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AN INVESTIGATION OF THE DI-GRIGNARD APPROACH TO METALLABENZOCYCLOBUTENES OF GROUP 14

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Summary

The reactions of 1,2-dihydro-1-magnesabenzocyclobutene (**5**) with dichlorodimethylsilane (**12a**), dichlorodimethylgermane (**12b**) and dichlorodimethylstannane (**12c**) are reported; 1,2-dihydro-1,1-dimethyl-1-silabenzocyclobutene (**14a**) and 1,2-dihydro-1,1-dimethyl-1-germabenzocyclobutene (**14b**) were formed in high yields, but the tin analogue **14c** was not obtained. Eight-membered ring species, the dimers **17** and **18**, were isolated for all three metals. Other products gave useful indications of the probable course of these interesting and complex reactions.

Introduction

Metallabenzocyclobutenes of Group 14 are known only for silicon [1,2]. For germanium and tin, the smallest-ring representatives of the metallabenzocycloalkenes are 2,3-dihydro-1,1-dimethyl-1-germabenzocyclopentene and its tin analogue, which were obtained by rearrangement of the corresponding *p*-trimethylmetalphenylcarbenes [3].

Recently, we reported the synthesis of a titanabenzocyclobutene from titanocene dichloride and a novel 1,3-divalent organomagnesium reagent, i.e. (an oligomer of) 1,2-dihydro-1-magnesabenzocyclobutene [4]. In view of the general usefulness of 1,3-di-Grignard reagents for the synthesis of metallacyclobutanes [5–8], it was tempting to explore the applicability of the new reagent for the preparation of metallabenzocyclobutenes of silicon, germanium and tin.

Results and discussion

(Oligomeric) 1,2-dihydro-1-magnesabenzocyclobutene (5)

An obvious starting material for the preparation of the required 1,3-di-Grignard reagent **3** is 1-bromo-2-bromomethylbenzene (**1a**). However, in contrast to its higher homologues 2-(2-bromophenyl)ethylbromide and 3-(2-bromophenyl)propylbromide,

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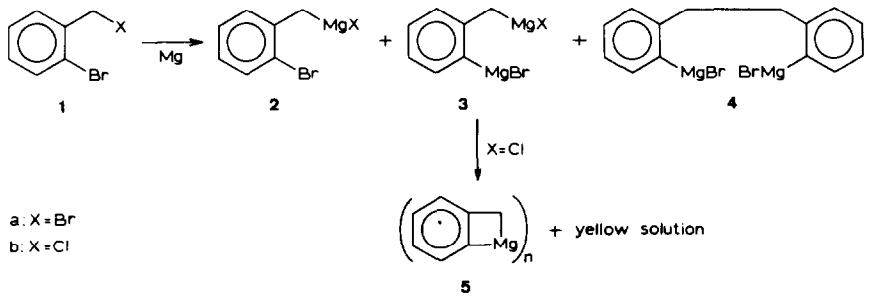


SCHEME 1

which are readily converted to the corresponding di-Grignard reagents by magnesium in tetrahydrofuran [9], **1a** is not an easy halide to convert into a Grignard reagent. Under the same conditions it underwent a quantitative Wurtz coupling followed by Grignard formation to give **4** (Scheme 1 and Table 1, entry 2). When the reaction was performed in diethyl ether instead of tetrahydrofuran as solvent, the mono-Grignard reagent **2** was obtained in reasonable yield [10–13]. Our own attempts to improve these yields (Table 1, entry 1) or to convert **2a** to **3a** (Table 1, entries 3 and 4) were only partly successful.

Better results were obtained with 1-bromo-2-chloromethylbenzene (**1b**) as starting material. In diethyl ether, Wurtz coupling (**4**) was a minor side reaction, and **2b** was obtained in good yield (Table 1, entry 5). Compound **2b** could be converted to **3b** in a separate step; this process was imcomplete in diethyl ether (Table 1, entry 7) but worked satisfactorily when diethyl ether was displaced by tetrahydrofuran as the solvent (Table 1, entry 8). However, the best procedure turned out to involve the slow addition of a dilute solution of **1b** in tetrahydrofuran to magnesium metal which had been sublimed, then powdered (10 mesh) and activated with a little 1,2-dibromoethane (Table 1, entry 6). This gave a greenish suspension, which contained **3b** in more than 95% yield; sometimes, **4** and other minor byproducts

TABLE 1

GRIGNARD REAGENTS FROM DIHALIDES AND MAGNESIUM

Entry	Dihalide	Solvent	Yield (%)		
			2a	**3a**	**4**
1	**1a**	Et_2O	79–81	0	19–21
2	**1a**	THF	0	0	100
3	**2a**	Et_2O	94–100	0–6	–
4	**2a**	THF	86–88	12–14	–
			2a	**3b**	**4**
5	**1b**	Et_2O	90–94	0	6–10
6	**1b**	THF	0	96–100	0–4
7	**2b**	Et_2O	74–77	23–26	–
8	**2b**	THF	1–21	79–99	–
9	**1a** [a]	THF	0	82	18

[a] Reaction with magnesium anthracene.

