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Synthesis of Polysilanylmagnesium Compounds

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The synthesis of several bis(polysilanyl)magnesium, polysilanylmagnesium bromide compounds was accomplished by metathesis of the respective potassium polysilanyls with magnesium bromide. The compounds were isolated as adducts of THF, TMEDA, or 1,4-dioxane. The use of Grignard reagents PhMgBr and MeMgBr instead of magnesium bromide led to the formation of mixed alkyl/polysilanylmagnesium compounds.

Introduction

Organomagnesium compounds play a pivotal role in both organic and organometallic chemistry. In contrast to carbanions, where the frequent use of organomagnesium compounds preceded the development of organolithium compounds, the chemistry of silyl anions was long dominated by alkali metal and especially lithium organosilyls. One reason for this concentration on group 1 metal compounds certainly stems from the fact that reaction of elemental magnesium with silyl halides does not lead to the formation of organosilylmagnesium compounds but rather to Wurtz-type silicon−silicon coupling products. Only recently was the direct synthesis of sila-Grignard compounds accomplished by reaction of activated magnesium with trimethylsilyl bromide and -iodide in the presence of tetramethylethylenediamine (TMEDA) or pentamethyldiethylenetriamine.[1]

Evidence for the existence of silylmagnesium compounds was reported as early as in 1959.[2] However, only in 1977 did Roesch[3] and Oliver[4] synthesize bis(trimethylsilyl)magnesium by reaction of bis(trimethylsilyl)mercury with magnesium.[5] Soon after, mixed alkyl-silylmagnesium compounds such as $PhMe_2SiMgMe$, obtained by the reaction of phenyldimethylsilyllithium and methylmagnesium bromide, gained some importance for the silylmetalation of unsaturated compounds.[6] Later Tamao et al. introduced aminosilylmagnesium compounds, which became useful reagents for organic synthesis as hydroxyl anion equivalents.[7]

The reaction of silyllithium compounds with magnesium halides is currently the most useful method for the preparation of silylmagnesium compounds.[8,9] In this way Oehme and coworkers prepared tris(trimethylsilyl)silylmagnesium bromide (**1**) from tris(trimethylsilyl)silyllithium[10] by reaction with magnesium bromide.[11] Isolation and structure determination of this compound and also bis[tris(trimethylsilyl)silyl]magnesium (**2**) were reported shortly after.[12] These and related compounds have gained importance as alternatives to polysilanyllithiums, as they are less reactive and frequently more selective. A recent report of the first synthesis of a hafnium disilene complex employed a disilanyldimagnesium compound in a case where the respective dipotassium compound did not give the desired product.[13] Reaction of such silyl dianions with magnesium bromide can lead to the formation of magnesacyclosilanes.[14,21]

Results and Discussion

As stated above, metathesis reaction of silyllithium or -potassium compounds with magnesium bromide is an excellent means of moderating the reactivity of silyl anions. As shown by us[12] and others,[11] this works very well for tris(trimethylsilyl)-

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

[2] (a) Selin, T. G.; West, R. *Tetrahedron* **1959**, *5*, 97−98. (b) Roesch, L.; Erb, W.; Mueller, H. *Z. Naturforsch.* **1976**, *31B*, 281−282. (c) Colomer, E.; Corriu, R. *J. Chem. Soc., Chem. Commun.* **1976**, 176−177.

[3] (a) Roesch, L. *Angew. Chem.* **1977**, *89*, 257−258. (b) Roesch, L.; Starke, U. *Z. Naturforsch.* **1983**, *38B*, 1292.

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

[5] For a recent example of a transmetalation reaction for the synthesis of silylmagnesium compounds by conversion of a silylborane with methylmagnesium bromide see: Kawachi, A.; Minamimoto, T.; Tamao, K. *Chem. Lett.* **2001**, 1216−1217.

[6] (a) Morizawa, Y.; Oda, H.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, *25*, 1163−1166. (b) Okuda, Y.; Sato, M.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1983**, *24*, 2015−2018. (c) Okuda, Y.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, *25*, 2483−2486. (d) Tang, J.; Shinokubo, H.; Oshima, K. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 245−251. (e) Oestreich, M.; Weiner, B. *Synlett* **2004**, 2139−2142.

[7] Tamao, K.; Kawachi, A.; Tanaka, Y.; Ohtani, H.; Ito, Y. *Tetrahedron* **1996**, *52*, 5765−5772.

[8] Dysard, J. M.; Tilley, T. D. *J. Am. Chem. Soc.* **2000**, *122*, 3097−3105.

[9] Lerner, H.-W.; Scholz, S.; Bolte, M.; Wiberg, N.; Nöth, H.; Krossing, I. *Eur. J. Inorg. Chem.* **2003**, 666−670.

[10] (a) Gilman, H.; Holmes, J. M.; Smith, C. L. *Chem. Ind. (London)* **1965**, 848−849. (b) Gilman, H.; Smith C. L. *J. Organomet. Chem.* **1968**, *14*, 91−101. (c) Gutekunst, G.; Brook, A. G. *J. Organomet. Chem.* **1982**, *225*, 1−3.

[11] (a) Krempner, C.; Oehme, H. *J. Organomet. Chem.* **1994**, *464*, C7−C10. (b) Krempner, C.; Reinke, H.; Oehme, H. *Chem. Ber.* **1995**, *128*, 143−149.

[12] (a) Farwell, J. D.; Lappert, M. F.; Marschner, C.; Strissel, C.; Tilley, T. D. *J. Organomet. Chem.* **2000**, *603*, 185−188. (b) Wiberg, N.; Niedermayer, W.; Lerner, H.-W.; Bolte, M. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1043−1047.

[13] Fischer, R.; Zirngast, M.; Baumgartner, J.; Marschner, C. *J. Am. Chem. Soc.* **2005**, *127*, 70−71.

[14] Fischer, R.; Konopa, T.; Baumgartner, J.; Marschner, C. *Organometallics* **2004**, *23*, 1899−1907.

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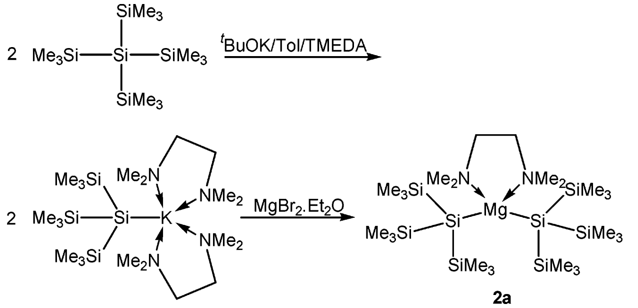
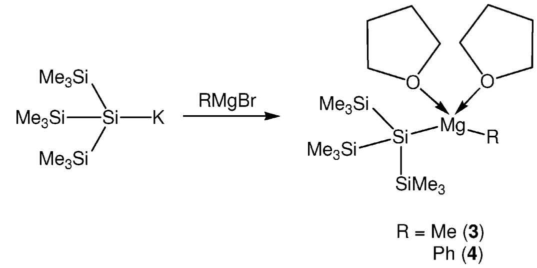
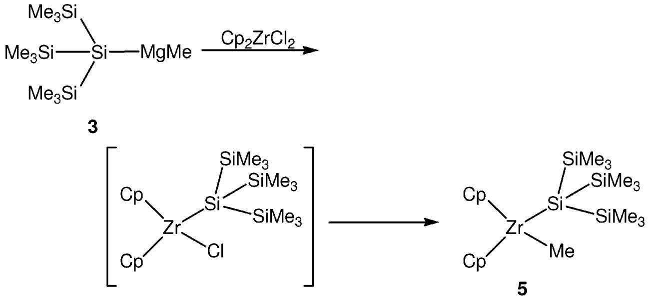
silyllithium and -potassium. Tris(trimethylsilyl)silylmagnesium bromide (**1**) and bis[tris(trimethylsilyl)silyl]magnesium (**2**) can be obtained as adducts with two THF molecules.[12] As we have encountered problems with coordinated ether molecules in reactions with very Lewis acidic transition metal salts, we recently reported the synthesis of tris(trimethylsilyl)silylpotassium[15] in toluene in the presence of TMEDA.[16] The adduct with two molecules of TMEDA was further reacted with magnesium bromide, and bis[tris(trimethylsilyl)silyl]magnesium coordinated with one molecule of TMEDA (**2a**) was obtained.



