Silicon Compounds

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Synthesis, Isolation, and Characterization of 1,1-DiGrignard and 1,1-Dizincio Silanes**

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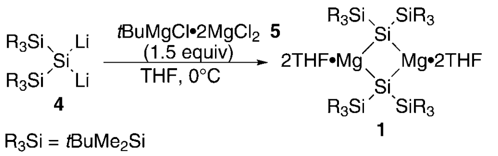
Geminal dimetallosilanes have already proved their great potential for the synthesis of novel silicon compounds.[1] However, the variety and number of isolated geminal dimetallosilanes is very small.[1–3] For example, all known geminal dimetallosilanes are alkali metal or mercury derivatives.[2] Furthermore, only one example of a geminal dimetallosilane with two different metals, that is, a mercury bridged bis(silyllithium) species, was reported recently by our research group.[1b,3] This contrasts with the large variety of available geminal dimetallorganic reagents, which are very useful synthons in organic synthesis.[4] In particular, diGrignard reagents and dizinc reagents are widely used in organic chemistry.[5] In contrast, silicon analogues, (i.e. geminal diGrignard or dizincio silanes) are yet to be reported. The vast synthetic potential of such reagents remains to be explored.

Herein we report the synthesis, isolation, and X-ray molecular structure of the first cyclic 1,1-dimagnesiosilane **1**, the first diGrignard silane 1,1-di(chloromagnesio)silane **2**, and the analogous 1,1-di(chlorozincio)silane **3**. We also report the selective redox reactions of **1** with *t*Bu$_2$MeSiLi and with 1,1-dilithiosilane **4**,[2a,6] thus leading to novel metallosilane species.

We initially believed that geminal dimetallosilanes could be prepared by a transmetalation reaction of dilithiosilane derivatives with metal salts such as MgX$_2$ or ZnX$_2$, in analogy to the synthesis of metallosilanes.[7] However, transmetalation reactions with strong electron donors often involve redox processes that lead to nonselective reactions.[8] This is the case also with (*t*BuMe$_2$Si)$_2$SiLi$_2$ (**4**). Thus, reaction of **4** with MX$_2$ (MX$_2$ = MgCl$_2$, MgBr$_2$ ZnCl$_2$, HgCl$_2$, HgF$_2$), leads to a complex mixture of products and a metallic M^0 residue.[9]

In contrast, mixing 1,1-dilithiosilane **4** with 1.5 equivalents of *t*BuMgCl·2 MgCl$_2$ (**5**) in THF[10] at 0 °C gave, after stirring for 30 minutes, cyclic 1,1-dimagnesiosilane **1** [Eq. (1); THF = tetrahydrofuran]. Tetrahydrofuran was replaced by *n*-hexane and the *n*-hexane solution was separated from the insoluble residue.[11] Compound **1** was isolated in 70 % yield by crystallization from *n*-hexane at room temperature and its molecular structure was determined by X-ray crystallography (Figure 1).[12]



(1)

Compound **1** has a planar four-membered ring (Si1-Mg1-Si2-Mg2 0.0(7)°) constructed from two Mg and two Si atoms. Each of the Mg atoms is bonded to two THF molecules. The planar Mg$_2$Si$_2$ ring has a rhombus shape with nearly tetrahedral angles around the Mg atoms (Si1-Mg1-Si2 104.32(7)°) and acute Mg1-Si1-Mg2 and Mg2-Si2-Mg1 angles (75.69(11)°

