Journal of Organometallic Chemistry, 338 (1988) 159–168
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

The synthesis and some applications of new 1,3-dilithiopropanes: dimethylbis(α-lithiobenzyl)silane and its germanium analogue

O.S. Akkerman* and F. Bickelhaupt

Scheikundig Laboratorium, Vrije Universiteit, de Boelelaan 1083, 1081 HV Amsterdam (The Netherlands)

(Received June 16th, 1987)

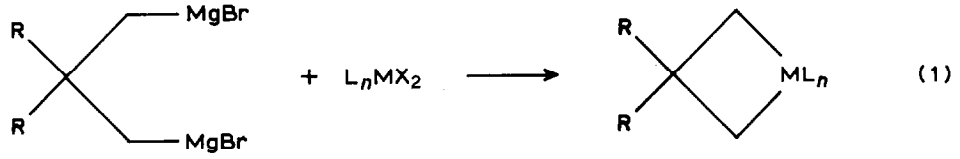
Abstract

The dimethylbis(α-lithiobenzyl)silanes and -germanes were prepared by the reaction of dimethylbis(α-thiophenylbenzyl)silane or -germane with lithium dispersion and their reactions with $Me_3M'Cl$ (M = Ge, Sn) investigated. The lithium compounds proved to be useful in the synthesis of 2,4-diphenyl-substituted 1,3-disila-, 1,3-digerma- and 1-germa-3-silacyclobutanes.

Introduction

Metallacyclobutanes have recently been the subject of much study. This is particularly the case for such species containing metals from groups 4, 5 and 6 and for the metal carbene complexes derived from them, since they are considered to be the active species in olefin-metathesis [1,2].

The most general method of synthesis of metallacyclobutanes involves the reaction of a 1,3-di-Grignard reagent [3,4] with a suitable metal dihalide, as shown in eq. 1.



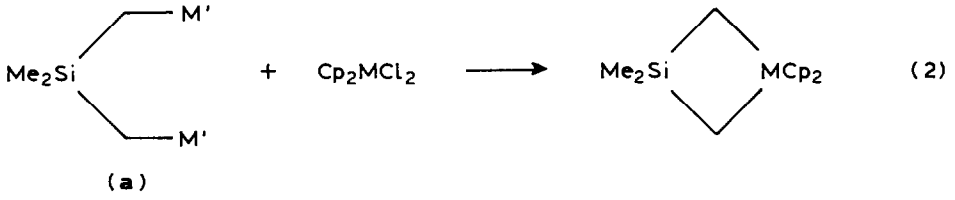
(1)

(L_n = Me_2 ; M = Ge [5], M = Sn [6] ;
L_n = Cp_2 ; M = Ti, Zr, Hf [7]; V [8] ;
R = H, Me)

0022-328X/88/$03.50

It was to be expected that 1,3-dilithiopropanes [9] could likewise be used for the synthesis of metallacyclobutanes. The drawback in their application is their rather complex synthesis; moreover the unsubstituted 1,3-dilithiopropane is unstable, decomposing even at −60 °C to allyllithium.

It has been shown by Sakurai [10] using lithium, and by Petersen [11,12] using magnesium, that 1,3-dimetal compounds having a $SiMe_2$ moiety in the 2-position can be used for the synthesis of 1,3-dimetallacyclobutanes (eq. 2), a reaction similar to the Barbier reaction of $Me_2Si(CH_2Cl)_2$ with Me_2SiCl_2 (or Me_2GeCl_2) and magnesium described by Seyferth et al. [13].



(a)

(M = Ti , Zr , Nb , Mo ;
M' = Li , Mg)

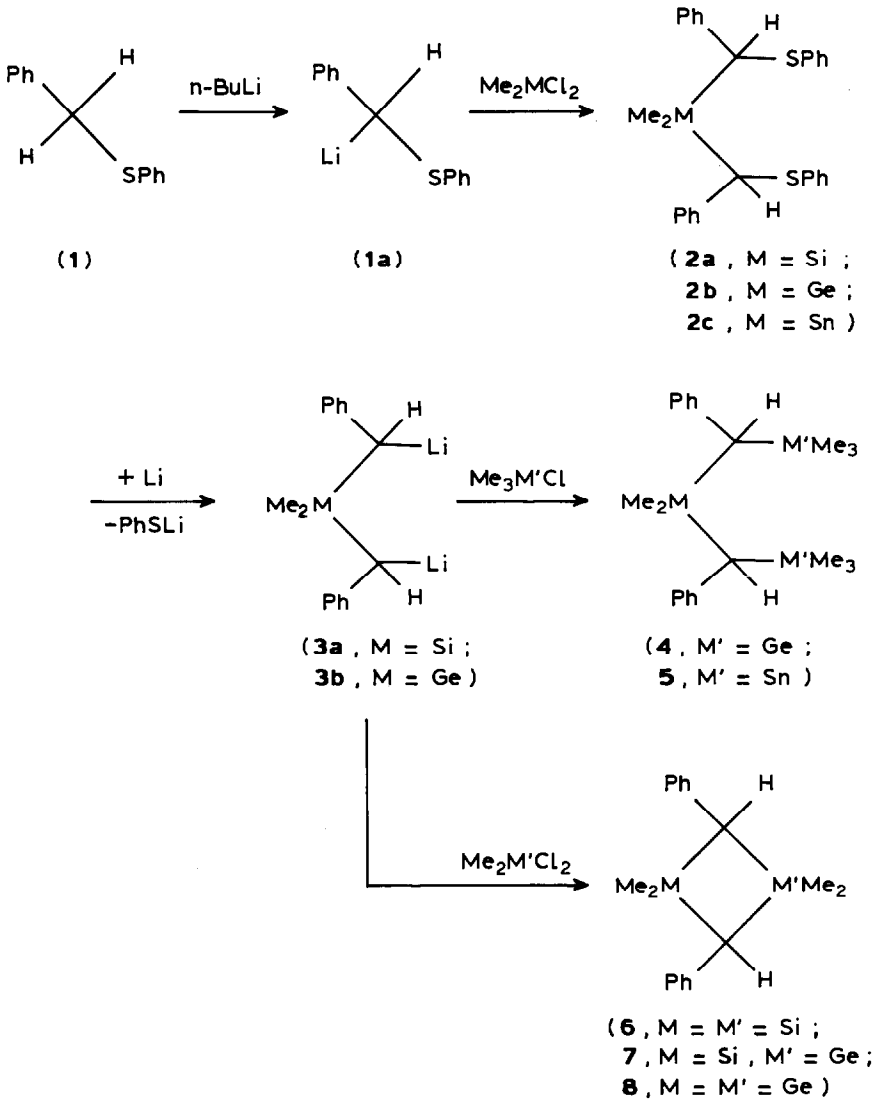
To extend the availability of 1,3-dilithio compounds we decided to examine the possibility of synthesizing compounds of the type **a** in eq. 2 by use of the thioether cleavage described by Screttas and Micha-Screttas [14].

