Synthesis and Structures of Alkaline-Earth Metal Supersilanides: *t*Bu$_3$SiMX and *t*Bu$_3$Si−M−Si*t*Bu$_3$ (M = Be, Mg; X = Cl, Br)

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The alkaline-earth metal silanides, (tBu$_3$Si)$_2$Be and (tBu$_3$Si)$_2$Mg, have been synthesized from the reaction of the sodium silanide tBu$_3$SiNa with BeCl$_2$ in Bu$_2$O and MgBr$_2$ in THF. The bissupersilylmagnesium THF adduct [(tBu$_3$Si)$_2$Mg(THF)$_2$] reacts with GaBr$_3$ in benzene at ambient temperature to form tBu$_3$SiGaBr$_2$ and tBu$_3$SiMgBr(THF). The structures of bissupersilyl silanides, (tBu$_3$Si)$_2$Be and (tBu$_3$Si)$_2$Mg(THF)$_2$, and the Grignard analogue, tBu$_3$SiMgBr(THF), have been determined by X-ray structure analysis.

Introduction

Silyl anions, which are conveniently accessible from silyl halides, are important and versatile organometallic reagents in synthesis. Various details of their molecular structures have, however, still not been fully elucidated and are therefore the subject of current investigations.[1] The best-studied class of silyl anions are the alkali metal silanides that feature monomeric,[2,3] dimeric,[2,3] and polymeric[4] arrangements as molecular units. Alkali metal silanides have not only become interesting for their molecular structures but have also attracted recent attention due to their synthetic utility. More recently, alkali metal tri-*tert*-butylsilanides (supersilanides), tBu$_3$SiM, have been used for the synthesis of new main group element clusters and compounds with elements in low coordination states. Accordingly, the reaction of sodium supersilanide with thallium(III) chloride produces the supersilylated thallium clusters [(tBu$_3$Si)$_6$Tl$_6$Cl$_2$] and [(tBu$_3$Si)$_4$Tl$_3$Cl],[5] and with [(Me$_3$Si)$_2$N]$_2$Sn leads to the tristannaallene, (tBu$_3$Si)$_2$Sn=Sn=Sn(SitBu$_3$)$_2$.[6]

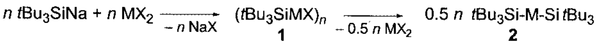
In contrast to the well-established silanides with alkali metals, only a few alkaline-earth metal silanides are known. Information regarding the structure and reactivity of these molecules is thus still rather limited.[1,7]

We have therefore become interested in the synthesis of alkaline-earth metal silanides, tBu$_3$SiMX and tBu$_3$Si−M−SitBu$_3$, and in their respective structures.

Results and Discussion

Synthesis

Several routes to silyl anions are known. In this study of the synthesis of alkaline-earth metal supersilanides only the metathesis of MX$_2$ (M = Be, X = Cl; M = Mg, X = Br) with sodium supersilanide, tBu$_3$SiNa, has been employed. We expected that the Grignard analogous compound, tBu$_3$SiMX, should be produced by reaction of MX$_2$ with one equivalent of tBu$_3$SiNa, and that tBu$_3$Si−M−SitBu$_3$- should be obtained upon elimination of MX$_2$ from two molecules of tBu$_3$SiMX.



$$n\ t\mathrm{Bu_3SiNa} + n\ \mathrm{MX_2} \xrightarrow[-n\ \mathrm{NaX}]{} \underset{\mathbf{1}}{(t\mathrm{Bu_3SiMX})_n} \xrightarrow[-0.5\ n\ \mathrm{MX_2}]{} 0.5\ n\ \underset{\mathbf{2}}{t\mathrm{Bu_3Si\text{-}M\text{-}Si}t\mathrm{Bu_3}}$$

1a: M = Be, X = Cl (1)
1b: M = Mg, X = Br
2a: M = Be
2b: M = Mg

The compounds tBu$_3$Si−M−SitBu$_3$ (M = Be, Mg) were indeed formed by the addition of two equivalents of tBu$_3$SiNa to BeCl$_2$ in dibutyl ether or to a tetrahydrofuran solution of MgBr$_2$. The Grignard analogous compound, tBu$_3$SiMgBr, was prepared by mixing tetrahydrofuran solutions of MgBr$_2$ and tBu$_3$SiNa in a 1:1 molar ratio at −78 °C, but no crystals suitable for X-ray crystallography could be obtained from this solution. While tBu$_3$SiMgBr(THF)$_n$ was transformed in a similar manner to the