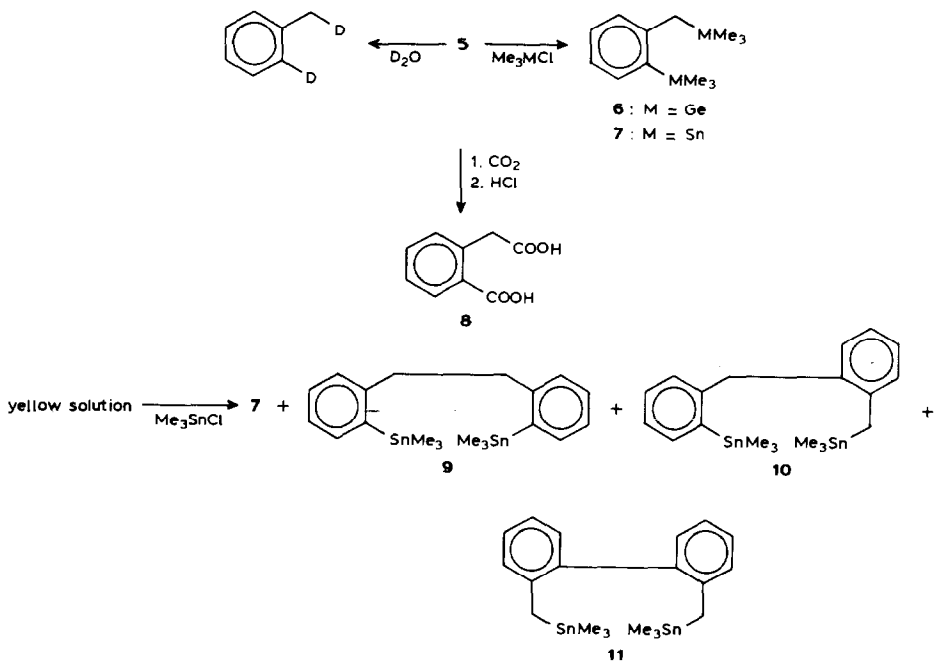
(vide infra) were practically absent. Nevertheless, in order to obtain a reliably pure reagent, it is advisable to let the greenish suspension settle and separate into a yellow solution and a greyish white precipitate. The solution contains most of the impurities and is decanted. The precipitate is washed twice with tetrahydrofuran; this removes not only residual impurities, but also all the halide, mostly as magnesium dihalide. The resulting sparingly soluble residue has the composition of pure **5** (vide infra), and is obtained in 84–90% yield relative to **1b** (Scheme 1 and Table 1).

The use of sublimed magnesium in the preparation is important, as commercially available magnesium turnings gave inferior results, e.g. more **4** was formed and the conversion of **2b** to **3b** was incomplete. We therefore also investigated the use of magnesium-anthracene as a substitute for the metal; this has been reported to give high yields of benzylic Grignard reagents [14]. The reaction of **1b** with two molar equivalents of magnesium anthracene in tetrahydrofuran did, indeed, give **5** in good yield, but there were also significant amounts of **4** (Table 1, entry 9). Another drawback of this method is the low solubility of anthracene in tetrahydrofuran, which makes the separation of **5** difficult.

The characterization of **5** as a diorganylmagnesium compound was initially by hydrolysis. Besides a quantitative yield of toluene, this gave an aqueous phase which on titration with HCl and EDTA [15] analyzed correctly for two equivalents of base per mol of magnesium. It has been well established that organomagnesium heterocycles are not stable as five or even higher-membered rings [8]; for this reason alone is highly unlikely that **5** occurs in the monomeric form. Moreover, the low solubility of pure **5** in tetrahydrofuran (1.6 mmol l^{-1}) or diethyl ether (0.7 mmol l^{-1}) is suggestive of a higher state of association, or even an oligomer–polymer equilibrium. The ready disproportionation of **3b** in tetrahydrofuran is yet another example of the growing number of short chain di-Grignard reagents showing the same tendency [16]. In all cases, this is probably caused by removal of the sparingly soluble oligomeric diorganylmagnesium from the Schlenk equilibrium.

The identity of **5** was confirmed by the derivatization reactions shown in Scheme 2. With D_2O, toluene-d_2 was obtained which, according to mass spectral analysis, contained 99% D_2; with an excess of chlorotrimethylgermane or chloromethylstannane, the expected derivatives **6** and **7**, respectively, were formed in 92–93% yield from unpurified **5**; addition of a suspension of **5** to dry ice yielded, after work-up 93% of homophtalic acid (**8**; 60% isolated yield).