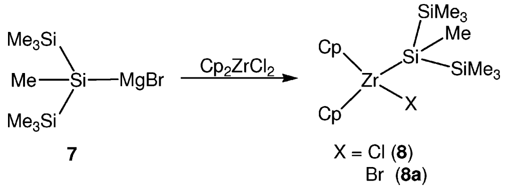
Instead of magnesium bromide, Grignard reagents can be used to obtain polysilanylmagnesium compounds. Reaction of tris(trimethylsilyl)silylpotassium with either methyl- or phenylmagnesium bromide gave the respective mixed silylmagnesium compounds (**3**, **4**) as THF adducts.



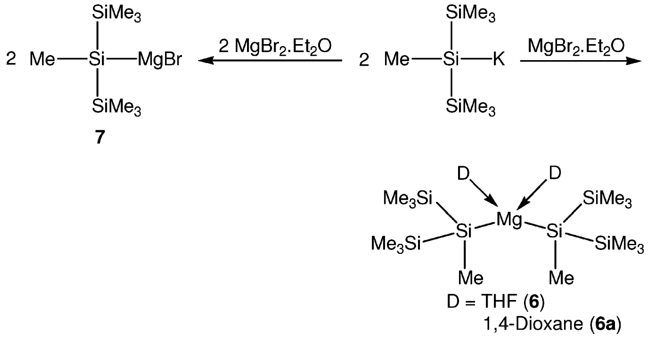
The methylsilylmagnesium compound **3** was reacted with zirconocene dichloride. NMR spectroscopic studies revealed that transfer of the bulky silyl group preceded methyl attack on the transiently formed tris(trimethylsilyl)silylzirconocene chloride.[17] Eventually, methyltris(trimethylsilyl)silylzirconocene (**5**)[17] was formed.



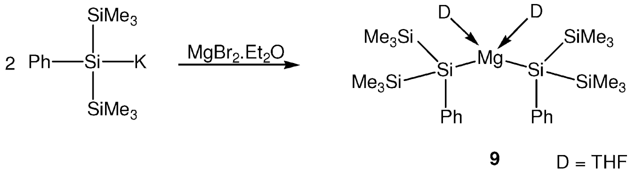
The methylbis(trimethylsilyl)silyl anion represents a good example of the necessity to employ silylmagnesium compounds. The reaction of methylbis(trimethylsilyl)silylpotassium[18] with zirconocene dichloride in THF gave a plethora of different silylzirconium compounds.[19] Change of solvent to toluene improved the situation and led to the wanted methylbis(trimethylsilyl)silylzirconocene chloride (**8**) as the main product, but still a considerable number of byproducts were detected. While the reason for this unexpected behavior is still not exactly understood, the use of the respective magnesium compounds (**6**, **7**) afforded selective formation of methylbis(trimethylsilyl)silylzirconocene chloride (**8**). The only detectible byproduct that was observed in differing quantities was methylbis(trimethylsilyl)silylzirconocene bromide (**8a**). This compound was formed via metathesis reaction of the zirconcene chloride with magnesium bromide.



The used mono- and bis[methylbis(trimethylsilyl)silyl]magnesium compounds (**6**, **7**) were obtained by reaction of methyl[bis(trimethylsilyl)]silylpotassium[18] with either one or half an equivalent of magnesium bromide.



In a similar way the reaction of phenylbis(trimethylsilyl)silylpotassium[18] with magnesium bromide gave bis[phenylbis(trimethylsilyl)silyl]magnesium (**9**).



Recently, we have prepared a number of different polysilanyldipotassium compounds.[20,30a] These silyl dianions are very reactive, and the need to moderate the reactivity is even higher than for monoanions. When dianions **10** and **11** were treated with magnesium bromide, cyclic products (**12**, **13**) were formed.

The use of a cyclic dianion gave a bicyclic polysilanylmagnesium compound. *trans*-1,4-Dipotassio-1,4-bis(trimethylsilyl)octamethylcyclohexasilane (**14**) was converted this way into the

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[15] Marschner, C. *Eur. J. Inorg. Chem.* **1998**, 221−226

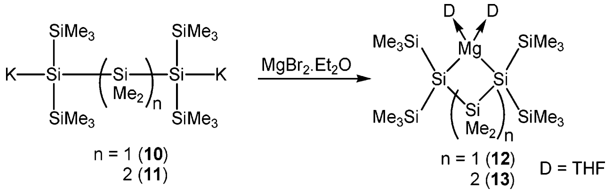
[16] (a) Frank, D.; Baumgartner, J.; Marschner, C. *Chem. Commun.* **2002**, 1190−1191. (b) Frank, D.; Baumgartner, J.; Marschner, C. *Organosilicon Chemistry VI*; Auner, N., Weis, J., Eds.; Wiley-VCH: Weinheim, Germany, 2005; pp 452−456.

[17] Campion, B. K.; Falk, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 2049−2056.

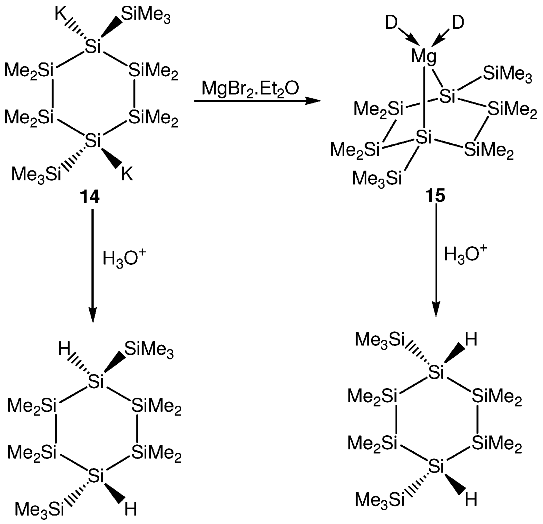
[18] Kayser, C.; Fischer, R.; Baumgartner, J.; Marschner, C. *Organometallics* **2002**, *21*, 1023−1030

[19] Kayser, C.; Marschner, C. *Monatsh. Chem.* **1999**, *130*, 203−206.