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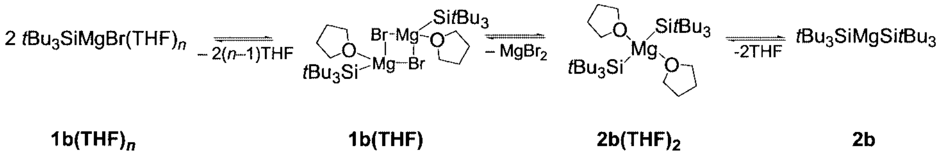
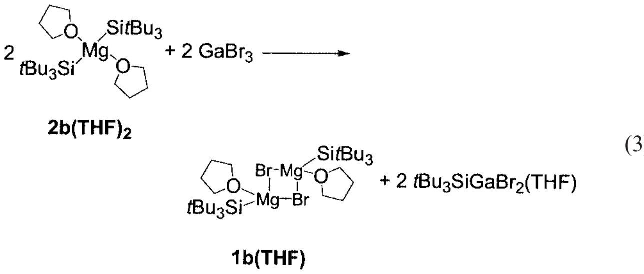


(2)

related hypersilyl compound $(\mathrm{Me_3Si})_3\mathrm{SiMgBr(THF)_2}$[8] in non-donor solvents, as indicated in Equation (2), obtaining X-ray quality crystals from $t\mathrm{Bu_3SiMgBr}$ was very difficult.-

Tetrahydrofuran molecules could be eliminated by heating the solid adduct $(t\mathrm{Bu_3Si})_2\mathrm{Mg(THF)_2}$ in vacuo. From the resulting residue, uncomplexed $(t\mathrm{Bu_3Si})_2\mathrm{Mg}$ could be recovered quantitatively. When two equivalents of sodium supersilanide reacted with $\mathrm{BeCl_2}$ in dibutyl ether only donor free $(t\mathrm{Bu_3Si})_2\mathrm{Be}$ was formed. The use of one equivalent of sodium supersilanide led to oligomeric $(t\mathrm{Bu_3SiBeCl})_n$ which shows broad signals in the ^{1}H and ^{29}Si NMR spectrum.

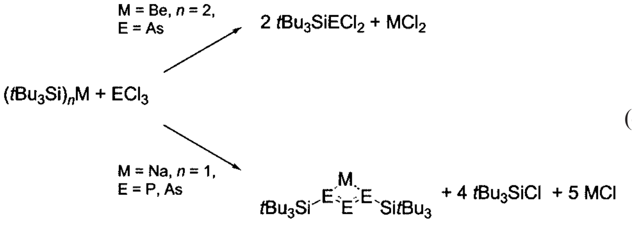


(3)

$\mathrm{GaBr_3}$ reacts with $(t\mathrm{Bu_3Si})_2\mathrm{Mg(THF)_2}$ in benzene at ambient temperature to give the Grignard analogous compound, $t\mathrm{Bu_3SiMgBr(THF)}$, and $t\mathrm{Bu_3SiGaBr_2(THF)}$. X-ray quality crystals of $t\mathrm{Bu_3SiMgBr(THF)}$ were grown from this benzene solution.