The by-products contained in the yellow solution were characterized by derivatization with chlorotrimethylstannane (Scheme 2). Product analysis by GC/MS showed the presence of **7**, **9**, **10** and **11** in the ratio 16/4/2/1. Compound **9** was identified by independent synthesis from **4** and chlorotrimethylstannane. Compounds **10** and **11** were isomers of **9**; the suggested structures are the only reasonable possibilities, but may have to be reversed as they are based on mass spectral evidence only. Compounds **9**–**11** indicate the presence of the corresponding di-Grignard reagents as precursors in the yellow solution. As mentioned above for the formation of **4** (which is the precursor of **9**), these dimerization products are a result of coupling of radical intermediates in the Grignard formation reaction. From **1b**, the two radicals **A** and **B** may be expected (Scheme 3). The combination **A** + **A** yields (after Grignard formation from the intermediate 2,2′-dibromodibenzyl) **4** and hence **9**; similarly the combination **A** + **B** leads to **10** and **B** + **B** to **11**. During the



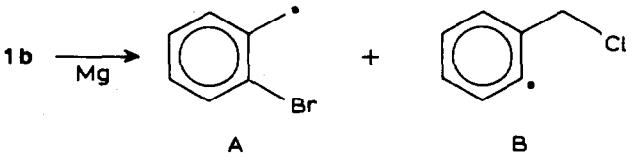
SCHEME 2

formation of **3b**, aliquots were taken from the reaction mixture and after hydrolysis product analysis by GC/MS showed the presence of more 2-bromotoluene than benzyl chloride (cf. the preferential formation of **2** from **1** in diethyl ether; Table 1, entry 5). Thus it is likely that **A** is present in a higher concentration than **B** during the Grignard formation, which is consistent with the observed ratio of **9**, **10** and **11**.

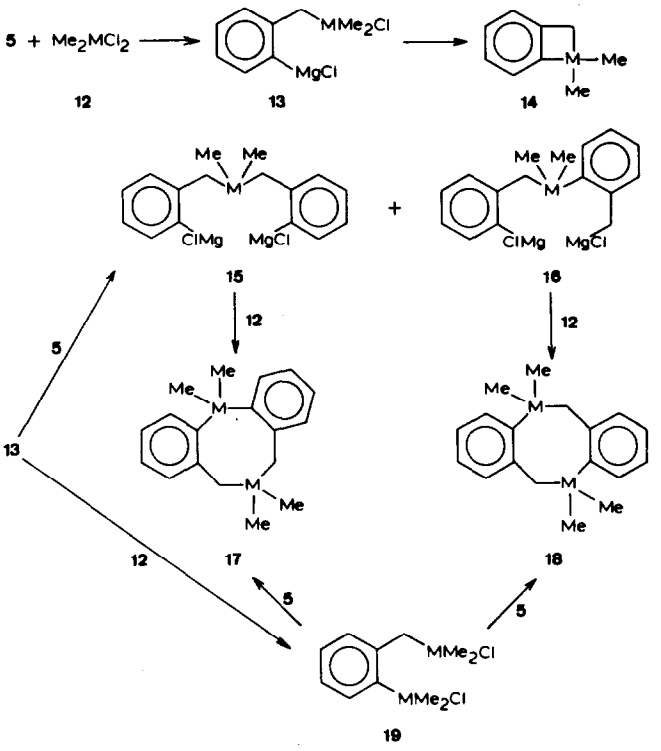
1,2-Dihydro-1,1-dimethyl-1-silabenzocyclobutene (14a)

The title compound **14a** [2a] and its 1,1-diphenyl analogue [1] have been prepared previously. The syntheses were performed under Barbier type conditions in diethyl ether by reaction of **1a**, magnesium, and dichlorodimethylsilane (**12a**) or dichlorophenylsilane; the yields were moderate (27–36%). Multistep alternatives to these procedures gave similar overall yields [2].

In order to test the new approach we treated pure **5** in tetrahydrofuran with **12a** in equimolar amount. Although the yield of **14a** (58%) was better than that obtained by the older methods, **14a** was not the only product; dibenzyldimethylsilane (12%) and the two isomeric dimers of **14a**, i.e. **17a** (5%) and **18a** (5%) were also isolated by preparative GLC. The rest is probably polymeric material.



SCHEME 3



SCHEME 4. a: M = Si; b: M = Ge; c: M = Sn.