Results and discussion

Screttas' method is analogous to the conversion of **1** into **3**, as depicted in Scheme 1 with the difference that Screttas treated **1a** with α,ω-dibromoalkanes having at least three carbon atoms between the bromines whereas we used dichlorodimethyl derivatives of Si, Ge and Sn to obtain (2-hetero) 1,3-dilithio reagents **2**. For the synthesis of **2**, an excess of **1** was lithiated in order to convert the Me_2MCl_2 completely. In all cases, mixtures of the *d,l* and *meso* forms were formed. Only in the case of **2a** (M = Si), were the diastereomers separated by crystallization.

The cleavage of the bis(phenylthio)ether **2** by lithium with formation of **3** was most successful when a large excess of lithium dispersion containing 1% of sodium was used. The progress of the cleavage was monitored by quenching a small sample of the reaction mixture with D_2O and subjecting the products to GC-MS analysis. The 1,3-dilithium compounds **3** were used directly for further reactions after the solution had been siphoned from the excess of lithium. Reaction of the tin compound **2c** with lithium led to fragmentation of carbon–tin bonds giving unidentified tin-containing products. The dilithio compounds **3** (M = Si: **3a**; M = Ge: **3b**) were quenched with $Me_3M'Cl$ (M' = Ge, Sn) to give the expected products **4** and **5**.

Application of **3** to the synthesis of 1,3-dimetallacyclobutanes as shown in Scheme 1 enabled us to synthesize compounds **6–8** in reasonable yields (after purification). The *cis*- and *trans*-isomers were formed in about equal amounts. In the case of **8** (Ge_2), the *trans*-isomer was selectively crystallized from a concentrated Et_2O solution at about −25 to −30 °C, and thus obtained in a nearly pure state. Attempts at ring closure reactions of **3a** or **3b** with Me_2SnCl_2 have so far been



Scheme 1

unsuccessful. Of these compounds, only **6** has previously been described; it was synthesized by pyrolysis at 500 °C of 1,1-dimethyl-2-phenyl-1-silacyclobutane [15].

A drawback of the described synthesis of **3** is the formation of PhSLi, which competes in the reaction with metal halides and metal dihalides. Therefore we tried to synthesize **3** by direct lithiation of dibenzyldimethylsilane or dibenzyldimethylgermane with n-butyllithium or s-butyllithium, but in all cases mixtures of mono- and dilithiated products were obtained. The synthesis of **3** by means of metal–halogen exchange in bis(α-bromobenzyl)dimethylsilane or its germanium analogue is under investigation.

Experimental

The experiments were carried out under argon. The THF was distilled from $LiAlH_4$ after treatment with solid KOH. Me_2SiCl_2 (Merck-Schuchardt, München), thiophenol, Me_2GeCl_2, Me_3GeCl (Ventron, Karlsruhe), Me_2SnCl_2, Me_3SnCl (Janssen Chimica, Beerse Belgium) were used without further purification.

The NMR spectra were measured in $CDCl_3$ with a Bruker WM-250 NMR spectrometer at 250 MHz (^1H) or 62.89 MHz (^{13}C). Mass spectra were recorded on a 5970 Hewlett Packard Mass Selective Detector connected to a HP 5890 Gas-chromatograph equipped with a 25 m CP sil 19 capillary column. Exact mass measurements were performed on the products with a Varian MAT CH-5 DF mass spectrometer after crystallization or GLC purification. The exact masses of the molecular ions were calculated using the most abundant isotopes e.g. ^{74}Ge, ^{120}Sn etc. The abundances of ions containing germanium and tin take account of all the ions in the isotopic cluster. The preparative scale GLC purifications were carried out with an Intersmat 120 gas-chromatograph with a 2 m 10% OV-101 or 3% OV-225 column.

Synthesis of benzylphenylsulfide (1)

Compound **1** was synthesized as described by Cutler [16] starting from 0.5 mol thiophenol (55 g), 450 ml aqueous NaOH solution (5%) and 0.55 mol benzyl bromide (94 g). The mixture was heated to 100 °C and stirred for 6 h. After cooling the solidified mass was filtered off and dissolved in Et_2O, and the solution washed, then dried over $MgSO_4$. Distillation (b.p. 95–100 °C/2 mmHg) yielded 97.5 g **1** (97.5% yield); mp. 42–43 °C.

^1H NMR (90 MHz, $CDCl_3$), δ: 7.21–7.36 (m, 10H, arom*H*), 4.14 ppm (s, 2H, C*H*$_2$). Mass spectrum, *m/z* (rel. int.) 200 (19.4) M^+, 109 (6.5), 91 (100).