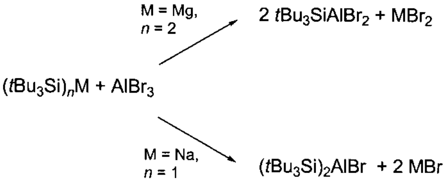
Reactivity

The supersilylated silanides of magnesium and beryllium are extremely sensitive to air and moisture. When a solution of $(t\mathrm{Bu_3Si})_2\mathrm{Mg(THF)_2}$ in benzene is treated with a small amount of water, the $\mathrm{Mg^{2+}}$ cation is substituted cleanly by two protons. When exposed to air, oxidation of $(t\mathrm{Bu_3Si})_2\mathrm{Mg(THF)_2}$ proceeds with the formation of superdisilane, $t\mathrm{Bu_3Si{-}Si}t\mathrm{Bu_3}$, and $(t\mathrm{Bu_3SiO})_2\mathrm{Mg}$. Nucleophilic substitution reactions of alkali metal supersilanides with element halides EX_n often occur with the reduction of E and the formation of E−E bonds. As reported previously, the reaction of $t\mathrm{Bu_3SiNa(THF)_2}$ with $\mathrm{ECl_3}$ (E = P, As) leads surprisingly to the sodium disupersilyltriphosphenide, $t\mathrm{Bu_3Si(Na)P{-}P{=}PSi}t\mathrm{Bu_3}$, and the disupersilyltriarsenide, $t\mathrm{Bu_3Si(Na)As{-}As{=}AsSi}t\mathrm{Bu_3}$, as shown in Equation (4).[9]



(4)

This result demonstrates the high reduction potential of alkali metal supersilanides. On the other hand, $(t\mathrm{Bu_3Si})_2\mathrm{Be}$ reacts with $\mathrm{AsCl_3}$ to produce $t\mathrm{Bu_3SiAsCl_2}$ in high yield.



(5)

We have reported that the reaction of sodium supersilanide with triel halides, $\mathrm{EX_3}$, does not depend on the starting material ratio (1:1 or 2:1) and always produces the disupersilylated compounds, $(t\mathrm{Bu_3Si})_2\mathrm{EX}$.[10] However, the reactions between $(t\mathrm{Bu_3Si})_2\mathrm{Mg(THF)_2}$ and $\mathrm{EBr_3}$ (E = Al, Ga) take a different course, as depicted in Equations (3) and (5), and only the monosupersilylated compounds $t\mathrm{Bu_3SiEBr_2}$ (E = Al, Ga) are formed. $t\mathrm{Bu_3SiAlBr_2}$ could be isolated as its $\mathrm{MgBr_2}$ adduct[10] and $t\mathrm{Bu_3SiGaBr_2}$ as its THF adduct.

Structures

Figure 1 shows the molecular structure of **2a**. Similar to the isoelectronic compound $(t\mathrm{Bu_3Si})_2\mathrm{Zn}$,[11] the Si−Be−Si unit is perfectly linear. The alkaline-earth metal silanide **2a** crystallizes in the triclinic space group $P\bar{1}$. The Be−Si distance of 2.1930(10) Å in the donor-free silanide **2a** is a little longer than the sum of the atomic radii (2.10 Å).[12]

The crystal structure of **2b(THF)₂** is shown in Figure 2; selected bond lengths and angles are listed in Table 1. X-ray-quality crystals of **2b(THF)₂** (orthorhombic, *Pbca*) were

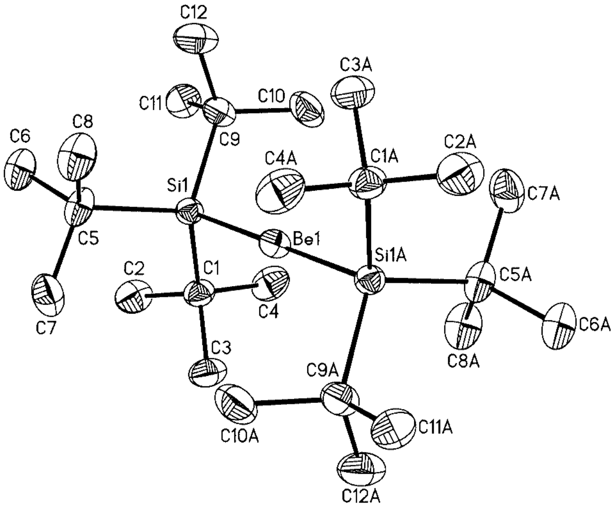


Figure 1. Thermal ellipsoid plot of **2a** showing the atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level

grown from pentane. Its Si−Mg−Si unit deviates from linearity [bond angle Si(1)−Mg−Si(2) = 132.82(4)°], due to interactions between Mg and two O atoms from tetrahydrofuran molecules. The distance between the Mg and Si atom is 2.777(2) Å. This distance is characteristic of a Mg−Si bond (sum of the atomic radii: 2.77 Å),[12] but is longer than in $(Me_3Si)_2Mg{\cdot}TMEDA$,[13] $(Me_3Si)_2Mg{\cdot}TMDAP$,[14] and $(Me_3Si)_2Mg{\cdot}DME$.[15]