The eight-membered ring compounds **17a** and **18a** were identified from their spectroscopic data (see Experimental); in particular, the distinction between the two structures is based on the observation of two Me_2Si groups for **17a** ($\delta(^1H)$: −0.11 and 0.49 ppm, respectively) and one for **18a** ($\delta(^1H)$: −0.02 ppm). The product formation can be accounted for as shown in Scheme 4.

Although in principle, the first reaction between **5** and **12a** may occur either at the benzyl or the aryl position of **5**, our experience with dichloromethylstannane (vide infra) suggests that the benzyl Grignard function is by far more reactive; therefore, **13a** may be expected to be the major primary intermediate. Intramolecular reaction between the two functions in **13a** gives **14a**; this is the entropically-favoured main pathway. It is, however, not unexpected [17] that a combination of two reactive bifunctional reagents such as **5** and **12a** also gives rise to higher condensation products. Two of the possible reaction sequences starting from **13a**, are shown in Scheme 4. The reaction of **13a** with **5** will give **15a** and **16a**; both may react with **12a** to furnish in two steps, **17a** and **18a**. We consider this course of events less likely for two reasons, firstly, **5** is only slightly soluble and its concentration is low; secondly, the observed 1/1 ratio of **17a** and **18a** requires an equal reactivity of the benzyl and aryl functions of **5** in this step, which is in contradiction with the observation above mentioned. More consistent with our result is rapid reaction of **13a** with **12a** to give **19a**, since the concentration of **12a** is high, and, as a dichlorosilane, it is more reactive than the monochlorosilane **13a**. The two mono-

chlorosilane functions of **19c**, however, will have a comparable reactivity and will be attacked by the benzylic position of **5** with approximately equal probability. As the regiochemistry for the formation of **17a** and **18a** is determined in this step, their 1/1 ratio can be easily understood. The reason for the rather high yield of dibenzyldimethylsilane is not clear. Probably this product comes from **15a**, because upon deuteration with D_2O before work-up, **15a**-d_2 containing more than 90% D_2 was detected by GC/MS.

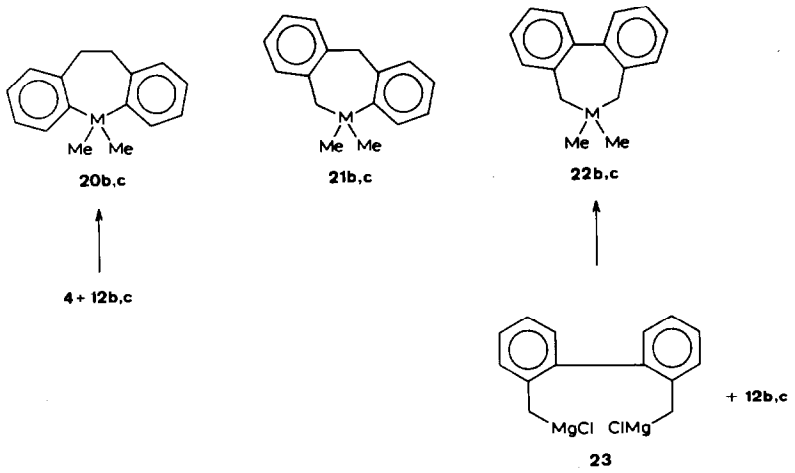
*1,2-Dihydro-1,1-dimethyl-1-germabenzocyclobutene (**14b**)*

In comparison to those containing silicon, four-membered rings containing germanium are generally less stable [20,21] and, indeed, **14b** had not been reported previously and turned out to be highly reactive.

In our initial experiments, we treated unpurified **5** with dichloromethylgermane (**12b**) at room temperature. The greenish suspension of **5** immediately turned colourless, and after the usual work up, no **14b** was obtained. Instead, we isolated benzylchlorodimethylgermane ($PhCH_2GeMe_2Cl$; 6%), **17b** (16%), **18b** (20%) and a mixture of the germepins **20b** (3%), **21b** (1%), and **22b** (1%), by preparative GLC. Again, the structure assignment is based on spectroscopic data, including on the observation of two Me_2Ge signals for **17b** ($\delta(^1H)$: 0.04 and 0.44 ppm, respectively) and one signal for **18b** ($\delta(^1H)$ 0.32 ppm). Interestingly, **17b** occurs in a conformation which is frozen on the NMR time scale, since the CH_2 protons show an AB-pattern (δ(A) 2.62, δ(B) 2.56 ppm, J(AB) 3 Hz) (cf. the next paragraph on the tin analogues). The identity of the germepins was established by ^1H NMR spectroscopy and by GC/MS (see Experimental). The structures of **20b** and **22b** were confirmed by independent synthesis from the di-Grignard reagents **4** and **23**, respectively (Scheme 5); the structure of **21b** as an isomer of **20b** and **22b** follows by exclusion and from the nonequivalence of the two methylene groups in the ^1H NMR spectrum.