α-Lithiobenzylphenylsulfide (1a)

The lithiation of **1** was carried out as described by Screttas and Micha-Screttas [14]. In a typical experiment, a solution of 30 mmol of **1** (6 g) in 75 ml of THF was cooled to −65 °C. Subsequently, 24 mmol of n-butyllithium in hexane (16.5 ml of a 1.45 molar solution) was added. The solution immediately turned yellow. After 1 h stirring at −65 °C, the mixture was allowed to warm to room temperature. Stirring was continued for another 5 h, giving a dark yellow-green solution. A sample was quenched with D_2O and the content of monodeuterated **1** shown mass spectroscopically to be 98%. This was confirmed by ^1H NMR spectroscopy, ^2J(DH) 2.4 Hz.

The reaction of 1a with Me_2MCl_2 (M = Si, Ge, Sn)

In these reactions, an excess of compound **1** was used in order to convert all of the Me_2MCl_2 into the desired product.

Compound **1** was lithiated as described above starting from 35 mmol **1** (7.0 g) in 100 ml THF. After the lithiation was complete (vide supra), 15 mmol Me_2MCl_2 (M = Si, 1.94 g; M = Ge, 2.60 g; M = Sn, 3.33 g) in 10 ml anhydrous THF was added with stirring during 5 min at −10 °C. The mixture was then allowed to warm to room temperature and stirred overnight after which it turned pale orange. Next, the THF was removed by distillation under reduced pressure, the residue was dissolved in Et_2O, and the solution washed with water until neutral then dried over

$MgSO_4$. After filtration and removal of the solvent by vacuum distillation, the residue was submitted to "short path distillation" at 100 °C and 2×10^{-2} mmHg. The distillate consisted of pure crystalline **1**: 1.27 g in the case of **2a**; 1.23 g in the case of **2b**; 1.03 g for **2c**. The residue consisted of **2** with a purity of more than 95% as determined for **2a** and **2b** from GLC (OV-101, 250 °C isothermal) and from the ^{1}H NMR spectrum for **2c**.

The "crude" yields of **2a–2c** were 6.54 g, 7.18 g and 7.61 g respectively; with respect to converted **1**, these yields are nearly quantitative. Compounds **2a** and **2b** can be crystallized from ethanol. Compound **2c** is a very viscous oil. In the case of **2a**, the *d,l* and *meso* forms were separated by fractional crystallization from ethanol. M.p. *meso*-2a: 78–79 °C; m.p. *d,l*-**2a**: 113–115 °C. Since several experiments yielded meso and *d,l* mixtures of varying compositions, no melting points of these mixtures are reported.

Dimethylbis(α-phenylthiobenzyl)silane (2a): meso-2a. ^{1}H NMR, δ: 7.59–6.67 (m, 20H, arom*H*), 3.78 (s, 2H, PhC*H*SPh), 0.45 (s, 3H, Si*Me*), 0.09 ppm (s, 3H, Si*Me*). ^{13}C NMR, δ: 140.54 (q, ^2J(CH) = ^3J(CH) = 7.2 Hz, *C(1)*Ph), 137.46 (br.m., *C(1)*SPh), 129.11–127.90 (overlap of signals *C(2)* + *C(3)* of Ph and SPh), 125.68 (d of t, ^1J(CH) 138.5, ^3J(CH) 6.9 Hz, *C(4)*Ph), 39.54 (d, ^1J(CH) 132.5 Hz, PhCSPh), −6.13 ppm (q, ^1J 121.4 Hz, Si*Me*).

d,l-**2a**. ^{1}H NMR, δ: 7.26–7.14 (m, 20H, arom*H*), 4.19 (s, 2H, PhC*H*SPh), 0.03 ppm (s, 6H, Si*Me*). ^{13}C NMR, δ: 140.31 (q, ^2J(CH) = ^3J(CH) = 7.2 Hz, *C(1)*Ph), 137.46 (br.m., *C(1)*SPh), 129.11–127.90 (overlap of signals *C(2)* + *C(3)* of Ph and SPh), 38.62 (d, ^1J(CH) 132.7 Hz, PhCSPh), −5.70 ppm (q, ^1J(CH) 121.4 Hz, Si*Me*).

2a mass spectrum, *m/z* (rel. int.) 456 (2.6) M^+, 347 (10.9), 257 (9.2), 199 (100), 179 (23.6), 167 (15.4), 151 (12.3). Exact mass: 456.1417; $C_{28}H_{28}S_2Si$ calc.: 456.1402.

Dimethylbis(α-thiophenylbenzyl)germane (2b), meso-2b. ^{1}H NMR, δ: 7.36–7.02 (m, 20H, arom*H*), 3.96 (s, 2H, PhC*H*SPh), 0.57 (s, 6H, Ge*Me*), 0.00 ppm (s, 2H, Ge*Me*). ^{13}C NMR, δ: 140.97 (q, ^2J(CH) = ^3J(CH) = 7.4 Hz, *C(1)*arom), 137.68 (q, ^2J(CH) = ^3J(CH) = 7.1 Hz, *C(1)*Sarom), 128.56–127.48 (overlap of signals *C(2)* + *C(3)* of arom and Sarom), 127.32 (d of t, ^1J(CH) 158.0, ^3J(CH) 7.0 Hz, *C(4)*arom), 125.52 (d of t, ^1J(CH) not known through overlap, ^3J(CH) 7.5 Hz, *C(4)*arom), 39.24 (d, ^1J(CH) 144.3 Hz, PhCSPh), −6.10 ppm (q, ^1J(CH) 128.3 Hz, Ge*Me*).