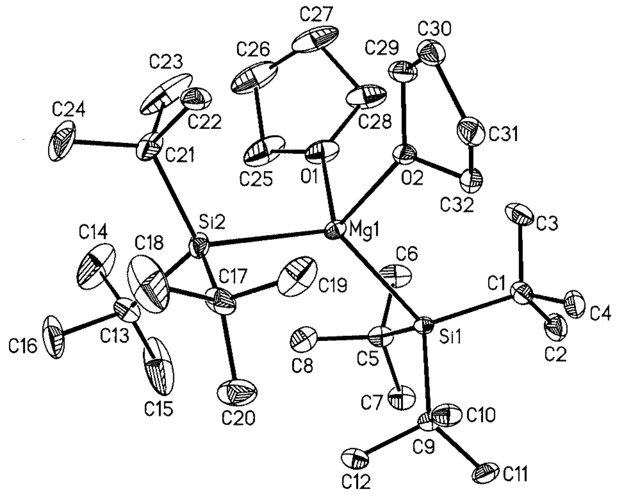


Figure 2. Thermal ellipsoid plot of **2b(THF)$_2$** showing the atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level

Table 1. Selected bond lengths (average) [Å] and angles (average) [°] for **1b(THF)**, **2a**, and **2b(THF)$_2$**

	1b(THF)	2a	2b(THF)$_2$
M−Si	2.6075(11)	2.1930(10)	2.777(2)
C−C	1.543(4)	1.540(5)	1.531(12)
Si−C	1.963(3)	1.952(3)	1.973(7)
Mg−O	2.040(2)	−	2.153(2)
Si−M−Si	−	180	132.82(4)
C−Si−M	108.97(9)	107.34(10)	111.5(4)

Complex **1b(THF)** crystallizes with a molecule of benzene in the monoclinic space group *C*2/*c*, as shown in Figure 3. The central framework of the Grignard analogous compound **1b(THF)** forms a planar four-membered ring. The corners of this ring are alternately occupied by Mg and Br atoms [angle of **1b(THF)**: Br−Mg−Br 98.2(2)°, Mg−Si−Mg 81.4(2)°]. Apart from these two Br atoms, the Mg atom is surrounded by one Si atom and one molecule of tetrahydrofuran. Contrary to the Mg center in **1b(THF)**, the Mg atoms in $(Me_3Si)MgBr{\cdot}TMEDA$[13] and $(Me_3Si)_2Mg{\cdot}MeN(CH_2CH_2NMe_2)_2$[14] are pentacoordinate. Complex **1b(THF)** features two Mg−Si contacts with a Mg−Si distance of 2.6075(11) Å. However, the Mg−Si distances in **1b(THF)** are significantly shorter than in **2b(THF)$_2$**. The Mg−Br bond in **1b(THF)** has a length of 2.5929(9) Å. This distance is characteristic of a Mg−Br bond (sum of the ionic radii: 2.53 Å).[12]

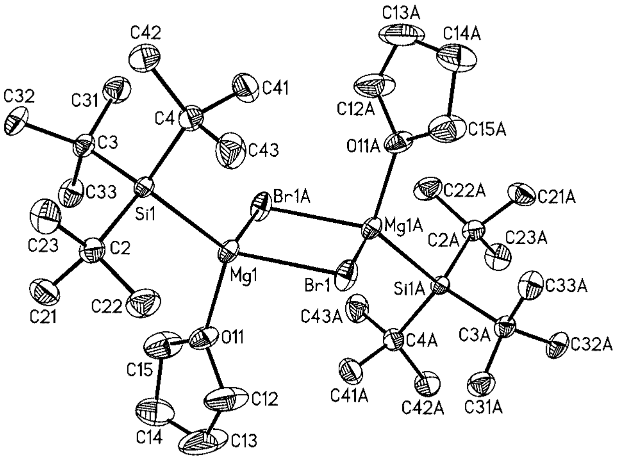


Figure 3. Thermal ellipsoid plot of **1b(THF)** showing the atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level

The disupersilylmagnesium compound **2b(THF)$_2$** shows an C−Si−C angle smaller than 110° [107.81(13)°], indicating a negatively polarized Si atom.[11]

Experimental Section

General Procedures: All experiments were carried out under dry argon or nitrogen with strict exclusion of air and moisture using standard Schlenk techniques. $t\mathrm{Bu}_3\mathrm{SiNa}$[2] was prepared according to literature procedures. The solvents (benzene, heptane, toluene, tetrahydrofuran) were distilled from sodium/benzophenone prior to use.