Under identical conditions, purified **5** reacted with **12b** to give **14b** in the reasonable yield of 56%; in this case **17b** (8%) and **18b** (16%) were the only by-products. Incidentally, this latter observation shows that **20b**, **21b** and **22b** from the previous experiment are not derived from or related to **5** or **14b**, and must instead be formed from di-Grignard precursors such as **4** [22] and **23**, which are side products from the reaction of **1b** with magnesium and present only in the "yellow solution" (vide supra).

The characterization of **14b** was difficult because of its extreme reactivity and its sensitivity to air and moisture. Its yield was determined by quantitative GLC analysis (hexamethylbenzene as internal standard), but even under these conditions **14b** decomposed to some extent. By use of preparative GLC with rigorous exclusion of oxygen and water, we succeeded in isolating a small sample for spectroscopy identification. The ^1H NMR spectrum (see Experimental) was consistent with the proposed structure. The monomeric formula of **14b** follows unequivocally from the mass spectrum. First of all, the highest mass ion was $\mathbf{14b}^{+\cdot}$ ($m/z = 194$), whereas the dimers **17b** and **18b** had molecular ion peaks at $m/z = 388$ and no detectable ions at $m/z = 194$. Secondly, the molecular ions $\mathbf{17b}^{+\cdot}$ (5%) and $\mathbf{18b}^{+\cdot}$ (4%) have low intensities, while $\mathbf{14b}^{+\cdot}$ (63%) is unusually intense. This is an indication of the high strain in **14b**, which in $\mathbf{14b}^{+\cdot}$ causes ring opening of the four-membered ring (without change of mass) to compete effectively with the normal fragmentation



SCHEME 5

mode, i.e. loss of a methyl group to give $[\mathbf{14b} - Me]^+$ (100%). This phenomenon has also been observed for stannacyclobutanes [23], and seems to be diagnostic for highly strained four-membered metallacycles.

*Attempts to prepare 1,2-dihydro-1,1-dimethyl-1-stannabenzocyclobutene (**14c**)*

Four-membered rings containing tin as a heteroatom are even less stable than those of germanium, presumably because the ring strain is even greater owing to the greater length of tin–carbon bonds; in keeping with this, only a limited number of four-membered tin rings is known [6,8,17,23]. Consequently, in addition to the problems already encountered in the synthesis of **14a** and **14b**, specific difficulties were envisaged in the attempt to prepare **14c**, and **14c** could not, in fact, be obtained; even the indirect evidence for its formation was not conclusive in spite of considerable efforts. The outcomes of the reactions between **5** and dichloromethylstannane (**12c**) are summarized briefly in Table 2. (See also Schemes 4 and 6, and Experimental). The following aspects are noteworthy.

(a) Product formations can in general be accounted for by the sequences depicted in Scheme 4. Additional evidence for postulated intermediates comes from **7** (derived from **19c**) and the tentatively identified regioisomers **28** (derived from **19c** plus **5**).

(b) As discussed for **14a**, products resulting from reaction of **5** at the benzyl position are normally dominant (i.e. **24**, **25** and/or **27**). If substitution at the aryl position occurs, it mostly does so in combination with benzyl substitution (**7** and **28**).

(c) The reaction with unpurified **5** (Table 2, entry 1) gave the additional products **20c**, **21c** and **22c**; **20c** and **22c** were independently synthesized as described for the germanium analogues (Scheme 5). Their formation can be accounted for as for the germanium series. In contrast to the flexible germepins **20b** and **22b** both **20c** and **22c** have a conformation which is frozen on the NMR time scale, as evidenced by AB-patterns for the CH_2 protons.

(d) The "dimers" of **14c**, the eight-membered ring compounds **17c** and **18c**, were formed in yields varying between 7 and 20%; the high yield obtained in entry 6 is noteworthy. Also noteworthy is that again (see **17a** and **18a**) these products were in

TABLE 2

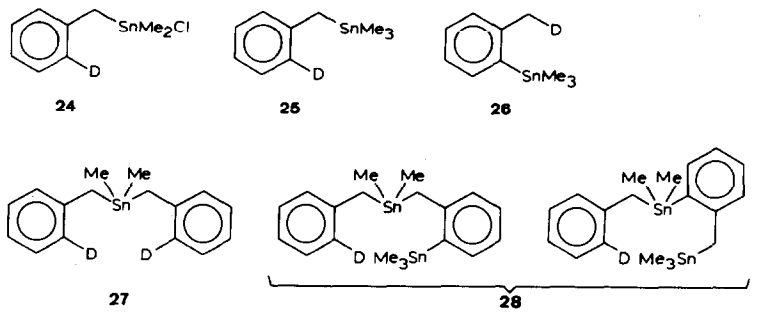
PRODUCT FORMATION FROM **5** AND **12c** [a]