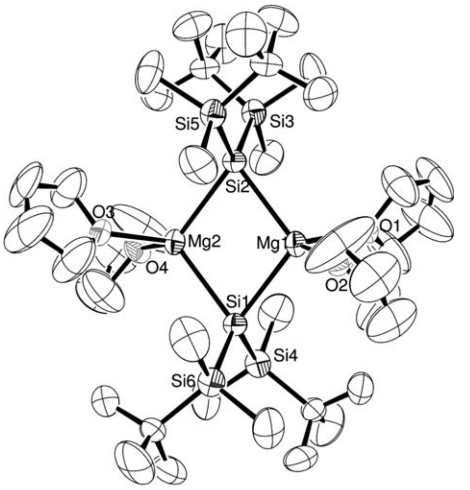


Figure 1. Molecular structure of **1** (ORTEP drawing). Hydrogen atoms were omitted for clarity and the thermal ellipsoids are set at the 40% probability level. Selected bond lengths [Å], bond angles and dihedral angles [°]: Si1–Mg1 2.668(3), Si1-Mg2 2.668(3), Si2–Mg1 2.668(3), Si2–Mg2 2.668(3), Mg2–O1 2.091(4), Mg2–O2 2.096(4), Mg1–O3 2.091(4), Mg1–O4 2.096(4), Mg1–Mg2 3.273(3), Si1–Si3 2.335(2), Si1–Si4 2.335(2), Si2–Si5 2.334(2), Si2–Si6 2.334(2); Si1-Mg1-Si2 104.32(7), Mg1-Si2-Mg2 75.69(11), Si2-Mg2-Si1 104.32(7), Mg2-Si1-Mg1 75.67(11), Si4-Si1-Si6 114.94(14), Si3-Si2-Si5 116.09(14), Si1-Mg1-Si2-Mg2 0.0(7), Mg2-Si1-Si2-Si5 90.4(7), Mg2-Si1-Si2-Si6 −89.6(7), Mg1-Si2-Si1-Si3 92.1(9), Mg1-Si2-Si1-Si4 −87.9(9).

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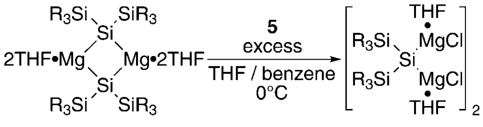
and 75.67(11)°, respectively). The Si–Mg bond lengths in **1** (2.668(3) Å) are close to those in cyclic monomagnesiosilanes (Si–Mg 2.679 Å).[7b] The *exo* cyclic Si4-Si1-Si6 and Si3-Si2-Si5 bond angles are nearly tetrahedral as well (114.94(14)° and 116.09(14)°, respectively).

The reaction of dilithiosilane **4** with an excess amount of **5** or of $MgCl_2$ in THF, led to a complex mixture of products.[9] In contrast, the reaction of **1** with an excess amount of **5** in a 1:1 mixture of THF/benzene gave the desired bisGrignard reagent, $(t\text{BuMe}_2\text{Si})_2\text{Si(MgCl)}_2$ (**2**) in 95% yield [Eq. (2)]. Compound **2** was crystallized from *n*-hexane and its structure was determined by X-ray crystallography (Figure 2).[13] Both **1** and **2** are the first bisGrignard-type silane reagents to be synthesized, isolated, and characterized.



(2)

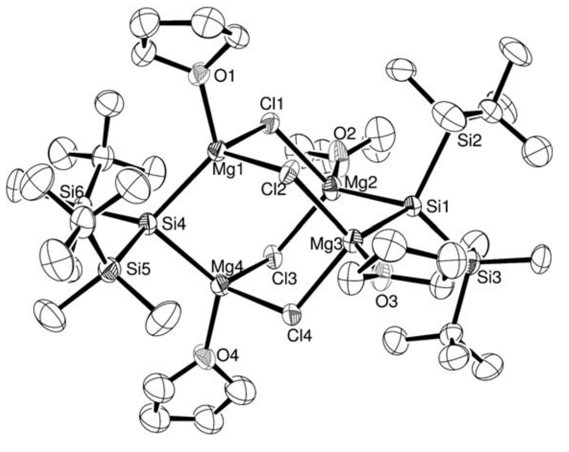
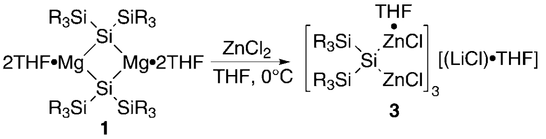


Figure 2. Molecular structure of **2** (ORTEP drawing). Hydrogen atoms were omitted for clarity and the thermal ellipsoids are set at the 40% probability level. Selected bond lengths [Å], bond angles and dihedral angles [°]: Si1–Mg2 2.569(2), Si1–Mg3 2.549(2), Si4–Mg1 2.549(2), Si4–Mg4 2.569(2), Mg2–Cl1 2.438(2), Mg2–Cl3 2.459(2), Mg3–Cl2 2.450(2), Mg3–Cl4 2.431(2), Mg1–Cl2 2.450(2), Mg1–Cl1 2.431(2), Mg4–Cl4 2.438(2), Mg4–Cl3 2.459(2), Si1–Si2 2.339(2), Si1–Si3 2.341(2), Si4–Si5 2.339(2), Si4–Si6 2.341(2); Si2-Si1-Si3 109.91(6), Si5-Si4-Si6 109.91(6), Mg1-Si4-Mg4 91.23(5), Mg2-Si1-Mg3 91.23(5), Cl1-Mg2-Cl3 99.93(6), Cl4-Mg3-Cl2 102.24(6), Cl1-Mg1-Cl2 102.24(6), Cl4-Mg4-Cl3 99.93(6), Mg1-Si4-Si1-Mg2 −91.73(6), Mg1-Si4-Si1-Mg3 93.6(5), Mg4-Si4-Si1-Mg2 82.94(5).

