylsilylphosphanediides of magnesium[39] and zinc[10,40] are well-known.

Experimental Section

General Remarks. All reactions were performed in an argon atmosphere using standard Schlenk techniques. All solvents were dried and thoroughly deoxygenated according to standard procedures prior to use. The NMR spectra were recorded on a JEOL Eclipse-400 spectrometer operating at 400.18 MHz for ^{1}H, 100.63 MHz for ^{13}C, and 79.50 MHz for ^{29}Si. Chemical shifts are given with respect to SiMe$_4$. The NMR data are listed in Table 1. The IR spectra were recorded at Nujol suspensions between KBr windows. The starting materials were prepared by known literature procedures as described earlier.[1]

(tmeda)Mg[N(H)SiiPr$_3$]$_2$ (1). Triisopropylsilylamine (2.0 mL, 9.49 mmol) was dissolved in 10 mL of toluene, and 9.49 mL of a 1.0 M solution of diethylzinc in diethyl ether (9.49 mmol) was added. After the mixture was stirred for 10 h at room temperature, this solution was refluxed for additional 2 h. After the mixture was cooled to room temperature, 5.9 mL of a 1.6 M diethylmagnesium solution in diethyl ether (9.44 mmol) and, then, 1.43 mL of TMEDA (9.49 mmol) in 5 mL of toluene were added dropwise. After the mixture was stirred for 10 h, all volatile materials were removed in vacuo at room temperature. The oily residue was recrystallized from pentane. When the solution cooled to 5 °C, 0.73 g of colorless cuboid crystals of **1** (1.51 mmol, 16%) precipitated. m.p.: >250 °C. IR: ν 3407 vw, 3326 vw 1545 vw, 1461 vs, 1410 vw, 1382 vw, 1373 w, 1356 w, 1288 m, 1263 sh, 1237 w, 1189 vw, 1162 w, 1124 w, 1099 w, 1074 m, 1062 s, 1015 s, 999 sh, 988 s, 976 s, 949 m, 907 vs, 883 vs, 820 w, 794 s, 770 vw, 653 vs, 645 sh, 619 m, 605 w, 584 vw, 514 w, 491 w, 477 w, 443 m, 423 w, 394 w, 328 vw. Anal. calcd for C$_{24}$H$_{60}$MgN$_4$Si$_2$ (485.250): C, 59.40; H, 12.46; N, 11.55. Found: C, 59.95; H, 12.48; N, 10.43 (the low nitrogen value could be the result of the formation of metal nitrides).

[Me(thf)MgN(H)SiiPr$_3$]$_2$ (2). Triisopropylsilylamine (1.05 mL, 5.0 mmol) was dissolved in 30 mL of THF. At 0 °C, 5 mL of a 1 M dimethylmagnesium solution in THF was added dropwise. The evolution of methane was observed immediately. After the mixture

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Table 3. Crystallographic Data for **1** and **2** and Information on the Refinement Procedures

	1	**2**
chemical formula	$C_{24}H_{60}MgN_4Si_2$	$C_{28}H_{66}Mg_2N_2O_2Si_2$
fw (g/mol)	485.25	567.62
T (K)	200(2)	200(3)
λ (Å)	0.71073	0.71073
space group	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)
a (Å)	22.696(2)	19.8237(16)
b (Å)	10.2958(5)	20.3413(12)
c (Å)	15.9320(12)	9.0722(6)
β (deg)	120.826(8)	95.021(9)
V (Å^3)	3196.9(4)	3644.2(4)
Z	4	4
D_{calc} (g/cm^3)	1.008	1.035
μ (mm^{-1})	0.147	0.156
wR_1 (on F^2, $I > 2\sigma(I))^a$	0.0461	0.0439
wR_2 (on F^2, $I > 2\sigma(I))^b$	0.1207	0.1177
R_2 (on F^2, all data)^b	0.1282	0.1235
CCDC number	CCDC-264916	CCDC-264915

^{a} $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$. ^{b} $R_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$.

was stirred at room temperature for several hours, the volume of the solution was reduced to half of the original amount. After the mixture was cooled to 0 °C, 2.69 g of colorless needles of **2** (4.75 mmol, 95%) precipitated. For the melting behavior, see the text. IR: ν 3487 vw, 3407 w, 1646 w, 1544 m, 1473 m, 1433 w, 1383 w, 1364 w, 1341 w, 1296 vw, 1246 m, 1179 vw, 1102 m, 1071 m, 1061 m, 1027 s, 1010 s, 993 s, 975 m, 916 w, 882 vs, 819 vs, 661 vs, 616 m, 587 m, 576 m, 519 vs, 492 sh, 461 w, 382 w, 333 w. MS (EI, 70 eV, m/z): 283 (4), 209 (23), 132 (100), 104 (97). Anal. Calcd for $C_{28}H_{66}Mg_2N_2O_2Si_2$ (567.63): C, 59.24; H, 11.72; N, 4.93. Found: C, 58.72; H, 11.30; N, 4.92.

Crystal Structure Determinations. Data were collected on a STOE-IPDS diffractometer with graphite-monochromated Mo Kα radiation using oil-coated rapidly cooled single crystals. Crystal-

lographic parameters, details of data collection and refinement procedures are summarized in Table 3.

All structures were solved by direct methods with the program SIR-97[41] and refined with the software package SHELXL-97.[42] Neutral scattering factors were taken from Cromer and Mann[43] and for the hydrogen atoms from Stewart et al.[44] The non-hydrogen atoms were refined anisotropically. The H atoms were considered with a riding model under the restriction of ideal symmetry at the corresponding carbon atoms; however, the N-bound hydrogen atoms were refined isotropically.

Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data can also be obtained free of charge on application to the Cambridge Crystallographic Data Centre [12 Union Road, Cambridge, CB2 1EZ, U.K.; fax (international) + 44(0)1223/336033; E-mail deposit@ccdc.cam.ac.uk].

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