d,l-**2b**: ^{1}H NMR, δ: 7.36–7.02 (m, 20H, arom*H*), 4.25 (s, 2H, PhC*H*SPh), 0.18 ppm (s, 6H, Ge*Me*). ^{13}C NMR, δ: 140.80 (q, ^2J(CH) = ^3J(CH) = 7.4 Hz, *C(1)*arom), 137.68 (q, ^2J(CH) = ^3J(CH) = 7.1 Hz, *C(1)*Sarom), 128.56–127.48 (overlap of signals of *C2* + *C3* of arom and Sarom), 127.20 (d of t, ^1J(CH) 157.9, ^3J(CH) 7.1 Hz, *C4*Sarom), 125.66 (d of t, ^1J(CH) not known through overlap, ^3J(CH) 7.5 Hz, *C4*arom), 38.35 (d, ^1J(CH) 139.8 Hz, PhCSPh), −5.95 ppm (q, ^1J(CH) 129.1 Hz, Ge*Me*).

2b mass spectrum, *m/z* (rel. int) 502 (3.2) M^+, 393 (0.6), 303 (93.5), 225 (56.8), 199 (100), 167 (49.2). Exact mass: 502.0871; $C_{28}H_{28}GeS_2$ calc: 502.0844.

Dimethylbis(α-phenylthiobenzyl)stannane (2c), meso-2c. ^{1}H NMR, δ: 7.67–6.59 (m, 20H, arom*H*), 4.15 (s, 2H, ^2J(SnH) 67.68/64.56 Hz, PhC*H*SPh), 0.43 (s, 3H, ^2J(SnH) 54.6/52.2 Hz, Sn*Me*), 0.06 ppm (s, 3H, ^2J(SnH) 51.6/54.0 Hz, Sn*Me*). ^{13}C NMR, δ: 142.31 (d of t, ^2J(CH) 7.4, ^3J(CH) 10.5, ^2J(SnC) 25.0 Hz, *C(1)*arom), 138.84 (d of t, ^2J(CH) 6.9, ^3J(CH) 15.0 Hz, *C(1)*Sarom), 130.07–127.42 (overlapping signals of *C(2)* + *C(3)* of arom + Sarom), 125.23 (d of t, ^1J(CH) 160.5, ^3J(CH) 6.8 Hz, *C(4)*arom), 34.92 (d, ^1J(CH) 143.2 Hz, long-range coupling 3.7 Hz, ^1J(SnC)

251.5/264.5 Hz, PhCSPh), −10.23 ppm (q, ^1J(CH) 131.9, ^1J(SnC) 331/340 Hz, Sn*Me*).

d,l-2c. ^{1}H NMR, δ: 7.67–6.59 (s, 20H, arom*H* + Sarom*H*), 4.24 (s, 2H, ^2J(SnH) 66.61/63.38 Hz, PhC*H*SPh), 0.15 ppm (s, 6H, ^2J(SnH) 51.64/53.99 Hz, Sn*Me*). ^{13}C NMR, δ: 142.27 (d of t, ^2J(CH) 7.4, ^3J(CH) 10.0, ^2J(SnC) 25.0 Hz, *C(1)*arom), 138.84 (d of t, ^2J(CH) 6.9, ^3J(CH) 15.0 Hz, *C(1)*Sarom), 130.07–127.42 (unres.m, *C(2)* + *C(3)* of arom and Sarom), 125.47 (d of t, ^1J(CH) 160.3, ^3J(CH) 7.0 Hz, *C(4)*arom), 35.38 (d, ^1J(CH) 143.3 Hz, long range J(CH) 4.7, ^1J(SnC) 264.5/251.5 Hz, PhCSPh), −10.57 ppm (q, ^1J(CH) 131.8, ^1J(SnC) 330.0/340.0 Hz, Sn*Me*).

2c mass spectrum, *m/z* (rel. int.) 548 (3.2) M^+, 349 (52.3), 259 (8.1), 229 (3.7), 199 (94.0), 167 (100). Exact mass: 548.0653; $C_{28}H_{28}S_2Sn$ calc: 548.0653.

Preparation of dimethylbis(α-lithiobenzyl)silane (3a) and its germanium analogue (3b)

The reaction of **2a–2c** with lithium was carried out as described by Screttas and Screttas [14]. About 500 mg of a 30% lithium dispersion containing 1% sodium in paraffin oil was washed four times with 5 ml anhydrous THF. After addition of 10 ml of THF the mixture was cooled to −65°C and a solution of 1 mmol of **2** (456 mg **2a**, 502 mg of **2b** or 548 mg **2c**) in 10 ml of THF was slowly added with vigorous stirring. A yellow colour appeared within 5 min. Stirring was continued for 7–8 h to give a dark brown-red solution. A sample was taken with D_2O and GC-MS revealed the formation of more than 95% of dimethylbis(α-lithiobenzyl)silane (**3a**) and dimethylbis(α-lithiobenzyl)germane (**3b**). The solution of the dilithium compounds was separated from the residual lithium metal by siphoning into another vessel through a stainless steel capillary (internal diameter 1 mm) and used for the subsequent experiments.