[20] (a) Fischer, R.; Frank, D.; Gaderbauer, W.; Kayser, C.; Mechtler, C.; Baumgartner, J.; Marschner, C. *Organometallics* **2003**, *22*, 3723−3731. (b) Fischer, R.; Konopa, T.; Baumgartner, J.; Marschner, C. *Organometallics* **2004**, *23*, 1899−1907.

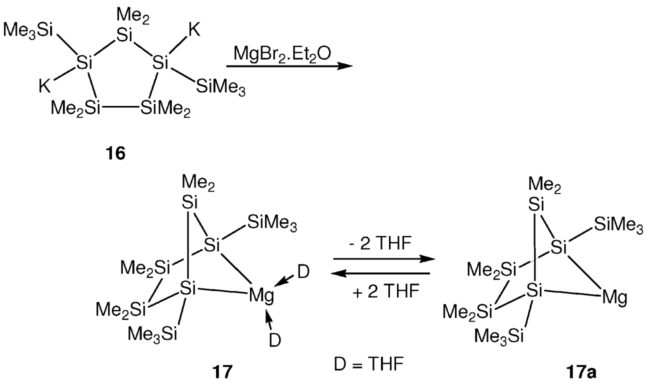


respective magnesa[2.2.1]bicycloheptasilane (**15**).[21] This transformation has important implications for the stereochemistry of the dianion. While hydrolysis of the dipotassium compound **14** gave mainly the *trans*-1,4-dihydrocyclohexasilane, treatment of the magnesium compound **15** with aqueous sulfuric acid afforded the respective *cis*-isomer, exclusively.[21] Similar to organomagnesium compounds, magnesium silyls have higher inversion barriers than the corresponding alkali metal derivatives.[2c,22] Therefore the configuration of the remaining anionic silicon atom is preserved after the first hydrolysis step.



In an analogous way *trans*-1,3-dipotassio-1,3-bis(trimethylsilyl)hexamethylcyclopentasilane (**16**)[23] was converted to the bicyclic product (**17**) with magnesium bromide. In the course of the isolation of **17** we encountered an interesting issue: during removal of the solvent also THF can be removed either partially or with extended exposure to vacuum also completely. The obtained compound **17a** has significantly different NMR properties. Upon addition of 2 equiv of THF, the adduct **17** was regained.

^{29}Si NMR Spectroscopy. ^{29}Si NMR spectroscopy provides most valuable insight into the electronic situation of the silylanions. For the tris(trimethylsilyl)silyl unit the replacement of a trimethylsilyl group ($\delta = -135.6$ for $(Me_3Si)_4Si$) with a potassium counterion ($\delta = -195.8$ for $(Me_3Si)_3SiK$) is accompanied by an upfield shift of ~60 ppm (see Table 1). For the investigated tris(trimethylsilyl)silylmagnesium compounds the chemical shift ranged from −168.7 to −174.5 ppm. While tris(trimethylsilyl)silylmagnesium bromide (**1**) showed a resonance for the metalated silicon atom at −168.7 ppm, the double-silylated magnesium (**2**, **2a**) is shifted slightly to higher field. For the mixed silyl/methyl (**3**) and silyl/phenyl (**4**) compounds another 3 ppm of increased field shift was observed. The same trend as for the tris(trimethylsilyl)silyl group was also observed for the methylbis(trimethylsilyl)silyl unit. Chemical shifts of −127.4 ppm for the silylpotassium compound, −117 ppm for the double-silylated magnesium compounds (**6**, **6a**), and −109.2 ppm for the silylmagnesium bromide (**7**) were found. Phenylated silylanions usually resonate at lower field than alkylated ones. This was also true for **9** (−92.5 ppm) compared to **6** (−117 ppm). The four-membered cyclic compound **12** resonated at very low field, at −137.3 ppm. This is close to the shift of tetrakis(trimethylsilyl)silane (−135.6 ppm) and rather unusual for a trisilylated silylanion. However, octakis(trimethylsilyl)cyclotetrasilane,[24] which should be similar in geometry to **12**, displays a shift at −92.1 ppm, which is also at unusually low field. Extending the ring size to five (**13**) reestablished expected NMR values (−176.6 ppm). The bicyclic compound **17** also contains a four-membered ring, and again a low-field shift was observed (−156.6 ppm). The removal of the THF molecules (**17a**) caused another shift to lower field (−148. ppm), which is a common behavior also for silylpotassium compounds.[15]



X-ray crystallography. Compounds **2a**, **4**, **6**, **6a**, **7**, **9**, and **13** could be subjected to crystal structure analysis (Tables 2 and 3). Structural data for silylmagnesium compounds are known only for the trimethylsilyl, tris(trimethylsilyl)silyl, and tri-*tert*-butylsilyl groups. Bis(trimethylsilyl)magnesium has been studied as adducts with TMEDA,[3] tetramethyltrimethylenediamine,[3] and dimethoxyethane.[4] Si−Mg bond lengths were found in the range between 2.61 and 2.67 Å. For the corresponding trimethylsilylmagnesium bromide TMEDA adduct[1] a value of 2.63 Å was found. For the tri-*tert*-butylsilyl group also the bissilylmagnesium and the silylmagnesium bromide were studied.[9] While the Si−Mg bond length for the former compound is relatively long (2.80 Å), the same distance in ^{t}Bu$_3$SiMgBr is, at 2.61 Å, astonishingly short. For compound **2** two structural investigations are known.[12a,25] The structures that are THF adducts and solvates of either pentane or hexane feature Si−Mg bond lengths of 2.65 and 2.67 Å. The published structure of tris(trimethylsilyl)silylmagnesium bromide gave a Si−Mg bond lengths around 2.59 Å.[12a]

Replacement of the two THF molecules by TMEDA in **2a** (Figure 1) elongated the Si−Mg bond length to 2.71/2.75 Å. In contrast to this, the bond length in the mixed silyl/phenylmagnesium compound **4** (Figure 2), at 2.65 Å, is comparable to **2**. The bissilylmagnesium compounds **6** (Figure 3), **6a** (Figure 4), **9** (Figure 6), and **13** (Figure 7) investigated in this paper all show similar Si−Mg bond lengths of around 2.64 Å. Methylbis(trimethylsilyl)magnesium bromide (**7**) (Figure 5) displayed the

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[21] Fischer, R.; Konopa, T.; Ully, S.; Baumgartner, J.; Marschner, C. *J. Organomet. Chem.* **2003**, *685*, 79−92.

[22] Fischer, R.; Marschner, C. *Organosilicon Chemistry V: From Molecules to Materials*; Auner, N., Weis, J., Eds.; Wiley-VCH: Weinheim, Germany, 2003; pp 190−194.

[23] Fischer, J.; Gaderbauer, W.; Baumgartner, J.; Marschner, C. *Heterocycles* **2006**, *67*, 507−510.

[24] Shen, Y.-S.; Gaspar, P. *Organometallics* **1982**, *1*, 1410−1412.

[25] Uffing, C.; Baum, E.; Schnockel, H. Cambridge Crystallographic Data Centre, private communication UCIXIN, 2001.

