

THE SYNTHESIS OF FOUR-MEMBERED SPIRO COMPOUNDS OF SILICON AND GERMANIUM: 2,2,6,6-TETRAMETHYL-4-METALLASPIRO[3.3]HEPTANES

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Summary

The reaction of the 1,3-di-Grignard reagent 1,3-bis(bromomagnesio)-2,2-dimethylpropane (**2**) with silicon or germanium tetrachloride gave the 2,2,6,6-tetramethyl-4-metallasp[3.3]heptanes (**1**) in 15% (Si) and 48% (Ge) isolated yield, respectively. The spectroscopic properties of **1** are briefly discussed.

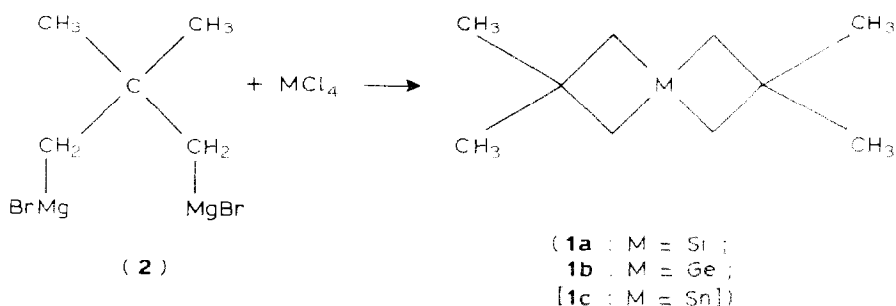
Introduction

Examples of spiro compounds which contain a Group 14 metal as spiro atom in a four-membered ring are scarce [1,2]. Several 4-silaspiro[3.3]heptanes are known [1,3–6], their synthesis usually involving formation of the second silacyclobutane ring from a dihalo precursor under Barbier-type conditions. Even less is known about germaspiroalkanes; the smallest representatives contain two five-membered rings or the combination of a four- and five-membered ring [2,7,8].

After the successful application of the 1,3-di-Grignard route to the synthesis of monocyclic metallacyclobutanes [9–15], it seemed of interest to explore the extension of this approach to the synthesis of metallasp[3.3]heptanes **1**.

Results and discussion

We chose the substituted 1,3-di-Grignard reagent **2** [11,14] for the preparation of the 2,2,6,6-tetramethyl-4-metallasp[3.3]heptanes **1a** (M = Si) and **1b** (M = Ge). The reactions were performed in a straightforward fashion by addition at room temperature of two molar equivalents of **2** in diethyl ether to one molar equivalent of silicon tetrachloride (in n-pentane) or germanium tetrachloride (in benzene), respectively (Scheme 1). A white precipitate of magnesium chloride bromide formed, and after stirring for 15 or 1 h, respectively, the mixture was quenched with water and worked up in the usual way. Compound **1a** was formed in ca. 50% and **1b** in ca.

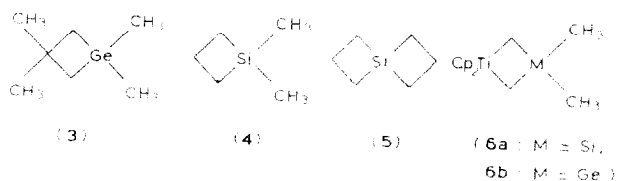


SCHEME 1

80% yield (GLC); preparative gas chromatography yielded pure **1a** (15%) and **1b** (48%).

Several attempts to synthesize the tin analogue **1c** were unsuccessful. According to GC/MS, the product mixture contained many unidentified products; ^1H NMR and mass spectroscopy yielded no indication of the presence of **1c**. This is not surprising in view of the inherent instability of stannacyclobutanes [10,13]. In general the trend observed here for the spiro series, i.e. an optimum in the ease of formation of four-membered rings for germanium, completely parallels our earlier observations for monocyclic analogues [12]; in both cases, it can be attributed to the operation of two opposing trends in the sequence Si-Ge-Sn: the higher reactivity of the metal-chlorine bond and the higher polarizability of the metal favour the closure of four-membered rings, while the increasing ring strain due to the longer metal-carbon bonds acts in the opposite direction.