The reaction of the dilithium compounds 3 with $Me_3M'Cl$ (M' = Ge, Sn)

To a freshly prepared solution of 1 mmol of **3a** or **3b** (vide supra) in 20 ml of THF was added during 5 min a solution of a twofold excess of $Me_3M'Cl$ (4 mmol Me_3GeCl (618 mg) or Me_3SnCl (802 mg)) in 20 ml of THF at −65°C. After the addition the intense color had disappeared. The mixture was allowed to warm to room temperature overnight and 200 μl water was then added. The THF was distilled off under reduced pressure and the residue was dissolved in Et_2O and worked up in the usual way to give dimethylbis(α-trimethylgermylbenzyl)silane (**4a**), dimethyl(α-trimethylstannylbenzyl)silane (**5a**), dimethylbis(α-trimethylgermylbenzyl)germane (**4b**) and dimethylbis(α-trimethylstannylbenzyl)germane (**5b**). The crude yields as determined with GLC or ^{1}H NMR spectroscopy were: **4a**, 70%; **5a**, 72%; **4b**, 76%; **5b**, 70%. The compounds were purified by preparative GLC for ^{1}H NMR and ^{13}C NMR spectroscopy and exact mass measurements (isothermal, 225°C). The isolated yields ranged from 55–60%.

***4a**: meso-4a*. ^{1}H NMR, δ: 7.18–6.72 (m, 10H, arom*H*), 1.69 (s, 2H, PhC*H*), 0.35 (s, 3H, Si*Me*), −0.06 (s, 3H, Si*Me*), 0.12 ppm (s, 18H, Ge*Me*). ^{13}C NMR, δ 143.49 (d of t, ^2J(CH) 7.1, ^3J(CH) 7.0 Hz, *C(1)*arom), 128.77 (d of d, ^1J(CH) 156.2, ^3J(CH) 6.5 Hz, *C(3)*arom), 127.96 (d of t, ^1J(CH) 157.0, ^3J(CH) 7.5 Hz, *C(2)*arom), 123.24 (d of t, ^1J(CH) 160.2, ^3J(CH) 7.3 Hz, *C(4)*arom), 27.51 (d, ^1J(CH) 113.0 Hz, PhC), 1.51 (q, ^1J(CH) 117.0 Hz, Si*Me*), −0.38 (q, ^1J(CH)) 118.6 Hz, Si*Me*), −0.18 ppm (q, ^1J(CH) 125.0 Hz, Ge*Me*).

d,l-**4a**. ^{1}H NMR, δ: 7.18–6.72 (m, 10H, arom*H*), 1.63 (s, 2H, PhC*H*), 0.25 (s, 6H, Si*Me*), 0.10 ppm (s, 18H, Ge*Me*). ^{13}C NMR, δ: 143.15 (d of t, ^2J(CH) 7.4, ^3J(CH) 7.0 Hz, *C(1)*arom), 128.91 (d of d, ^1J(CH) 156.2, ^3J(CH) 6.5 Hz, *C(3)*arom), 127.78 (d of t, ^1J(CH) 157.0, ^3J(CH) 8.1 Hz, *C(2)*arom), 123.14 (d of t, ^1J(CH) 160.12, ^3J(CH) 6.9 Hz, *C(4)*arom), 27.51 (d, ^1J(CH) 113.0 Hz, PhC), 0.71 (q, ^1J(CH) 119.9 Hz, Si*Me*), −0.18 ppm (q, ^1J(CH) 125.0 Hz, Ge*Me*).

4a mass spectrum, *m/z* (rel. int.) 476 (3.7) M^+, 461 (6.9), 342 (21.6), 327 (27.1), 267 (68), 194 (31.6), 163 (74.9), 147 (25.3), 135 (13.9), 119 (100), 105 (5.70), 98 (20.3), 73 (43.2). Exact mass: 476.0977; $C_{22}H_{36}Ge_2Si$ calc: 476.1010.

5a**: meso-**5a. ^{1}H NMR, δ: 7.19–6.72 (m, 10H, arom*H*), 1.89 (s, 2H, ^2J(SnH) 80.7/77.3 Hz, PhC*H*), 0.28 (s, 3H, Si*Me*), 0.08 (s, 3H, Si*Me*), 0.04 ppm (s, 18H, ^2J(SnH) 50.0/52.2 Hz, Sn*Me*). ^{13}C NMR, δ: 144.55 (q, ^2J(CH) = ^3J(CH) = 7.2 Hz, ^2J(SnC) 36.8 Hz, *C(1)*arom), 128.52–127.49 (unresolved m, ^1J(CH) 156.9 Hz, *C(2)* + *C(3)*arom), 122.72 ppm (d of t, ^1J(CH) 160.5, ^3J(CH) 7.6 Hz, *C(4)*arom), 24.18 (d, ^1J(CH) 115.6, ^1J(SnC) 222.3/208.6 Hz, PhC), 1.81 (q, ^1J(CH) 120.8, ^4J(CH) 2.3 Hz, Si*Me*), 0.13 (q, ^1J(CH) 118.7, ^4J(CH) 2.3 Hz, Si*Me*), −7.93 ppm (q, ^1J(CH) 128.6, ^1J(SnC) 325.8/313.7 Hz, Sn*Me*).

d,l-**5a**. ^{1}H NMR, δ: 7.19–6.72 (m, 10H, arom*H*), 1.86 (s, 2H, ^2J(SnH) 75.3/78.6 Hz, PhC*H*), 0.25 (s, 6H, Si*Me*), 0.05 ppm (s, 18H, ^2J(SnH) 52.1/49.8 Hz, Sn*Me*). ^{13}C NMR, δ: 144.28 (q, ^2J(CH) = ^3J(CH) = 7.0 Hz, ^2J(SnC) 36.6 Hz, *C(1)*arom), 128.52–127.49 (unresolved m, ^1J(CH) 156.9 Hz, *C(2)* + *C(3)*arom), 122.61 (d of t, ^1J(CH) 160.1, ^3J(CH) 7.5 Hz, *C(4)*arom), 24.07 (q, ^1J(CH) 115.6, ^1J(SnC) 222.1/210.4 Hz, PhC), 0.95 (q, ^1J(CH) 118.7 Hz, Si*Me*), −8.01 ppm (q, ^1J(CH) 128.5, ^1J(SnC) 322.6/310.4 Hz, Sn*Me*).