Entry	Reaction conditions			Products (yield in %)							
	Addition temp. (°C)	Reaction temp. (°C); time (h)	MeMgBr	**7**	**17c**	**18c**	**24**	**25**	**26**	**27**	**28**
1 [b]	25	25; 4	no	–	8	8	1	0	0	1 [b]	–
2	−20	−20; 4	no	–	9.5	9.5	34	–	–	9	–
3	−20	−20; 48	no	–	11.5	11.5	14	–	–	11	–
4	−20	−20; 48	yes	9	10	10	0	14	0	10	0
5	−70	−70; 4 −20; 3	yes	20	10	10	0	2	1	1	8
6 [c]	−20	−20; 3	yes	8	20	20	0	1	0	1	0
7	−20 [d]	25; 4	yes	9	11.5	11.5	0	10	1	13	5
8	−20	25; 4	yes	9	7	7	0	2	0	9	0
9	−110; 0.5 h	−20; 17	yes	23	12	12	0	3	2	1	8
10	25 [e]	23; 3	yes	0	11	11	0	14	9	16	0

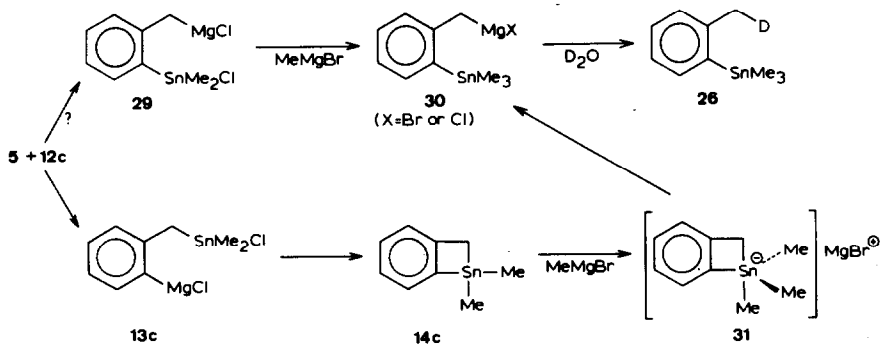
[a] Except for entry 1, purified **5** was used and the reaction mixture was quenched with D_2O; see also Experimental. [b] For entry 1, unpurified **5** was used. Quenching was performed with H_2O and the undeuterated analogues of **25** and **27** were obtained. Other products were **20c** (2%), **21c** (1%) and **22c** (1%). [c] Reaction conditions: additions of **12c** at −20°C; after 4 h, THF was distilled off and replaced by n-pentane and filtered; the filtrate was reacted with MeMgBr, followed by quenching with D_2O. [d] Before warming to room temperature, the reaction mixture was diluted with a 10-fold volume of THF. [e] Reaction conditions: **12c** and **5** were simultaneously added during 2 h to a large volume of THF (dilution 1/10), as in entry 7.

1/1 ratio, in spite of the very different conditions. As with silicon and germanium analogues, distinction between **17c** and **18c** was possible because **17c** has two different Me_2Sn groups while those of **18c** are identical (^1H NMR). In connection with flexibility of the eight-membered rings we note the interesting trend that on the NMR time scale in the tin series, both **17c** and **18c** are frozen (AB-pattern of the CH_2 protons), while in the germanium series **17b** is frozen and **18b** not, and the silicon compounds **17a** and **18b** are both flexible. This confirms the trend observed for the seven-membered ring systems (vide supra).

(e) Although the reaction conditions were varied considerably, **14c** was never observed directly. The only indicator for its possible intermediacy is **26**; as shown in Scheme 7, this may be formed from **14c** and methylmagnesium bromide via the ate



SCHEME 6



SCHEME 7

complex **31**, followed by ring opening to **30** (X = Br) and deuterolysis. Such ate complexes have been postulated in the analogous ring opening of stannacyclobutanes [23]; tin ate complexes with all carbon substituents have recently been observed directly [24]. For the formation of **31** from **14c**, relief of angle strain provides the driving force; the cleavage of the benzylic bond in **31** is expected from intuition and from analogous cleavage of **14a** by nucleophiles [1,2a,d].

The following argument can be raised in favour of the formation of **26** via the intermediate **14c**. From Table 2 it can be concluded that **26** is only formed in reactions which are performed either at low temperature (entries 5 and 9) or at high dilution (entries 7 vs. 8, and entry 10). These conditions must be favourable for the survival of the unstable **14c**, which is not only endangered by thermal self-decomposition or polymerization, but also by attack from the various organomagnesium reagents and intermediates in the reaction mixture (see Scheme 4). However, this item of evidence is not compelling, as the combination of **5** and **12c** to give **29**, though less likely, cannot be excluded; **29** could after transformation to **30** (X = Cl) and deuterolysis also lead to **26** (Scheme 7).