Table 1. Comparison of ^{29}Si NMR Spectroscopic Data for R−E

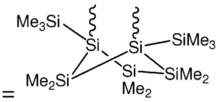
E	-SiMe$_3$	-K	-Mg-R'
R = Si(SiMe$_3$)$_3$, R'=Br	-9.6, -135.6	-3.9; -195.8	-6.5,-168.7 (**1**)
R, R' = Si(SiMe$_3$)$_3$	-9.6, -135.6	-3.9; -195.8	-6.4, -171.9 (**2**)
	-9.6, -135.6	-3.9; -195.8	-7.5, -170.2 (**2a**)
R = Si(SiMe$_3$)$_3$, R'= Me	-9.6, -135.6	-3.9; -195.8	-6.2, -174.5 (**3**)
R = Si(SiMe$_3$)$_3$, R'= Ph	-9.6, -135.6	-3.9; -195.8	-6.5, -174.2 (**4**)
R, R' Si(SiMe$_3$)$_2$Me	-12.5, -87.9	-7.8, -127.4	-9.1, -116.9 (**6**)
	-12.5, -87.9	-7.8, -127.4	-9.2, -117.3 (**6a**)
R = Si(SiMe$_3$)$_2$Me, R' = Br	-12.5, -87.9	-7.8, -127.4	-9.5, -109.2 (**7**)
R, R' Si(SiMe$_3$)$_2$Ph	-12.8, -76.8	-9.8, -99.3	-10.8, -92.5 (**9**)
R = R' [Si(SiMe$_3$)$_2$]$_2$SiMe$_2$	-8.6, -25.2, -117.7.	-5.3, -16.4, -171.9	-6.9, -25.4, -137.3 (**12**)
R = R' [Si(SiMe$_3$)$_2$]$_2$(SiMe$_2$)$_2$	-8.8, -29.1, -127.4	-4.1, -26.7, -191.6	-5.4, -27.8, -176.6 (**13**)
R = R'= 	-7.6, -19.9, -24.8, -129.4	-3.8, -5.4, -11.3, -178.4	-5.0, -9.0, -23.5, -156.6 (**17**)
	-7.6, -19.9, -24.8, -129.4	-3.8, -5.4, -11.3, -178.4	-6.0, -13.5, -26.2, 148.1 (**17a**)

Table 2. Selected Structural Properties of 2, 2a, 4, 6, 6a, 7, 9, and 13

	Si−Mg [Å]	Si−Mg−Si [deg]	∑Si−Si−E [deg]
2	2.682(2)	131.2	308.3/310.2
2a	2.708(3)/ 2.749(4)	130.9	306.0/308.0
4	2.6504(16)	128.2 (Si−Mg−C)	314.0
6	2.6378(10)	133.9	313.1
6a	2.646(3)	134.1	
7	2.568(3)	120.5 (Si−Mg−Br)	320.4
9	2.635(3)	120.2	318.9/319.7
13	2.646(3)	107.6	319.4

shortest of all Si−Mg distances (2.57 Å). As already shown for the case of tri-*tert*-butylsilylmagnesium bromide,[9] also **7** is dimeric in the solid state. Magnesium coordinates to two bromide atoms and one THF molecule. Interestingly, tris(trimethylsilyl)magnesium bromide was found to be monomeric and coordinated by two THF molecules.[12a] With the exception of trimethylsilylmagnesium bromide all other examples of silylmagnesium bromides feature considerably shorter Si−Mg bond distances than the analogous bissilylmagnesium compounds.

The Si−Mg−Si angles of the known bissilylmagnesium compounds range from 115.3° for $(Me_3Si)_2Mg{\cdot}TMEDA$[3] to 135.7° for $[(Me_3Si)_3Si]_2Mg{\cdot}2THF$.[25] With the exceptions of compounds **7**, **9**, and **13** the structures investigated in this study display Si−Mg−Si angles close to 130°. For the cyclic compound **13** (Figure 7) the Si−Mg−Si angle is constrained to 107.6°.

Conclusion

The synthesis of either bis(polysilanyl)magnesium compounds or (polysilanyl)magnesium bromides by metathesis reaction of (polysilanyl)potassium compounds with magnesium bromide was found to be very convenient and straightforward. In this way a number of adducts with different donor molecules (THF, TMEDA, 1,4-dioxane) were prepared. The use of silyldipotassium compounds gave magnesacyclosilanes, while a cyclic silyldipotassium compound led to the formation of a magnesabicyclosilane. Methylbis(trimethylsilyl)silylmagnesium compounds were found to be superior to the analogous potassium compounds in the reaction with zirconocene dichloride.

Also mixed alkyl/polysilanylmagnesium compounds were prepared by reaction of tris(trimethylsilyl)silylpotassium with either methyl- or phenylmagnesium bromide.

Several of the obtained polysilanylmagnesium compounds were characterized by single-crystal X-ray diffraction analysis.

Experimental Section

General Remarks. All reactions involving air-sensitive compounds were carried out under an atmosphere of dry nitrogen or argon using either Schlenk techniques or a glovebox. All solvents besides $CDCl_3$ were dried over sodium/potassium alloy under nitrogen and were freshly distilled prior to use. Potassium *tert*-butyl alcoholate was purchased exclusively from Merck. All other chemicals were bought from different suppliers and were used without further purification. ^{1}H (300 MHz), ^{13}C (75.4 MHz), and ^{29}Si (59.3 MHz) NMR spectra were recorded on Varian INOVA 300 or Bruker DRX 500 spectrometers. Samples for ^{29}Si spectra were either dissolved in a deuterated solvent or measured with a D_2O capillary in order to provide an external lock frequency signal. To compensate for the low isotopic abundance of ^{29}Si, the INEPT pulse sequence was used for the amplification of the signal.[26] Elementary analysis was carried out using a Heraeus Vario Elementar.

Tetrakis(trimethylsilyl)silane,[27] methyltris(trimethylsilyl)silane,[10a,18] phenyltris(trimethylsilyl)silane,[18,28] bis[tris(trimethylsilyl)silyl]dimethylsilane,[15] 1,2-bis[tris(trimethylsilyl)silyl]tetramethyldisilane,[29] 1,1,3,3-tetrakis(trimethylsilyl)hexamethylcyclopentasilane,[30] and magnesium bromide etherate[31] were prepared following known procedures.

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(26) (a) Morris, G. A.; Freeman, R. *J. Am. Chem. Soc*. **1979**, *101*, 760−762. (b) Helmer, B. J.; West, R. *Organometallics* **1982**, *1*, 877−879.

(27) Gilman, H.; Smith, C. L. *J. Organomet. Chem.* **1967**, *8*, 245−253.

(28) Gilman, H.; Atwell, W. H.; Sen, P. K.; Smith, C. L. *J. Organomet. Chem.* **1965**, *4*, 163−167.

(29) Whittaker, S. M.; Brun, M.-C.; Cervantes-Lee, F.; Pannell, K. H. *J. Organomet. Chem.* **1995**, *499*, 247−52.