5a mass spectrum, *m/z* (rel. int.) 568 (6.9 M^+, 553 (100), 338 (22.4), 283 (7.8), 223 (7.2), 165 (51.1), 150 (16.1), 135 (21.6), 120 (28.9). Exact mass: 568.0598; $C_{22}H_{36}SiSn_2$ calc: 568.0071.

4b**: meso-**4b. ^{1}H NMR, δ: 7.19–6.72 (m, 10H, arom*H*), 1.81 (s, 2H, PhC*H*), 0.47 (s, 3H, Ge*Me*$_2$), 0.03 (s, 3H, Ge*Me*$_2$), 0.11 ppm (s, 18H, Ge*Me*$_3$). ^{13}C NMR, δ: 144.18 (q, ^2J(CH) = ^3J(CH) = 7.1 Hz, *C(1)*arom), 128.50 (d of d, ^1J(CH) 152.4, ^3J(CH) 7.7 Hz, *C(3)*arom), 127.95 (d of t, ^1J(CH) 156.4, ^3J(CH) 8.2 Hz, *C(2)*arom), 123.20 (d of t, ^1J(CH) 160.2, ^3J(CH) 7.4 Hz, *C(4)*arom), 27.8 (d, ^1J(CH) 119.4 Hz, PhC), 1.24 (q, ^1J(CH) 124.8 Hz, Ge*Me*$_2$), −1.05 (q, ^1J(CH) 125.0 Hz, Ge*Me*$_2$), −0.48 ppm (q, ^1J(CH) 125.0 Hz, Ge*Me*$_3$).

d,l-**4b**. ^{1}H NMR, δ: 7.19–6.72 (m, 10H, arom*H*), 1.79 (s, 2H, PhC*H*), 0.33 (s, 6H, Ge*Me*$_2$), 0.10 ppm (s, 18H, Ge*Me*$_3$). ^{13}C NMR, δ: 143.94 (q, ^2J(CH) = ^3J(CH) = 7.2 Hz, *C(1)*arom), 128.55 (d of d, ^1J(CH) 151.7, ^3J(CH) 7.7 Hz, *C(3)*arom), 127.80 (d of t, ^1J(CH) 156.6, ^3J(CH) 7.9 Hz, *C(2)*arom), 123.10 (d of t, ^1J(CH) 160.4, ^3J(CH) 7.2 Hz, *C(4)*arom), 27.66 (d, ^1J(CH) 119.4 Hz, PhC), 0.44 (q, ^1J(CH) 125.0 Hz, Ge*Me*$_3$), 0.25 ppm (q, ^1J(CH) 126.1 Hz, Ge*Me*$_2$).

4b mass spectrum, *m/z* (rel. int.) 522 (18.6) M^+, 507 (4.7), 313 (100), 209 (62.2), 194 (30.7), 119 (67.1), 104 (23.7), 89 (12.4). Exact mass: 522.0462; $C_{22}H_{36}Ge_3$ calc: 522.0453.

5b**: meso-**5b. ^{1}H NMR, δ: 7.17–6.72 (m, 10H, arom*H*), 1.98 (s, 2H, ^2J(SnH) 70.2/67.1 Hz, PhC*H*), 0.37 (s, 3H, Ge*Me*), 0.12 (s, 3H, Ge*Me*), 0.013 ppm (s, 18H, ^2J(SnH) 50.4/51.9 Hz, Sn*Me*). ^{13}C NMR, δ: 145.45 (q, ^2J(CH) = ^3J(CH) = 7.3 Hz, *C(1)*arom), 128.14–127.80 (unresolved m, ^1J(CH) 155.8 Hz, *C(2)* + *C(3)*arom), 122.68 (d of t, ^1J(CH) 160.5, ^3J(CH) 7.5 Hz, *C(4)*arom), 23.78 (d, ^1J(CH) 122.9, ^1J(SnC)

246.1/234.5 Hz, PhC), 1.29 (q, ^1J(CH) 124.5 Hz, GeMe), −0.62 (q, ^1J(CH) 124.2 Hz, GeMe), −8.22 (q, ^1J(CH) 128.4, ^1J(SnC) 309.6/324.3 Hz, SnMe).
d,l-5b. ^{1}H NMR, δ: 7.17–7.62 (m, 10H, aromH), 1.97 (s, 2H, PhCH), 0.30 (s, 6H, GeMe), 0.03 ppm (s, 18H, ^2J(SnH) 50.02/52.25 Hz, SnMe). ^{13}C NMR, δ: 145.28 (q, ^2J(CH) = ^3J(CH) = 7.3 Hz, *C(1)*arom), 128.14–127.80 (unresolved m, ^1J(CH) 155.8 Hz, *C(2)* + *C(3)*arom), 122.55 (d of t, ^1J(CH) 160.5, ^3J(CH) 7.4 Hz, *C4*), 23.74 (d, ^1J(CH) 122.8, ^1J(SnC) 246.0/234.0 Hz, PhC), 0.27 (q, ^1J(CH) 126.1 Hz, GeMe), −8.22 ppm (q, ^1J(CH) 128.4, ^1J(SnC) 324.3/309.6 Hz, SnMe).

5b mass spectrum, *m/z* (rel. int.) 614 (93) M^+, 599 (63.0), 522 (6.2), 434 (8.8), 359 (21.8), 313 (38.8), 209 (50.5), 165 (54.3), 135 (49.7), 120 (100). Exact mass: 614.0085; $C_{22}H_{36}GeSn_2$ calc: 614.0071.