The NMR spectra were recorded on a Jeol GSX 270 ($^1H/^{13}C/^{29}Si$: 270.17/67.94/53.67 MHz), a Jeol EX 400 ($^1H/^{13}C/^{29}Si$: 399.78/100.53/79.31 MHz), a Bruker AM 250 ($^1H/^{13}C$: 250.133/62.896 MHz), a Bruker DPX 250 ($^1H/^{13}C/^{29}Si$: 250.130/62.895/49.69 MHz) or a Bruker AMX 400 ($^1H/^{29}Si$: 400.130 MHz/79.495 MHz) spectrometer. The ^{29}Si NMR spectra were recorded using the INEPT pulse sequence with empirically optimized parameters for polarization transfer from the *t*Bu substituents.

Caution! In view of the extreme toxicity of beryllium compounds, all experimental work was carried out in a well-ventilated fume cupboard used exclusively for this work. Any spillage of the beryllium solutions was washed out immediately. Established procedures for handling dangerous materials were followed rigorously in all phases of the synthetic work and measurements.

Synthesis of $t\mathrm{Bu}_3\mathrm{SiBeCl}$ [1a]: A solution of $t\mathrm{Bu}_3\mathrm{SiNa(THF)}_n$ (0.146 g, 0.40 mmol) in 10 mL of tetrahydrofuran was added to a solution of $BeCl_2$ (0.093 g, 1.16 mmol) in 5 mL of tetrahydrofuran at ambient temperature. After concentrating the solution to 5 mL, **1a** was obtained as an air- and moisture-sensitive precipitate at −25 °C. Yield: 0. 101 g of **1a** (80%). ^1H NMR (C_6D_6, internal TMS): δ = 1.105 (s, 27 H, *t*Bu$_3$Si) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, internal TMS): δ = 22.3 (s, *C*Me$_3$), 30.7 (s, C*Me$_3$*) ppm. $^{29}Si\{^1H\}$ NMR (C_6D_6, internal TMS): δ = 6.5 (s, Si*t*Bu$_3$) ppm.

Synthesis of $t\mathrm{Bu}_3\mathrm{SiMgBr(THF)}_n$ [1b(THF)$_n$]: A solution of $t\mathrm{Bu}_3\mathrm{SiNa(THF)}_n$ (0.792 g, 2.16 mmol) in 1.8 mL of tetrahydrofuran was added to a cooled solution (−78 °C) of $MgBr_2(THF)_4$ (0.403 g, 2.10 mmol) in 20 mL of tetrahydrofuran. After allowing the mixture to attain ambient temperature and concentrating the solution to 10 mL, **1b(THF)*n*** was obtained at −25 °C as air- and moisture-sensitive, colorless crystals. Yield: 0.482 g (0.82 mmol) of **1b(THF)*n*** (39%). Decomposition at 144 °C. ^{1}H NMR ([D$_8$]THF internal TMS): δ = 1.056 (s, 27 H, *t*Bu$_3$Si) ppm. ^{13}C{^{1}H} NMR ([D$_8$]THF internal TMS): δ = 24.0 (s, *C*Me$_3$), 33.6 (s, C*Me$_3$*) ppm. ^{29}Si{^{1}H} NMR ([D$_8$]THF external TMS): δ = 26.4 (s, Si*t*Bu$_3$) ppm.

Remark: **1b(THF)*n*** dissolved in [D$_6$]benzene transforms into **2b(THF)$_2$** (by ^{1}H and ^{29}Si NMR spectroscopy).

Synthesis of (*t*Bu$_3$Si)$_2$Be (2a): A slurry of BeCl$_2$ (0.154 g, 1.93 mmol) and *t*Bu$_3$SiNa(Bu$_2$O)$_2$ (1.40 g, 3.80 mmol) in 10 mL of heptane was stirred for two days at ambient temperature. The reaction mixture became colorless. The solid that formed was removed by filtration. Colorless crystals of **2a** were grown from the filtrate at −25 °C. Yield: 0.632 g (1.55 mmol) of **2a** (80%). m.p. 208−210 °C. ^{1}H NMR (C$_6$D$_6$, internal TMS): δ = 1.250 (s, 54 H, *t*Bu$_3$Si) ppm. ^{29}Si{^{1}H} NMR (C$_6$D$_6$, external TMS): δ = 6.9 (s, Si*t*Bu$_3$) ppm. X-ray structure analysis: see Figure 1.