Table 3. Crystallographic Data for Compounds 2a, 4, 6, 6a, 7, 9, and 13

	2a	**4**	**6**	**6a**	**7**	**9**	**13**
empirical formula	$MgSi_8NC_{24}H_{70}$	$MgSi_4O_2C_{23}H_{48}$	$MgSi_6O_2C_{22}H_{58}$	$MgSi_6O_4C_{22}H_{58}$	$Mg_2Br_2Si_6O_2C_{22}H_{58}$	$MgSi_6O_2C_{32}H_{62}$	$MgSi_8O_2C_{24}H_{64}$
M_w	635.85	493.28	547.53	579.53	731.66	671.67	633.78
temperature [K]	100(2)	158(2)	100(2)	100(2)	100(2)	100(2)	243(2)
size [mm]	0.75 × 0.25 × 0.08	0.21 × 0.07 × 0.05	0.55 × 0.34 × 0.15	0.32 × 0.28 × 0.22	0.42 × 0.28 × 0.20	0.55 × 0.45 × 0.38	0.59 × 0.29 × 0.16
cryst syst	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic	triclinic	orthorhombic
space group	*P*2(1)/*c*	*P*2(1)/*c*	*Pccn*	*Pccn*	*P*2(1)/*n*	$P\bar{1}$	*P*2(1)2(1)2(1)
a [Å]	13.682(3)	9.240(2)	10.020(2)	10.069(2)	8.043(2)	10.592(2)	13.009(3)
b [Å]	17.080(3)	14.820(4)	17.796(4)	18.334(4)	24.718(5)	11.069(2)	15.913(3)
c [Å]	18.966(4)	22.998(7)	19.966(4)	19.739(4)	10.042(7)	18.403(4)	20.961(4)
α [deg]	90	90	90	90	90	99.82(3)	90
β [deg]	106.36(3)	95.88(2)	90	90	97.01(3)	97.80(3)	90
γ [deg]	90	90	90	90	90	104.30(3)	90
V [Å^3]	4252.7(2)	3133(2)	3560(2)	3644(2)	1981(2)	2024(7)	4339(2)
Z	4	4	4	4	2	2	4
ρ_{calc} [g cm^{-3}]	0.993	1.046	1.022	1.056	1.226	1.102	0.970
abs coeff [mm^{-1}]	0.283	0.225	0.267	0.268	2.274	0.247	0.279
F(000)	1408	1080	1208	1272	758	732	1392
θ range [deg]	$2.03 < \theta < 22.50$	$1.64 < \theta < 23.26$	$2.04 < \theta < 26.40$	$2.06 < \theta < 20.00$	$1.65 < \theta < 25.00$	$1.14 < \theta < 23.00$	$1.61 < \theta < 20.81$
no. of reflns collected/unique	21 810/5432	12 383/4489	26 728/3663	14 977/1701	14 101/3495	12 204/5605	14 767/4524
completeness to *θ* [%]	97.4	99.6	100	99.8	100	99.4	99.9
no. of data/restraints/params	5432/0/340	4489/0/280	3663/0/148	1701/0/157	3495/0/161	5605/0/382	4524/0/332
goodness of fit on F^2	1.01	0.98	1.07	1.22	1.08	1.07	1.02
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.101, wR2 = 0.254	R1 = 0.057, wR2 = 0.120	R1 = 0.055, wR2 = 0.136	R1 = 0.100, wR2 = 0.217	R1 = 0.066, wR2 = 0.125	R1 = 0.099, wR2 = 0.275	R1 = 0.064, wR2 = 0.158
R indices (all data)	R1 = 0.151, wR2 = 0.290	R1 = 0.114, wR2 = 0.135	R1 = 0.085, wR2 = 0.146	R1 = 0.111, wR2 = 0.223	R1 = 0.096, wR2 = 0.135	R1 = 0.126, wR2 = 0.291	R1 = 0.078, wR2 = 0.170
largest diff peak/hole [e$^-$/Å^3]	0.07/−0.06	0.34/−0.25	0.53/−0.38	0.32/−0.35	0.70/−0.75	1.59/−0.64	0.33/−0.18

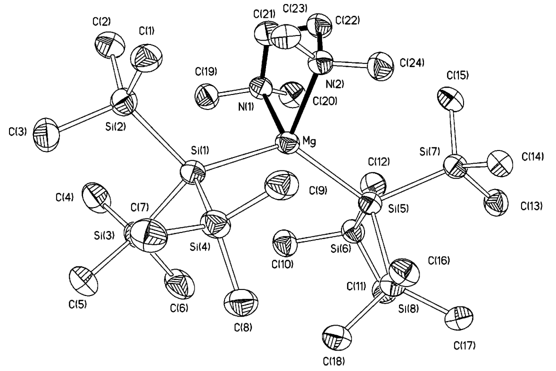

Figure 1. Molecular structure and numbering of **2a** with 30% probability thermal ellipsoids; all hydrogen atoms omitted for clarity. Selected bond lengths [Å] and bond angles [deg] with SE's: Mg−N(2) 2.243(7), Mg−N(1) 2.248(7), Mg−Si(1) 2.708(3), Mg−Si(5) 2.749(4), Si(1)−Si(4) 2.353(3), Si(1)−Si(2) 2.371(4), Si(1)−Si(3) 2.375(4), Si(2)−C(2) 1.891(9), Si(5)−Si(6) 2.359(4), Si(5)−Si(7) 2.365(3), Si(5)−Si(8) 2.369(3), N(2)−Mg−Si(1) 107.7(2), N(1)−Mg−Si(1) 106.44(19), N(2)−Mg−Si(5) 109.8(2), N(1)−Mg−Si(5) 109.3(2), Si(1)−Mg−Si(5) 130.89(11).

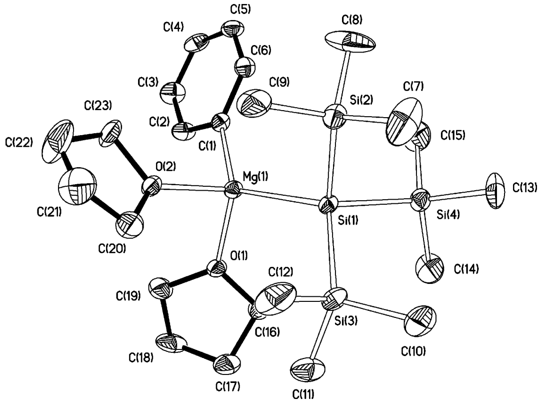

Figure 2. Molecular structure and numbering of **4** with 30% probability thermal ellipsoids; all hydrogen atoms omitted for clarity. Selected bond lengths [Å] and bond angles [deg] with SE's: Si(1)−Si(2) 2.3323(16), Si(1)−Si(4) 2.3359(16), Si(1)−Si(3) 2.3495(15), Si(1)−Mg(1) 2.6504(16), Si(2)−C(8) 1.846(5), Mg(1)−O(2) 2.051(3), Mg(1)−O(1) 2.059(3), Mg(1)−C(1) 2.150(4), Si(2)−Si(1)−Si(4) 103.79(6), Si(2)−Si(1)−Si(3) 104.28(6), Si(4)−Si(1)−Si(3) 105.87(6), Si(2)−Si(1)−Mg(1) 108.92(6), Si(4)−Si(1)−Mg(1) 113.81(6), Si(3)−Si(1)−Mg(1) 118.77(6), C(1)−Mg(1)−Si(1) 128.18(12), O(2)−Mg(1)−O(1) 95.41(12), O(2)−Mg(1)−C(1) 100.98(13), O(1)−Mg(1)−C(1) 108.45(14), O(2)−Mg(1)−Si(1) 110.13(9), O(1)−Mg(1)−Si(1) 108.62(9).