Experimental

^{1}H NMR spectra were recorded on a Bruker WH 90 or a Bruker WM 250 spectrometer, operating at a frequency of 90 or 250 MHz, respectively. ^{13}C NMR spectra and ^{29}Si NMR spectra were recorded on a Bruker WM 250 spectrometer, operating at frequencies of 63 and 50 MHz, respectively; the ^{29}Si NMR signal was enhanced by polarization transfer (INEPT) [25]. All products were analyzed by GC/MS, using a Hewlett Packard 5360 mass spectrometer or a Finnigan 4000 mass spectrometer, respectively; high resolution measurements were performed with a Varian CH5DF mass spectrometer, operating at an ionization potential of 70 eV. The ions containing Si, Ge or Sn showed the expected isotope pattern; when more than one metal atom was present, only the ions containing exclusively the most abundant isotope (i.e. ^{29}Si, ^{94}Ge or ^{120}Sn) are listed. Boiling points and melting points are uncorrected. GLC analyses and purifications were performed on a Intersmat GC120 (10% OV101, 1/8″, 1.5 m, FID and 10% OV101, 1/4″, 1.5 m, TCD). The experiments with **1**, as well as with unpurified **5**, were performed under nitrogen, using standard glass equipment; the other experiments were performed in

a completely sealed and evacuated glass apparatus [15]. Microanalyses were performed by the Instituut voor Toegepaste Chemie, TNO, Zeist, The Netherlands, under the supervision of Mr. G.J. Rotscheid.

Grignard formation reactions

The starting dihalides **1a** [26] and **1b** [27] were prepared by published procedures; they were distilled twice and found to be more than 99.5% pure by GLC. Magnesium metal was sublimed and powdered and only particles passing through a 10 mesh sieve were used; other forms of the metal, in particular commercial magnesium turnings, gave inferior results in the preparation of **5**.

The reactions between **1** and magnesium (Table 1) were conducted on a 3–10 mmol scale of **1**; magnesium was used in a ten-fold excess in 100–300 ml diethyl ether or THF. At various times, samples were hydrolyzed and analyzed by acid/base and EDTA-titration [15] as well as by quantitative GLC analysis with authentic samples as standards.

1,2-Dihydro-1-magnesabenzocyclobutene (5)

To 40.8 mmol of magnesium (0.98 g, 10 mesh) was added a solution of 0.2 mmol 1,2-dibromoethane (0.037 g) in 7 ml THF. After 15 min stirring a solution of 4.1 mmol of **1b** (0.85 g) in 50 ml THF was added during 4 h. When the addition was complete, the mixture was stirred for 3 h, then 100 ml THF was added. The greenish suspension was filtered through a coarse glass-filter to remove the residual magnesium, and the filtrate allowed to settle and to separate into the yellow solution and a greyish white precipitate. The solution was decanted and the precipitate washed twice with THF. After drying of the precipitate under vacuum, 200 ml of THF was added. Titration of an aliquot of the suspension with acid/base and EDTA [15] revealed two equivalents of base per mol magnesium. The purity of the suspension of **5** in THF was checked by reaction of a sample with chlorotrimethylstannane; GC/MS analysis showed only the presence of **7**. The yellow solution was also analyzed by acid/base and EDTA titration; the first titration furnishes equivalents of "basic" (i.e. originally carbon bond) magnesium, the second gives the "total" gram-atom equivalents of magnesium; thus, 100% yield of **3b** (or **5** + MgBrCl) should yield 2 equivalents of "basic" magnesium and 2 gram-atom equivalents of "total" magnesium; the accuracy of the titration is estimated to be 2–3%. For the yellow solution, the results were 0.20 to 0.32 equivalents of "basic" magnesium and 1.0–1.16 gram-atom equivalents of "total" magnesium; the corresponding values for the precipitate (i.e. **5**) formed in the same experiment were 1.80 to 1.68 equivalents of "basic" magnesium and 0.90 to 0.84 equivalents of "total" magnesium.

A sample of the yellow solution was derivatized with chlorotrimethylstannane; GC/MS analysis (column: Chrompack, CP Sil 19 CB, length 51 m, diameter 0.21 mm; temperature: first 3 min at 80°C, then raised by 20°C/min. **7**, **9**, **10**, **11** retention times: 7.612, 11.202, 11.403, 11.039 min, respectively; ratio: 16/4/2/1). Compounds **10** and **11** were characterized by their mass spectra only; their structure assignment may therefore have to be reversed. **10**. Mass spectrum *m/z* (relative intenstiy): 345 (5) $[M - Me_3Sn]^+$, 330 (10), 315 (100), 179 (40), 165 (55), 91 (3). **11**. Mass spectrum *m/z* (relative intensity): 345 (3) $[M - Me_3Sn]^+$, 315 (5), 179 (100), 165 (76), 91 (16).