Synthesis of (*t*Bu$_3$Si)$_2$Mg(THF)$_2$ [2b(THF)$_2$]: A solution of *t*Bu$_3$SiNa(THF)$_n$ (2.64 g, 7.20 mmol) in 6 mL of tetrahydrofuran was added to a cooled solution (−78 °C) of MgBr$_2$(THF)$_4$ (1.718 g, 3.63 mmol) in 20 mL of tetrahydrofuran. After allowing the mixture to attain ambient temperature, the solvent was removed in vacuo. The remaining residue was treated with 20 mL of heptane. After filtrating the insoluble material and concentrating the filtrate to 10 mL, **2b(THF)$_2$** was obtained at −25 °C as air- and moisture-sensitive colorless crystals, which were suitable for X-ray diffraction analysis (Figure 2). Yield: 1.402 g (2.48 mmol) of **2b(THF)$_2$** (68%). decomposition 116 °C. ^{1}H NMR (C$_6$D$_6$, internal TMS): δ = 1.328 (s, 54 H, *t*Bu$_3$Si), 1.269 (m, 8 H, CH$_2$), 3.566 (m, 8 H, OCH$_2$) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, internal TMS): δ = 24.1 (s, *C*Me$_3$), 33.5 (s, C*Me$_3$*), 24.7 (CH$_2$), 68.3 (OCH$_2$) ppm. ^{29}Si{^{1}H} NMR (C$_6$D$_6$, external TMS): δ = 31.2 (s, Si*t*Bu$_3$) ppm. C$_{32}$H$_{70}$Si$_2$O$_2$Mg (567.38): calcd. C 67.79, H 12.45; found C 62.15, H 11.40.

According to the ^{1}H and ^{29}Si NMR spectra solvent-free (*t*Bu$_3$Si)$_2$Mg was obtained quantitatively after (*t*Bu$_3$Si)$_2$Mg(THF)$_2$ (0.040 g, 0.07 mmol) was heated to 80 °C for 2 h in high vacuo. ^{1}H NMR (C$_6$D$_6$, internal TMS): δ = 1.380 (s, 54 H, *t*Bu$_3$Si) ppm. ^{29}Si{^{1}H} NMR (C$_6$D$_6$, external TMS): δ = 38.0 (s, Si*t*Bu$_3$) ppm.

Reaction of (*t*Bu$_3$Si)$_2$Be [2a] with AsCl$_3$: A solution of (*t*Bu$_3$Si)$_2$Be (0.054 g, 0.13 mmol) in 2 mL of heptane was added to a cooled solution (−78 °C) of AsCl$_3$ (0.42 g, 2.90 mmol) in 20 mL of tetrahydrofuran. After allowing the mixture to attain ambient temperature, all volatile compounds were removed in vacuo. The remaining residue was treated with 10 mL of heptane. After filtrating the insoluble material and removing the solvent in vacuo, *t*Bu$_3$SiAsCl$_2$ remained as an air- and moisture-sensitive colorless oil. Yield: 0.061 g (0.176 mmol) of *t*Bu$_3$SiAsCl$_2$ (68%). ^{1}H NMR

Table 2. Crystallographic data and further details of the structure determination of **1b(THF)**, **2a**, and **2b(THF)$_2$**