Compounds **1a** and **1b** are new and were characterized spectroscopically (see Table 1 and Experimental).



Examination of the NMR data in Table 1 reveals some interesting trends. The shielding effect of the four methyl groups in **1a** on $\delta(^{29}\text{Si})$ (10.7 ppm) compared to the unsubstituted parent compound **5** (δ 37.2 ppm) is noteworthy. Similar effects in silacyclobutanes have been accounted for [6] on the assumption that electron-donating groups at C(3) polarize the electrons on silicon towards the nucleus owing to antibonding interactions between C(3) and Si. However, alternative explanations such as an anisotropic shielding by methyl groups cannot be excluded.

In contrast to the ^{29}Si chemical shifts, those of ^1H and ^{13}C show only small variations between monocyclic and spirocyclic four-membered ring systems. Nevertheless, some trends are apparent from the limited experimental material. Comparison of **4** with **5** and **1a** (unfortunately, the 3,3-dimethyl derivative of **4** is unknown) in the silicon series, and of **3** and **1b** in the germanium series reveal that the spiro

TABLE 1

NMR SPECTRAL DATA FOR SOME MONO- AND SPIRO-CYCLIC METALLACYCLOBUTANES OF SILICON AND GERMANIUM (in CDCl₃)

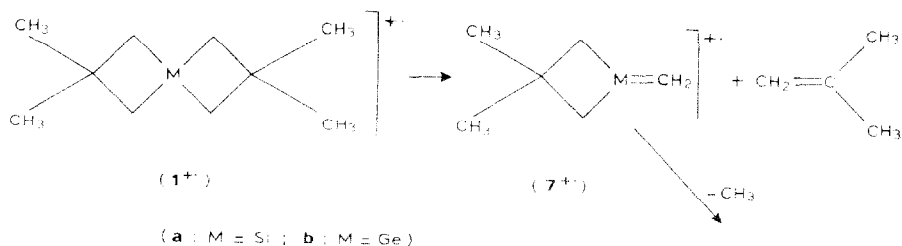
Compound	¹ H ^a			¹³ C ^b				²⁹ Si ^c
	δ(CH ₂)	δ(CCH ₃)	δ(MCH ₃)	δ(CH ₂)	δ(CCH ₃)	δ(M-CH ₃)	δ(C-quart) ^d	
1a	1.18	1.15	–	32.1 [t; 129]	34.2 [q quint; [124.5, 4.6]	–	35.6	10.7 ^e
1b	1.70	1.14	–	38.2 [t; 133]	33.6 [q quint; 124.5, 4.6]	–	38.0	
3 ^f	1.35	1.13	0.46	34.1 [tm; 131]	34.3 [q quint; 128, 5]	1.0	36.8	–
4 ^g	1.06	–	0.26	14.8 [–] ^h	–	–	–	18.4
5 ^g	1.25	–	–	18.3 [–] ^h	–	–	–	37.2
6a ⁱ	2.52	–	0.13	70.6 [t; 130]	–	1.0	–	–76.0
6b ⁱ	2.75	–	0.26	71.5 [t; 134]	–	–0.2	–	–

^a 90 MHz; δ in ppm; all signals were singlets. ^b 62.89 MHz; δ in ppm; [multiplicity; *J*(CH) in Hz]. ^c 49.63 MHz; δ in ppm. ^d All signals were singlets. ^e Nonet; ²*J*(SiH) 5.9 Hz. ^f From Ref. 12. ^g From Ref. 6. ^h Data not available. ⁱ From Ref. 15; C₆D₆.

compounds have slightly deshielded α-CH₂ groups. Similarly, both ¹H and ¹³C nuclei of the α-CH₂ groups of the germanium compounds **1b**, **3** and **6b** are deshielded in comparison with their silicon analogues **1a**, **4** (two C-methyl groups missing, vide supra) and **6a** in line with general experience. Consistently, the ¹*J*(CH) couplings of the α-CH₂ groups are larger for the germanium compounds, which is indicative of higher *s*-character in the CH bonds and thus of a larger H–C–H angle.