X-ray Structure Determination. For X-ray structure analyses the crystals were mounted onto the tip of glass fibers, and data collection was performed with Bruker-AXS SMART APEX and SMART 1000 CCD (**4**) diffractometers using graphite-monochromated Mo Kα radiation (0.71073 Å). The data were reduced to F_o^2 and corrected for absorption effects with SAINT[32] and SADABS[33] (except **4**), respectively. The structures were solved by direct methods and refined by full-matrix least-squares methods (SHELXL97).[34] If not noted otherwise all non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen

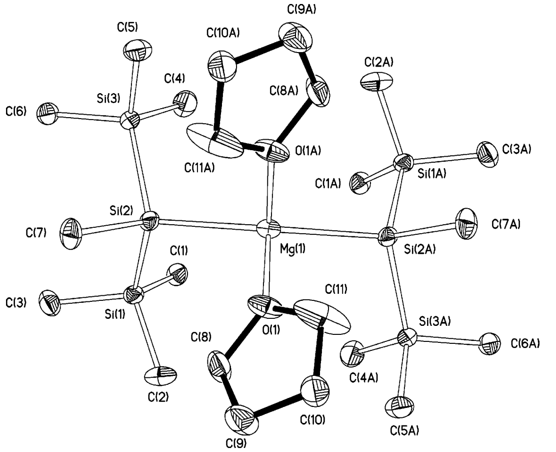

Figure 3. Molecular structure and numbering of **6** with 30% probability thermal ellipsoids; all hydrogen atoms omitted for clarity. Selected bond lengths [Å] and bond angles [deg] with SE's: Mg(1)−O(1) 2.053(2), Mg(1)−Si(2) 2.6378(10), Si(1)−C(2) 1.880(3), Si(1)−Si(2) 2.3340(11), Si(2)−Si(3) 2.3352(11), O(1)−Mg(1)−Si(2) 107.06(6), Si(2)#1−Mg(1)−Si(2) 133.94(6), Si(1)−Si(2)−Si(3) 107.81(4), C(7)−Si(2)−Mg(1) 114.51(11), Si(1)−Si(2)−Mg(1) 115.02(4), Si(3)−Si(2)−Mg(1) 112.92(4).

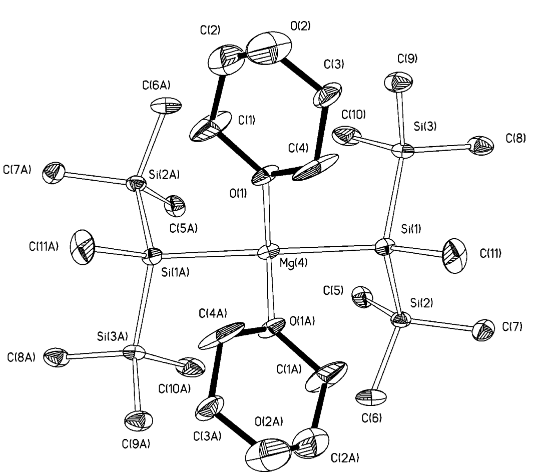

Figure 4. Molecular structure and numbering of **6a** with 30% probability thermal ellipsoids; all hydrogen atoms omitted for clarity. Selected bond lengths [Å] and bond angles [deg] with SE's: Mg(4)−O(1) 2.066(6), Mg(4)−Si(1) 2.646(3), Si(1)−Si(2) 2.337(4), Si(1)−Si(3) 2.340(4), O(1)#1−Mg(4)−O(1) 90.8(4), O(1)−Mg(4)−Si(1) 105.9(2), Si(1)−Mg(4)−Si(1)#1 134.1(2), Si(2)−Si(1)−Si(3) 106.47(14), C(11)−Si(1)−Mg(4) 113.7(4), Si(2)−Si(1)−Mg(4) 115.90(14), Si(3)−Si(1)−Mg(4) 112.24(13).

atoms were located in calculated positions to correspond to standard bond lengths and angles. Unfortunately, the obtained crystal quality of some substances was poor. This fact is reflected by quite high R and low θ values.

Crystallographic data (excluding structure factors) for the structures of compounds **2a**, **4**, **6**, **6a**, **7**, **9**, and **13** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-290184 (**2a**), CCDC-290187 (**4**), CCDC-290185 (**6**), CCDC-290778 (**6a**), CCDC-290777 (**7**), CCDC-290186 (**9**), and CCDC-290183 (**13**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

General Procedure. To a solution of the respective silane in THF was added potassium *tert*-butoxide (1.02 equiv). The solution

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(30) (a) Kayser, C.; Kickelbick, G.; Marschner, C. *Angew. Chem.* **2002**, *114*, 1031−1034; *Angew. Chem., Int. Ed.* **2002**, *41*, 989−992. (b) Blinka, T. A.; West, R. *Organometallics* **1986**, *5*, 128−33.

(31) Nützel, K. *Houben-Weyl, Methoden d. Org. Chem.* Müller, E., Ed.; Georg Thieme Verlag: Stuttgart, 1973; Vol. 13/2a, p 76.

(32) *SAINTPLUS: Software Reference Manual*, Version 6.45; Bruker-AXS: Madison, WI, 1997−2003.

(33) Blessing, R. H. *Acta Crystallogr. A* **1995**, *51*, 33−38; *SADABS*, Version 2.1; Bruker AXS: Madison, WI, 1998.

(34) Sheldrick, G. M. *SHELX97*, Programs for Crystal Structure Analysis (Release 97-2); Universität Göttingen: Göttingen (Germany), 1998.

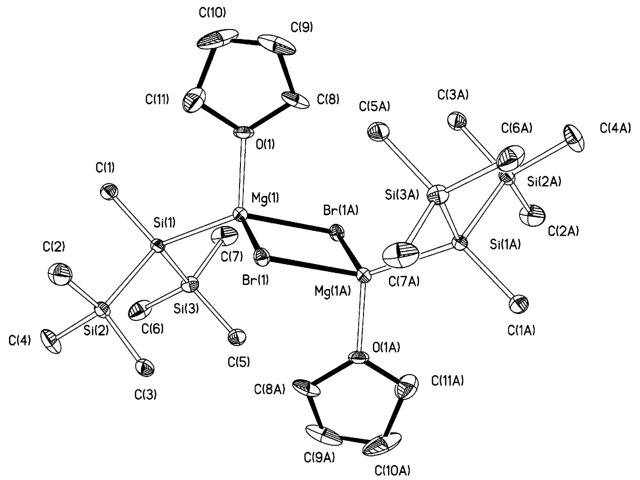

Figure 5. Molecular structure and numbering of **7** with 30% probability thermal ellipsoids; all hydrogen atoms omitted for clarity. Selected bond lengths [Å] and bond angles [deg] with SE's: Si(1)−Si(3) 2.331(2), Si(1)−Si(2) 2.338(2), Si(1)−Mg(1) 2.568(3), Mg(1)−O(1) 2.011(4), Mg(1)−Br(1) 2.592(2), Mg(1)−Mg(1)#1 3.532(4), Si(3)−Si(1)−Si(2) 108.50(10), Si(3)−Si(1)−Mg(1) 108.46(9), Si(2)−Si(1)−Mg(1) 111.08(9), O(1)−Mg(1)−Si(1) 116.62(16), O(1)−Mg(1)−Br(1) 98.35(15), Si(1)−Mg(1)−Br(1) 120.45(8), Br(1)#1−Mg(1)−Br(1) 93.61(7), Br(1)−Mg(1)−Mg(1)#1 46.53(5), Mg(1)#1−Br(1)−Mg(1) 86.39(7).