Synthesis of the 2,4-diphenyl-1,1,3,3-tetramethyl-1,3-dimetallacyclobutanes (M = M' = Si, 6; M = Si, M' = Ge, 7; M = M' = Ge, 8)

To a freshly prepared solution of 2.6 mmol of **3a** was added 2.6 mmol of Me_2SiCl_2 (338 mg, 317 μl) at −65 °C during 1 min. The mixture was allowed to warm to room temperature overnight, then 200 μl of H_2O was added and the work up the carried out as described above. The solid residue (1.00 g) contained over 75% of **6** according to GC-MS analysis. Compound **6** [14] was isolated by preparative scale GLC (isothermal 215 °C). The isolated yield was 68%.

For the synthesis of **7** (or **8**) 1 mmol of **2a** (456 mg) (or **2b** (502 mg)) was converted into the dilithium compound **3a** (or **3b**) as described above, then a solution of 2 mmol of Me_2GeCl_2 (350 mg, 235 μl) in 2 ml of THF was added at 65 °C during 1 min. The mixture was then immediately treated with 250 μl of saturated aqueous $NaHCO_3$ then quickly warmed to room temperature and worked up as described above. GC-MS analysis of the residue revealed the formation of 75% of **7**. The compound was isolated by preparative scale GLC (isothermal 225 °C) in a yield of 55%.

Compound **8** was formed in a yield of 70% as determined by GLC analysis. A solution of the residue in about 2 ml Et_2O was cooled to −30 °C, and the *trans* isomer crystallized in a nearly pure form (101 mg, 0.26 mmol). The mother liquor was submitted to preparative scale GLC on a 2m OV-225 column, isothermal 225 °C. After purification, the total yield was 45%.
6: trans-6. ^{1}H NMR, δ: 7.20–6.75 (m, 10H, aromH), 2.29 (s, 2H, PhCH), 0.31 ppm (s, 12H, SiMe). ^{13}C NMR, δ: 141.62 (q, ^2J(CH) = ^3J(CH) = 7.1 Hz, *C(1)*arom), 128.18 (d of d, ^1J(CH) 162.7, ^3J(CH) 7.7 Hz, *C(3)*arom), 127.63 (d of t, ^1J(CH) 155.6, ^3J(CH) 7.2 Hz, *C(2)*arom), 122.63 (d of t, ^1J(CH) 160.8, ^3J(CH) 7.3 Hz, *C(4)*arom), 31.02 (d, ^1J(CH) 112.2 Hz, PhC), −0.54 ppm (q, ^1J(CH) 120.4 Hz, SiMe).
cis-6. ^{1}H NMR, δ: 7.20–6.75 (m, 10H, aromH), 2.13 (s, 2H, PhCH), 0.42 (s, 6H, SiMe), 0.35 ppm (s, 6H, SiMe). ^{13}C NMR, δ: 142.56 (q, ^2J(CH) = ^3J(CH) = 7.2 Hz, *C(1)*arom), 128.24 (d of d, ^1J(CH) 162.7, ^3J(CH) 7.7 Hz, *C(3)*arom), 127.87 (d of t, ^1J(CH) 155.6, ^3J(CH) 7.2 Hz, *C(2)*arom), 122.95 (d of t, ^1J(CH) 160.6, ^3J(CH) 7.4 Hz, *C(4)*arom), 29.24 (d, ^1J(CH) 112.2 Hz, PhC), 2.73 (q, ^1J(CH) 120.3 Hz, SiMe), −2.91 ppm (q, ^1J(CH) 121.7 Hz, SiMe).

6 mass spectrum, *m/z* (rel. int.): 296 (58.2) M^+, 281 (100), 265 (12.5), 205 (25.0), 177 (19.8), 161 (13.0), 149 (14.6), 148 (43.9), 147 (14.6), 146 (29.1), 145 (87.8), 131 (23.4), 121 (25.0), 107 (14.2), 105 (11.0), 73 (58.2), 59 (29.1), 53 (14.2), 47 (27.3), 43 (58.2). Exact mass: 296.1413; $C_{18}H_{24}Si_2$ calc: 296.1417.

7: trans-7. ^{1}H NMR (400 MHz), δ: 7.24–7.19, 7.07–7.00 (m, 10H, *H*arom), 2.57 (s, 2H, PhC*H*), 0.49 (s, 6H, Ge*Me*), 0.30 ppm (s, 6H, Si*Me*). ^{13}C NMR, δ: 143.47 (q, ^2J(CH) = ^3J(CH) = 6.8 Hz, *C(1)*arom), 128.18 (d of d, ^1J(CH) 158.5, ^3J(CH) 7.7 Hz, *C(3)*arom), 127.58 (d of t, ^1J(CH) 155.5, ^3J(CH) 7.0 Hz, *C(2)*arom), 122.64 (d of t, ^1J(CH) 160.8, ^3J(CH) 7.3 Hz, *C(4)*arom), 33.43 (d, ^1J(CH) 120.2 Hz, PhC), −0.35 (q, ^1J(CH) 121.2 Hz, Ge*Me*), −0.45 ppm (q, ^1J(CH) 127.0 Hz, Si*Me*).
cis-7. ^{1}H NMR (400 MHz), δ: 7.24–7.19, 7.07–7.00 (m, 10H, arom*H*), 2.40 (s, 2H, PhC*H*), 0.60 (s, 3H, Ge*Me*), 0.57 (s, 3H, Ge*Me*), 0.38 (s, 3H, Si*Me*), 0.31 ppm (s, 3H, Si*Me*). ^{13}C NMR, δ: 142.78 (q, ^2J(CH) = ^3J(CH) = 7.0 Hz, *C(1)*arom), 128.18 (d of d, ^1J(CH) 158.5, ^3J(CH) 7.7 Hz, *C(3)*arom), 127.81 (d of t, ^1J(CH) 155.6, ^3J(CH) 7.1 Hz, *C(2)*arom), 122.89 (d of t, ^1J(CH) 160.7, ^3J(CH) 7.2 Hz, *C(4)*arom), 31.19 (d, ^1J(CH) 116.5 Hz, PhC), 3.50 (q, ^1J(CH) 120.5 Hz, Ge*Me*), 2.95 (q, ^1J(CH) 125.8 Hz, Ge*Me*), −3.11 (q, ^1J(CH) 119.9 Hz, Si*Me*), −3.30 ppm (q, ^1J(CH) 125.7 Hz, Si*Me*).