In the solid state **2** is a dimer of two $(t\text{BuMe}_2\text{Si})_2\text{Si(MgCl)}_2$ units that form an adamantane-type skeleton, in which each Cl atom bridges two Mg atoms. Each of the Mg atoms is bonded to a THF molecule. The average Si–Mg bond length in **2** (2.559(18) Å) is 0.1 Å shorter than in **1**. A similar trend is found in the comparison between $((\text{Me}_3\text{Si})_3\text{Si})_2\text{Mg}$ and $\text{Me}(\text{Me}_3\text{Si})_2\text{SiMgBr}$ (Si–Mg 2.725 Å vs. 2.568 Å, respectively).[7b]

Transmetalation of **1** with $ZnCl_2$ in THF at 0 °C gave 1,1-di(chlorozincio)silane (**3**; complexed with LiCl·THF), which was isolated in 90% yield by crystallization from *n*-hexane at room temperature [Eq. (3)],[14] and its molecular structure was determined by X-ray crystallography.[15]

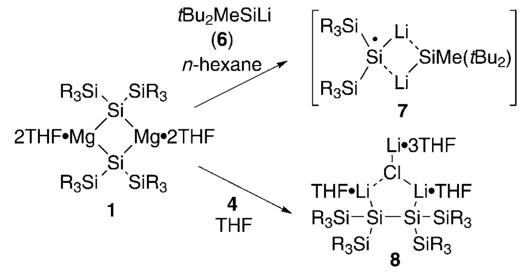


(3)

We suggest that the main reason for the more selective transmetalation reactions of 1,1-dimagnesiosilane **1** compared with 1,1-dilithiosilane **4** is its lower reductive ability, owing to the fact that the Si–Mg bond in **1** is less polarized than the Si–Li bond in **4**, thus making **1** a weaker electron donor compared with **4**. This suggestion is supported by the ^{29}Si NMR chemical shifts of the silicon atoms bonded to the metal. In cyclic dimagnesiosilane **1** Si1 and Si2 absorb at $\delta = -200$ ppm, and are deshielded by $\delta = 54$ ppm compared with **4** ($\delta = -254$ ppm[6]), thus indicating a lower negative charge on these silicon atoms in **1** compared with **4**. Also, in bisGrignard **2** the ^{29}Si signal ($\delta = -226$ ppm) is deshielded by $\delta = 26$ ppm compared with that of **1**.[16] In 1,1-dizinciosilane **3** the ^{29}Si signal of the metal-bonded Si atom appears at $\delta = -184$ ppm, and is deshielded by $\delta = 70$ ppm compared with 1,1-dilithiosilane **4** and by $\delta = 42$ ppm compared with the 1,1-dimagnesiosilane **2**. This trend in ^{29}Si chemical shifts is consistent with the metal's Pauling electronegativities; Zn (1.65) > Mg (1.31) > Li (0.98).[17] The same trend in ^{29}Si chemical shifts exists between $(\text{Me}_3\text{Si})_3\text{SiLi}$ (−189.4 ppm[18]) compared with $(\text{Me}_3\text{Si})_3\text{SiMgBr}$ (−168.7 ppm[7a]).[19]

Activation of R_2Mg by ate-complexation with RM (M=Li, Na, K) leads to interesting new properties of this reagent.[20,5e–f] Therefore, the reaction of **1** with RM (M = Li, Na, K) is of interest.

Reaction of **1** with $t\text{Bu}_2\text{MeSiLi}$ (**6**) in *n*-hexane produced a persistent lithium-substituted silyl radical $\text{Li}(t\text{BuMe}_2\text{Si})_2\text{Si}^{\bullet}$ that coaggregated with **6** and formed **7**, which was characterized by EPR spectroscopy (Scheme 1).[21] Reaction of **1** with $(t\text{BuMe}_2\text{Si})_2\text{SiLi}_2$ (**4**) in THF yielded the vicinal 1,2-dilithiosilane **8**[22] coaggregated with LiCl[14] (60% yield; Scheme 1). Compound **8** was isolated by crystallization form *n*-hexane and was characterized by X-ray crystallography.[23] We suggest that **8** may be formed by the coupling of two intermediate $\text{Li}(t\text{BuMe}_2\text{Si})_2\text{Si}^{\bullet}$ radicals.