	1b(THF)	**2a**	**2b(THF)$_2$**
Formula	C$_{38}$H$_{76}$Br$_2$Mg$_2$O$_2$Si$_2$	C$_{24}$H$_{54}$BeSi$_2$	C$_{32}$H$_{70}$MgO$_2$Si$_2$
Molecular weight [g/mol]	829.61	407.86	567.73
Temperature [K]	173	158	153
Wave length [Å]	Mo-K_α, 0.71073	Mo-K_α, 0.71073	Mo-K_α, 0.71073
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	*C*2/*c*	$P\bar{1}$	*Pbca*
Z	4	2	8
Cell parameters			
a [Å]	12.3504(9)	8.631(4)	15.583(6)
b [Å]	12.624(1)	11.871(4)	17.162(8)
c [Å]	29.853 (2)	14.942(6)	22.433(13)
α [°]	90	74.03(2)	90
β [°]	98.958(6)	87.64(2)	90
γ [°]	90	73.377(15)	90
Volume [Å ^{3}]	4597.7(7)	1409.2(9)	7336.6(6)
Calculated density [Mg/m^3]	1.199	0.961	1.027
Absorption coeff. [mm^{-1}]	1.870	0.132	0.138
F(000)	1768	460	2544
crystal dimensions [mm^3]	0.4 × 0.3 × 0.2	0.3 × 0.2 × 0.07	0.3 × 03 × 0.2
2θ$_{max}$ [°]	55.9	54.0	55.0
Index ranges	$-15 \le h \le 15$, $-15 \le k \le 15$, $-34 \le l \le 36$	$-10 \le h \le 10$, $-15 \le k \le 10$, $-19 \le l \le 19$	$-17 \le h \le 12$, $-7 \le k \le 22$, $-35 \le l \le 35$
Measured reflections	27623	8066	19444
Independent reflections	4700	4358	7363
R_{int}	0.0470	0.0379	0.0408
Reflections with $I > 2\sigma(I)$	3910	2911	4048
Data /Restraints/Parameter	4700/0/209	3610/0/265	4967/0/405
Weighting scheme *x*/*y*	0.0588/7.931	0.0292/1.2655	0.028/12.656
GooF	1.071	1.133	1.126
$R1$ [$I > 2\sigma(I)$]	0.0567	0.0502	0.0595
$wR2$ [$I > 2\sigma(I)$][a]	0.1027	0.1084	0.1221
$wR2$	0.1089	0.1336	0.1593
Difference electron density [e/Å^3]	0.862	0.543	0.357

[a] $w = 1/[\sigma^2(F_o^2) + (x \cdot P)^2 + y \cdot P]$; $P = (F_o^2 + 2F_c^2)/3$.

(C_6D_6, internal TMS): δ = 1.166 (s, 27 H, *t*Bu_3Si) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, internal TMS): δ = 26.5 (s, *C*Me_3), 30.7 (s, C*Me₃*) ppm. $^{29}Si\{^1H\}$ NMR (C_6D_6, external TMS): δ = 23.0 (s, Si*t*Bu_3) ppm.

Reaction of (*t*$Bu_3Si)_2Mg(THF)_2$ [2b($THF)_2$] with $GaBr_3$: $GaBr_3$ (0.085 g, 0.274 mmol) was added to a solution of **2b($THF)_2$** (0.150 g, 0.264 mmol) in 1.2 mL of C_6D_6. Colorless crystals of **1b(THF)**, *t*$Bu_3SiMgBr(THF)_2$, grew from this benzene solution within one week at ambient temperature. These crystals were suitable for X-ray diffraction analysis (Figure 3). Yield: 0.084 g (0.194 mmol) of **1b(THF)** (73%). For NMR of **1b(THF)** see above. For the reaction of (*t*$Bu_3Si)_2Mg(THF)_2$ (**2b**) with $AlBr_3$ see ref.[10]

The ^1H, ^{13}C, and ^{29}Si NMR spectra of the remaining benzene solution showed only the signals of *t*$Bu_3SiGaBr_2$(THF).[10] After removing the solvent in vacuo, colorless *t*$Bu_3SiGaBr_2$(THF) was obtained as a solid. ^1H NMR (C_6D_6, internal TMS): δ = 1.29 (s, 27 H, *t*Bu_3Si), 1.42 (m, 8 H, CH_2), 3.62 (m, 8 H, OCH_2) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, internal TMS): δ = 25.6 (s, *C*Me_3), 31.7 (s, C*Me₃*), 25.0 (CH_2), 68.2 (OCH_2) ppm. $^{29}Si\{^1H\}$ NMR (C_6D_6, external TMS): δ = 47.7 (s, Si*t*Bu_3) ppm.