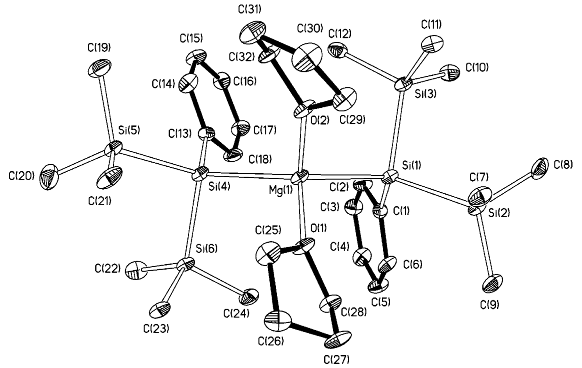

Figure 6. Molecular structure and numbering of **9** with 30% probability thermal ellipsoids; all hydrogen atoms omitted for clarity. Selected bond lengths [Å] and bond angles [deg] with SE's: Mg(1)−O(1) 2.050(5), Mg(1)−O(2) 2.059(5), Mg(1)−Si(1) 2.635(3), Mg(1)−Si(4) 2.656(3), Si(1)−Si(3) 2.349(3), Si(1)−Si(2) 2.358(3), Si(2)−C(9) 1.877(7), Si(4)−Si(6) 2.346(3), Si(4)−Si(5) 2.359(3), O(2)−Mg(1)−Si(1) 109.31(17), O(1)−Mg(1)−Si(4) 110.36(17), Si(1)−Mg(1)−Si(4) 120.17(10), Si(3)−Si(1)−Si(2) 104.44(10), Si(3)−Si(1)−Mg(1) 103.48(10), Si(2)−Si(1)−Mg(1) 116.44(10).

was stirred for 12 h and turned yellow or orange. The completeness of the conversion was verified by ^{29}Si NMR spectroscopy before the solvent was removed in a vacuum. The residue was dissolved in toluene, and $MgBr_2 \cdot Et_2O$ (0.51 equiv) was added. After stirring for 30 min the precipitated potassium bromide was removed by filtration and the solvent amount reduced in a vacuum. Crystallization was achieved by cooling to −70 °C.

Bis[tris(trimethylsilyl)silyl]magnesium·TMEDA (2a). **2a** was prepared according to the general procedure, but instead of THF a mixture of toluene and 3 equiv of tetramethylethylenediamine was used as solvent. Accordingly $MgBr_2 \cdot Et_2O$ was added after complete formation of the silylpotassium compound. Crystallization from pentane at −70 °C gave **2a** (87%) as colorless crystals (mp: 125−127 (dec) °C). ^{1}H NMR (C_6H_6, δ ppm): 2.11 (m, 4H); 2.07 (m, 9H); 0.45 (s, 27H). ^{13}C NMR (C_6D_6, δ ppm): 58.3; 56.0; 48.6; 45.9; 6.3. ^{29}Si NMR (C_6D_6, δ ppm): −7.5; −170.2. Anal. Calcd for $C_{24}H_{70}MgN_2Si_8$ (634.35): C 45.34, H 11.10, N 4.41. Found: C 45.00, H 10.94, N 4.27.

Tris(trimethylsilyl)silylmethylmagnesium·2THF (3). To a solution of tris(trimethylsilyl)silylpotassium in THF [generated from tetrakis(trimethylsilyl)silane (1.00 g, 3.12 mmol) and potassium *tert*-butoxide (0.360 g, 3.21 mmol)] was added methylmagnesium bromide (1.06 mL of a 3 M solution in ether, 3.18 mmol). Upon addition, the mixture decolorized and became gray and viscous. After 60 min the solvent was removed in a vacuum and the residue extracted with pentane. Colorless crystals (1.03 g, 2.39 mmol, 76%) were obtained at −30 °C. ^{1}H NMR (C_6D_6, δ ppm): 3.54 (m, 8H); 1.24 (m, 8H); 0.43 (s, 27H); −0.8 (s, 3H). ^{13}C NMR (C_6D_6, δ ppm): 68.7; 24.8; 5.1. ^{29}Si NMR (THF/D_2O, δ ppm): −6.2; −174.5. Anal. Calcd for $C_{18}H_{46}MgO_2Si_4$ (431.20): C 50.14, H 10.75. Found: C 50.11, H 10.63.

Tris((trimethylsilyl)silyl)phenylmagnesium·2THF (4). The reaction was carried out analogously to the synthesis of **3** with phenylmagnesium chloride (1.60 mL of a 2 M solution in THF, 3.20 mmol). From the pentane extract colorless crystals were grown (1.18 g, 2.40 mmol, 77%). ^{1}H NMR (C_6D_6, δ ppm): 7.90 (bs, 2H); 7.45 (m, 2H), 7.32 (m, 1H), 3.54 (m, 8H); 1.18 (m, 8H); 0.46 (s, 27H). ^{13}C NMR (THF/D_2O, δ ppm): 166.5; 140.0; 125.6; 71.7; 31.6; 5.0. ^{29}Si NMR (THF/D_2O, δ ppm): −6.5; −174.2. Anal. Calcd for $C_{23}H_{48}MgO_2Si_4$ (493.27): C 56.00, H 9.81. Found: C 55.62, H 10.02.

Bis[methylbis(trimethylsilyl)silyl]magnesium·2THF (6). Starting material was methyltris(trimethylsilyl)silane, and the reaction was carried out according to the general procedure. At cooling to −70 °C colorless crystals (57%) were obtained (mp: 113−115 °C). ^{1}H NMR (C_6D_6, δ ppm): 3.64 (m, 8H); 1.30 (m, 8H); 0.40 (s, 36H); 0.37 (s, 6H). ^{13}C NMR (C_6D_6, δ ppm): 69.6; 25.0; 2.6; 2.2. ^{29}Si NMR (C_6D_6, δ ppm): −9.1; −116.9. Anal. Calcd for $C_{22}H_{58}MgO_2Si_6$ (547.51): C 48.26, H 10.68. Found: C 47.92, H 10.45.

Bis[methylbis(trimethylsilyl)silyl]magnesium·2(1,4-dioxane) (6a). The same procedure as for compound **6** except for the addition of $MgBr_2 \cdot Et_2O$ was carried out in 1,4-dioxane. Colorless crystals (65%) were obtained (mp: 60−63 °C). ^{1}H NMR (C_6D_6, δ ppm): 3.40 (s, 16H); 0.36 (s, 36H); 0.26 (s, 6H). ^{13}C NMR (C_6D_6, δ ppm): 67.2, 2.6, −3.9. ^{29}Si NMR (1,4-dioxane/D_2O, δ ppm): −9.2; −117.3. Anal. Calcd for $C_{22}H_{58}MgO_4Si_6$ (579.51): C 45.60, H 10.09. Found: C 45.85, H 10.39.