Scheme 1. Reaction of 1,1-dimagnesiosilane (**1**) with $t\text{Bu}_2\text{MeSiLi}$ and 1,1-dilithiosilane, respectively.

In summary, by using transmetalation reactions the first cyclic 1,1-dimagnesiosilane **1** and diGrignard-type 1,1-di(chloromagnesio)silane **2** as well as the first 1,1-

di(chlorozincio)silane **3** were synthesized, isolated, and characterized by X-ray crystallography. Compound **1** is more selective than 1,1-dilithiosilane **4** in transmetalation reactions. We continue to study the chemistry of these novel dimetallosilane reagents, which have the potential to open new synthetic possibilities towards novel and interesting silicon compounds.

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Keywords: dianions · Grignard reagents · radicals · silicon · transmetalation

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[6] a) The synthesis and X-ray crystal structure of **4** is given in the Supporting Information. CCDC 773218 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif; b) A related 1,1-dilithiosilane was reported previously, see Ref. [2c].

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[8] For a review, see: D. Seyferth, *Organometallics* **2009**, *28*, 2–33.

[9] For more details, see the Supporting Information.

[10] Compound **5** is soluble in THF and probably serves as a source of soluble "activated" $MgCl_2$. For the synthesis and isolation of **5**, see the Supporting Information; for the X-ray structure of **5**, see: S. Sakamoto, T. Imamoto, K. Yamaguchi, *Org. Lett.* **2001**, *3*, 1793–1795.

[11] For experimental details of the preparation of **1**, see the Supporting Information.

[12] Crystallographic data for **1**: $C_{40}H_{92}Mg_2O_4Si_6$, $Mr=854.30$, monoclinic, space group $C\ 2/c$, $a=19.455(4)$, $b=14.477(3)$, $c=20.764(4)$ Å, $\beta=109.39(3)°$, $V=5399.9(19)$ Å^3, $Z=4$, Nonius appa CCD, Mo_{Ka} radiation (0.71073 Å), 240 K, $2\Theta_{max}=25°$, $R=0.0687$ ($I>2\sigma I$), $wR2=0.1942$ ($I>2\sigma I$), $Rw=0.1538$ (all data), GOF = 0.785. CCDC 773214 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[13] Crystallographic data for **2**: $C_{40}H_{92}Cl_4Mg_4O_4Si_6$, $Mr=1044.72$, monoclinic, space group $C\ 2/c$, $a=30.776(6)$, $b=11.059(2)$, $c=20.051(4)$ Å, $\beta=114.51(3)°$, $V=6209(2)$ Å^3, $Z=8$, Nonius Kappa CCD, Mo_{Ka} radiation (0.71073 Å), 240 K, $2\Theta_{max}=25°$, $R=0.0627$ ($I>2\sigma I$), $wR2=0.1803$ ($I>2\sigma I$), $Rw=0.1016$ (all data), GOF = 1.223. CCDC 773215 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[14] LiCl is a by-product in the reaction of **4** with **5** [Eq. (1)], which probably can not be fully separated from **1**. As a result, LiCl is present in the reactions (shown in [Eq. (3)] and in Scheme 1) and it crystallizes with the products, **3** and **8**, respectively.

[15] The synthesis and X-ray crystal structure of **3** is given in the Supporting Information. CCDC 773216 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[16] The difference in the ^{29}Si chemical shifts between **1** and **2** results from the cyclic structure of **1**. Similar behavior was observed for other cyclic magnesiosilanes.[7b]

[17] *Handbook of Chemistry and Physics*, 90th ed. (Ed.: D. R. Lide), CRC, Boca Raton, **2009–2010**.

[18] G. Korogodsky, M. Bendikov, D. Bravo-Zhivotovskii, Y. Apeloig, *Organometallics* **2002**, *21*, 3157–3161.

[19] The ^{29}Si chemical shift of $(Me_3Si)_3SiZnCl$ was not reported.

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[21] The EPR spectrum of **7** is reported in the Supporting Information.

[22] The preparation of compound **8** (without complexing LiCl·3THF) was reported previously, see: M. Kira, T. Iwamoto, D. Z. Yin, T. Maruyama, H. Sakurai, *Chem. Lett.* **2001**, 910–911, however, its X-ray structure was not reported.

[23] The synthesis and X-ray crystal structure of **8** is given in the Supporting Information. CCDC 773217 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.