Two factors may be responsible. In the first place, the degree of puckering in the germacyclobutanes may be higher than in silacyclobutanes, which leads to a reduction of the endocyclic angles. Silacyclobutanes are puckered [1,4], but the structures of germacyclobutanes are not known, though they are expected to be more puckered because the longer germanium–carbon bonds will lead to reduction of unfavourable 1,3 interactions across the ring. Secondly, carbon is expected to employ more *s*-character in its bond to germanium than to silicon. Given the constant sum of one *s* and three *p* orbitals participating in the four carbon hybrid orbitals, this will lead to a reduction of the endocyclic valence angle at the α-carbon [16].

An interesting feature in the mass spectra of **1a** and **1b** is the appearance of a relatively abundant fragment ion [*M*–C₄H₈]⁺. In view of the well-established cleavage of silacyclobutanes under electron impact conditions into silaethenes and ethylene [17], we suggest an analogous cleavage of **1a** and **1b** to isobutene and the 1-methylenemetallacyclobutanes **7a** and **7b**, respectively (Scheme 2). It should be pointed out that in contrast to observations on the monocyclic silacyclobutanes [17],



SCHEME 2

the $[M-C_4H_8]^+$ ions do not form the base peak; further fragmentation is evident, in particular the loss of an additional methyl group.

Experimental

All reactions were performed under dry nitrogen in a three-necked flask equipped with a magnetic stirrer. Solvents were distilled from sodium-potassium alloy. The metal tetrachlorides were distilled before use. The 1,3-di-Grignard reagent **2** was prepared as described previously [11].

The NMR spectra were recorded on a Bruker WH-90 (1H) or WM-250 spectrometer (^{13}C , ^{29}Si), respectively. Mass spectra were recorded on a Hewlett Packard 5970 Mass Selective Detector combined with a HP 5890 gas chromatograph equipped with a 25 m OV-101 capillary column; exact mass measurement was performed with a Varian Mat CH5-DF spectrometer; all peaks showed the expected isotope patterns.

General procedure for the synthesis of **1**

A solution of $SiCl_4$ (0.7 mmol in 5 ml pentane) or $GeCl_4$ (0.7 mmol in 5 ml benzene), was added to a solution of **2** (1.4 mmol) in diethyl ether (200 ml) at room temperature during 5 min. The mixture was stirred (15 h in the case of Si, 1 h in the case of Ge) and then poured into water. The organic phase was separated and dried ($MgSO_4$). The yield of **1** was determined by GLC with *o*-, *m*-, or *p*-xylene as internal standard. Isolation of **1** was achieved by careful concentration of the organic phase to about 2 ml and subsection of the residue to preparative GLC (OV 101; 10%).

2,2,6,6-Tetramethyl-4-silaspiro[3.3]heptane (1a). Isolated yield: 15%; GLC yield ca. 50%. NMR spectra: see Table 1. Mass spectra m/z (rel. intensity): 168(9) M^+ ; 153(7) $[M - CH_3]^+$; 112(55) $[M - C_4H_8]^+$; 97(100) $[M - C_4H_8 - CH_3]^+$; HRMS: Found: 168.1329. $C_{10}H_{20}^{28}Si$ calcd.: 168.1334.

2,2,6,6-Tetramethyl-4-germaspiro[3.3]heptane (1b). Isolated yield: 48%; GLC yield ca. 80%. NMR spectra: see Table 1. Mass spectra m/z (rel. intensity): 214(2) M^+ ; 199(3) $[M - CH_3]^+$; 158(47) $[M - C_4H_8]^+$; 143(60) $[M - C_4H_8 - CH_3]^+$; 89(100) $[GeCH_3]^+$; HRMS: Found: 214.0767. $C_{10}H_{20}^{74}Ge$ calcd.: 214.0777.

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