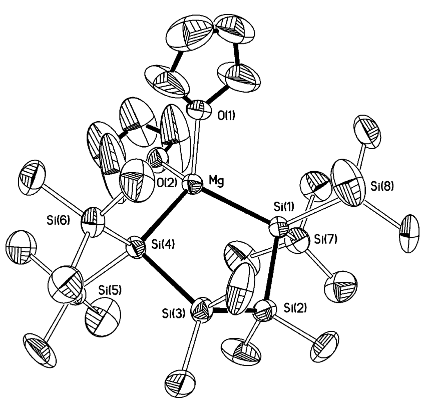

Figure 7. Molecular structure and numbering of **13** with 30% probability thermal ellipsoids; all hydrogen atoms omitted for clarity. Selected bond lengths [Å] and bond angles [deg] with SE's: Mg−O(1) 2.063(5), Mg−O(2) 2.137(5), Mg−Si(1) 2.646(3), Mg−Si(4) 2.713(3), Si(1)−Si(8) 2.326(3), Si(1)−Si(7) 2.368(3), Si(1)−Si(2) 2.442(3), Si(2)−C(1) 1.869(10), Si(2)−Si(3) 2.350(3), Si(3)−Si(4) 2.393(3), Si(4)−Si(5) 2.334(3), Si(4)−Si(6) 2.361(3), O(1)−Mg−O(2) 90.3(2), O(1)−Mg−Si(1) 113.28(19), O(1)−Mg−Si(4) 114.56(18), Si(1)−Mg−Si(4) 107.58(9), Si(8)−Si(1)−Si(7) 105.18(12), Si(8)−Si(1)−Si(2) 107.73(12), Si(7)−Si(1)−Si(2) 106.53(11), Si(8)−Si(1)−Mg 118.07(11), Si(7)−Si(1)−Mg 118.61(11), Si(2)−Si(1)−Mg 99.62(10).

Methylbis(trimethylsilyl)silylmagnesium Bromide·THF (7). The general procedure was followed starting with methyltris(trimethylsilyl)silane, but in this case 2.02 equiv of $MgBr_2 \cdot Et_2O$ was added. Colorless crystals (78%) (mp: 105−108 °C). ^1H NMR (C_6D_6, δ ppm): 3.86 (m, 8H); 1.24 (m, 8H); 0.44 (s, 18H); 0.16 (s, 3H). ^{13}C NMR (C_6D_6, δ ppm): 70.7, 24.8, 2.1, 0.5. ^{29}Si NMR (C_6D_6, δ ppm): −9.5; −109.2. Anal. Calcd for $C_{22}H_{58}Br_2Mg_2O_2Si_6$ (731.63): C 36.12, H 7.99. Found: C 35.95, H 7.87.

Bis[phenylbis(trimethylsilyl)silyl]magnesium·2THF (9). The reaction was done according to the general procedure with tris(trimethylsilyl)phenylsilane as starting material. By cooling to −70 °C colorless crystals (87%) were obtained. ^1H NMR (C_6H_6/D_2O, δ ppm): 7.63 (m, 4H); 7.21(m, 4H); 7.18 (m, 2H); 3.53 (m, 8H); 1.45 (m, 8H); 0.34 (s, 36H). ^{13}C NMR (C_6H_6/D_2O, δ ppm): 145.7; 137.6; 127.1; 67.8; 25.6; 3.3. ^{29}Si NMR (C_6H_6/D_2O, δ ppm): −10.8; −92.5. Anal. Calcd for $C_{32}H_{62}MgO_2Si_6$ (671.65): C 57.22, H 9.30. Found: C 56.93, H 9.49.

2,2,4,4-Tetrakis(trimethylsilyl)-3,3-dimethymagnesacyclotratrasilane·2THF (12). Starting from 1,1,1,3,3,3-hexakis(trimethylsilyl)-2,2-dimethyltrisilane and 18-crown-6 (2.1 equiv) the general procedure was followed. Colorless crystals (72%). ^1H NMR (C_6D_6, δ ppm): 3.48 (m, 8H); 1.59 (m, 8H); 0.43 (s, 6H); 0.09 (s, 36H). ^{13}C NMR (C_6D_6, δ ppm): 65.5; 20.8; 15.0; 5.7. ^{29}Si NMR (C_6D_6, δ ppm): −6.9; −25.4; −137.3. Anal. Calcd for $C_{22}H_{58}MgO_2Si_7$ (575.60): C 45.91, H 10.16. Found: C 45.85, H 10.16.

2,2,5,5-Tetrakis(trimethylsilyl)-3,3,4,4,-tetramethyl-magnesacyclopentasilane·2THF (13). Starting from 1,1,1,4,4,4-hexakis(trimethylsilyl)-2,2,3,3-tetramethylpentasilane and 18-crown-6 (2.1 equiv) the general procedure was followed. Colorless crystals (83%). ^1H NMR (C_6H_6/D_2O, δ ppm): 3.79 (m, 8H); 1.95 (m, 8H); 0.38 (s, 12H); 0.31 (s, 36H). ^{13}C NMR (C_6H_6/D_2O, δ ppm): 67.7; 25.8; 5.9; 0.3. ^{29}Si NMR (C_6H_6/D_2O, δ ppm): −5.4; −27.1; −176.6. Anal. Calcd for $C_{24}H_{64}MgO_2Si_8$ (633.75): C 45.48, H 10.18. Found: C 44.97, H 10.27.

6-Magnesa-1,4-bis(trimethylsilyl)hexamethylbicyclo[2.1.1]-hexasilane·2THF (17). Starting from 1,1,4,4-tetrakis(trimethylsilyl)-2,2,3,3,5,5-hexamethylcyclopentasilane and 18-crown-6 (2.1 equiv) the general procedure was followed. The addition of $MgBr_2 \cdot Et_2O$ was carried out at −36 °C, and the reaction mixture was allowed to warm slowly to rt. Colorless crystals (68%). ^1H NMR (C_6D_6, δ ppm): 3.53 (m, 8H); 1.48 (m, 8H); 0.98 (s, 3H); 0.70 (s, 3H); 0.63 (s, 6H); 0.60 (s, 6H); 0.44 (s, 18H). ^{13}C NMR (C_6D_6, δ ppm): 67.6; 25.7; 8.8; 8.1; 6.7; 2.6; 1.9. ^{29}Si NMR (C_6D_6, δ ppm): −5.0; −9.0; −23.5; −156.6. Anal. Calcd for $C_{20}H_{52}MgO_2Si_7$ (545.53): C 44.03, H 9.61. Found: C 44.06, H 9.81.

6-Magnesa-1,4-bis(trimethylsilyl)hexamethylbicyclo[2.1.1]-hexasilane (17a). The coordinated THF can be removed by treating **17** under reduced pressure. ^1H NMR (C_6D_6, δ ppm): 1.11 (s, 3H); 0.93 (s, 3H); 0.75 (s, 6H); 0.53 (s, 6H); 0.46 (s, 18H). ^{13}C NMR (C_6D_6, δ ppm): 6.9; 6.6; 6.1; 3.7; 3.5. ^{29}Si NMR (C_6D_6, δ ppm): −6.0; −13.5; −26.2; −148.1. Anal. Calcd for $C_{12}H_{36}MgSi_7$ (401.32): C 35.91, H 9.04. Found: C 35.82, H 9.21.

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Supporting Information Available: Crystallographic data for **2a**, **4**, **6**, **6a**, **7**, **9**, and **13** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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