7 mass spectrum, *m/z* (rel. int.): 342 (49.5) M^+, 327 (42.8), 162 (44.1), 149 (8.5), 148 (5.1), 147 (12.5), 73 (100). Exact mass: 342.0869; $C_{18}H_{24}GeSi$ calc: 432.0859.
8: trans-8. ^{1}H NMR, δ: 7.50–7.01 (m, 10H, arom*H*), 2.85 (s, 2H, PhC*H*), 0.46 ppm (s, 12H, Ge*Me*). ^{13}C NMR, δ: 144.27 (q, ^2J(CH) = ^3J(CH) = 6.8 Hz, *C(1)*arom), 128.15 (d of d, ^1J(CH) 158.6, ^3J(CH) 7.8 Hz, *C(3)*arom), 127.47 (d of q, ^1J(CH) 155.4, ^3J(CH) 7.0, ^3J(CH) 7.3 Hz, *C(2)*arom), 122.67 (d of t, ^1J(CH) 161.0, ^3J(CH) 7.4 Hz, *C(4)*arom), 36.59 (d, ^1J(CH) 125.1 Hz, PhC), −0.42 ppm (q, ^{1}J(CH) 126.4 Hz, long range coupling 1.85 Hz, Ge*Me*).
cis-8. ^{1}H NMR, δ: 7.50–7.01 (m, 10H, arom*H*), 2.74 (s, 2H, PhC*H*), 0.53 (s, 6H, Ge*Me*), 0.50 ppm (s, 6H, Ge*Me*). ^{13}C NMR, δ: 143.87 (q, ^2J(CH) = ^3J(CH) = 6.9 Hz, *C(1)*arom), 128.15 (d of d, ^1J(CH) 158.6, ^3J(CH) 7.8 Hz, *C(3)*arom), 127.66 (d of q, ^1J(CH) 155.4, ^3J(CH) 7.1 Hz, *C(2)*arom), 122.67 (d of t, ^1J(CH) 160.8, ^3J(CH) 7.7 Hz, *C(4)*arom), 34.18 (d, ^1J(CH) 123.1 Hz, PhC), 3.51 (q, ^1J(CH) 127.4 Hz, Ge*Me*), −3.83 ppm (q, ^1J(CH) 127.1 Hz, Ge*Me*).

8 mass spectrum, *m/z* (rel. int.): 388 (65.4) M^+, 373 (7.2), 208 (100), 193 (24.1), 149 (29.8), 119 (83.9), 104 (28.9), 91 (8.2), 74 (5.0), 77 (3.7). Exact mass: 388.0329; $C_{18}H_{24}Ge_2$ calc: 388.0302.

Acknowledgement

We thank Mr. R.F. Schmitz for the exact mass measurements.

References

1 A.K. Rappé and W.A. Goddard III, J. Am. Chem. Soc., 104 (1982) 297, 448 and references cited.
2 R.H. Grubbs, Prog. Inorg. Chem., 24 (1978) 1; N. Calderon, J.P. Lawrence and E.A. Ofstead, Adv. Organomet. Chem., 17 (1979) 449; K.J. Ivin, Olefin Metathesis, Academic Press, London, 1983.
3 J.W.F.L. Seetz, B.J.J. van de Heisteeg, G. Schat, O.S. Akkerman and F. Bickelhaupt, J. Organomet. Chem., 275 (1984) 173.
4 J.W.F.L. Seetz, F.A. Hartog, H.B. Böhm, C. Blomberg, O.S. Akkerman and F. Bickelhaupt, Tetrahedron Lett., 23 (1982) 1497.
5 J.W.F.L. Seetz, O.S. Akkerman and F. Bickelhaupt, J. Organomet. Chem., 277 (1984) 319.
6 J.W.F.L. Seetz, G. Schat, O.S. Akkerman and F. Bickelhaupt, J. Am. Chem. Soc., 105 (1983) 3336.
7 J.W.F.L. Seetz, O.S. Akkerman and F. Bickelhaupt, Angew. Chem., 95 (1983) 242.

8 J.W.F.L. Seetz, B.J.J. van de Heisteeg, G. Schat, O.S. Akkerman and F. Bickelhaupt, J. Organomet. Chem., 275 (1984) 173.
9 J.W.F.L. Seetz, G. Schat, O.S. Akkerman and F. Bickelhaupt, J. Am. Chem. Soc., 104 (1982) 6848.
10 H. Sakurai and H. Umino, J. Organomet. Chem., 142 (1977) C49.
11 W.R. Tikkanen, J.Z. Liu, J.W. Egan Jr. and J.L. Petersen, Organometallics, 3 (1984) 825.
12 W.R. Tikkanen, J.W. Egan Jr. and J.L. Petersen, Organometallics, 3 (1984) 1646.
13 D. Seyferth and C.J. Attridge, J. Organomet. Chem., 21 (1970) 103.
14 C.G. Screttas and M. Micha-Screttas, J. Org. Chem., 44 (1979) 713.
15 P.B. Valkovich, Th. Ito and W.P. Weber, J. Org. Chem., 39 (1974) 3543.
16 R.A. Cutler, R.J. Stenger and C.M. Suter, J. Am. Chem. Soc., 74 (1952) 5475.