Oxidation of (*t*$Bu_3Si)_2Mg(THF)_2$ [2b($THF)_2$]: N_2O (0.104 g, 0.61 mmol) was condensed into a solution of (*t*$Bu_3Si)_2Mg(THF)_2$ (0.017 g, 0.027 mmol) in 1 mL of benzene. The supersiloxide (*t*$Bu_3SiO)_2Mg$ and N_2 were formed in quantitative yield (by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy). Compound **2b** (0.2 mmol/1 mL of C_6D_6) reacts with dry air, forming superdisilane, *t*Bu_3SiSi*t*Bu_3,[10] and (*t*$Bu_3SiO)_2Mg$: ^1H NMR (C_6D_6, internal TMS): δ = 1.146 (s, 54 H, *t*Bu_3Si) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, internal TMS): δ = 22.1 (s, *C*Me_3), 30.8 (s, C*Me₃*) ppm. $^{29}Si\{^1H\}$ NMR (C_6D_6, external TMS): δ = −9.4 (s, Si*t*Bu_3) ppm.

X-ray Structure Determination: Data Collection (Table 2): Siemens CCD three-circle diffractometer, graphite-monochromated Mo-K_α radiation; empirical absorption correction using SADABS,[16] structure solution by direct methods,[17] structure refinement: full-matrix least-squares on F^2 with SHELXL-97.[17] Hydrogen atoms were placed at ideal positions and refined with fixed isotropic displacement parameters using a riding model. CCDC-192308 (**1b**), CCDC 192306 (**2a**), and CCDC-192307 (**2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] P. D. Lickiss, C. M. Smith, *Coord. Chem. Rev.* **1995**, *145*, 75−124.

[2] N. Wiberg, K. Amelunxen, H.-W. Lerner, H. Schuster, H. Nöth, I. Krossing, M. Schmidt-Amelunxen, T. Seifert, *J. Organomet. Chem.* **1997**, *542*, 1−18.

[3] K. W. Klinkhammer, *Chem. Eur. J.* **1997**, *3*, 1418−1441.

[4] H.-W. Lerner, S. Scholz, M. Bolte, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1638−1642.

[5] N. Wiberg, T. Blank, H.-W. Lerner, D. Fenske, G. Linti, *Angew. Chem.* **2001**, *113*, 1275−1278, *Angew. Chem. Int. Ed.* **2001**, *40*, 1232−1235.

[6] N. Wiberg, H.-W. Lerner, S.-K. Vasisht, S. Wagner, K. Karaghiosoff, H. Nöth, W. Ponikwar, *Eur. J. Inorg. Chem.* **1999**, 1211−1218.

[7] R. Goddard, C. Krüger, N. A. Ramadan, A. Ritter, *Angew. Chem.* **1995**, *107*, 1107−1109, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1030−1032.

[8] J. D. Farwell, M. F. Lappert, C. Marschner, C. Strissel, D. Tilley, *J. Organomet. Chem.* **2000**, *603*, 185−188.

[9] N. Wiberg, A. Wörner, H.-W. Lerner, K. Karaghiosoff, D. Fenske, G. Baum, A. Dransfeld, P. von Ragué Schleyer, *Eur. J. Inorg. Chem.* **1998**, 833−841.

[10] N. Wiberg, K. Amelunxen, H.-W. Lerner, H. Schuster, H. Nöth, J. Knizek, I. Krossing, *Z. Naturforschung, Teil B* **1998**, *53*, 333−348.

[11] N. Wiberg, K. Amelunxen, H.-W. Lerner, H. Nöth, A. Appel, J. Knizek, K. Polborn, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1861−1870.

[12] Holleman-Wiberg, *Lehrbuch der Anorganischen Chemie*, 101. Ed., de Gruyter, Berlin **1995**, p. XXXVI.

[13] D. W. Goebel Jr., J. L. Hencher, J. P. Oliver, *Organometallics* **1983**, *2*, 746−750.

[14] L. Rösch, J. Pickardt, S. Imme, U. Börner, *Z. Naturforschung, Teil B* **1986**, *41*, 1523−1526.

[15] A. R. Claggett, W. H. Ilsley, T. J. Anderson, M. D. Glick, J. P. Oliver, *J. Am. Chem. Soc.* **1977**, *99*, 1797−1801.

[16] G. M. Sheldrick, *SADABS*, a Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen, Germany, **1996**.

[17] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.

[18] G. M. Sheldrick, *SHELXL-97*, A Program for the Refinement of Crystal Structures; University of Göttingen, Germany, **1997**.

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