1-Trimethylgermyl-2-trimethylgermylmethylbenzene (6)

A suspension of 1.15 mmol of unpurified **5** in 17 THF was added at room temperature to a solution of 2.50 mmol of chlorotrimethylgermane (386 mg) in 4 ml of THF. The mixture was stirred for 1 h then saturated aqueous NH_4Cl was added and the aqueous layer was extracted twice with diethyl ether. The organic fractions were combined, dried and the solvent evaporated. The residue was purified by preparative GLC.

6. Yield: 92%. ^1H NMR ($CDCl_3$, 250 MHz): δ 0.16 (s, 9H, CH_3), 0.44 (s, 9H, CH_3), 2.39 (s, 2H, CH_2), 7.02–7.39 ppm (m, 4H, arom.). ^{13}C NMR ($CDCl_3$, 63 MHz): δ −1.6 (q, ^1J(CH) 125 Hz, C(9)), 0.2 (q, ^1J(CH) 125 Hz, C(8)), 26.7 (td, ^1J(CH) 125, ^3J(CH) 4 Hz, C(7)), 123.5 (dd, ^1J(CH) 161, ^3J(CH) 8 Hz, C(5)), 127.6 (dd, ^1J(CH) 155, ^3J(CH) 7 Hz, C(3)), 128.4 (dd, ^1J(CH) 159, ^3J(CH) 8 Hz, C(4)), 133.7 (dd, ^1J(CH) 158, ^3J(CH) 7 Hz, C(6), 138.9 (C(1)), 146.7 ppm (C(2)).

The aromatic ^{13}C chemical shifts were in good agreement with those calculated from the ^{13}C chemical shifts of toluene corrected for shifts produced in toluene by a trimethylgermyl substituent [28]. Mass spectrum *m/z* (relative intensity): 328 (1) $M^{+\cdot}$, 194 (74), 179 (41), 119 (100), HRMS ($C_{13}H_{24}Ge_2$): found 328.0308, calc 328.0315. Found: C, 49.33; H, 7.48; Ge, 43.19. $C_{13}H_{24}Ge_2$ calc: C, 48.97; H, 7.43; Ge, 43.60%.

1,2-Bis(2-trimethylgermylphenyl)ethane

Yield: 2%. For identification this was prepared from **4** [29] and chlorotrimethylgermane as described for **6**; yield: 96%. ^1H NMR ($CDCl_3$, 250 MHz): δ 0.47 (s, 18H, CH_3), 3.07 (s, 4H, CH_2), 7.20–7.49 ppm (m, 8H, arom.). ^{13}C NMR ($CDCl_3$, 63 MHz): δ 0.1 (q, ^1J(CH) 125 Hz), 37.7 (td, ^1J(CH) 129, ^3J(CH) 7 Hz), 125.5 (dd, ^1J(CH) 164, ^3J(CH) 6 Hz), 128.0 (dd, ^1J(CH) 151, ^3J(CH) 7 Hz, 128.8 (dd, ^1J(CH) 159, ^3J(CH) 8 Hz, 138.8 (dd, ^1J(CH) 158, ^3J(CH) 7 Hz), 140.7, 146.7 ppm. Mass spectrum *m/z* (relative intensity): 418 (2) $M^{+\cdot}$, 299 (19), 269 (75), 179 (25), 178 (38), 119 (100), 89 (40). HRMS ($C_{20}H_{30}Ge_2$): found 418.0771, calc: 418.0754.

1-Trimethylstannyl-2-trimethylstannylmethylbenzene (7)

This was prepared from unpurified **5**, as described for **6**; yield: 93%. ^1H NMR ($CDCl_3$, 250 MHz): δ 0.11 (s, 9H, $^2J(H^{117}Sn/^{119}Sn)$ 51/53 Hz, CH_3), 0.35 (s, 9H, $^2J(H^{117}Sn/^{119}Sn)$ 52/55 Hz, CH_3), 2.47 (AB, 2H, δ(A) 2.50, δ(B) 2.43, J(AB) 4, ^2J(HSn) 62 Hz, CH_2), 7.01–7.49 ppm (m, 4H, arom.). ^{13}C NMR ($CDCl_3$, 63 MHz): δ −9.5 (q, ^1J(CH) 128, ^1J(SnC) 320 Hz, C9), −8.2 (q, ^1J(CH) 128, ^1J(SnC) 338 Hz, C(8)), 24.0 (t, ^1J(CH) 128, ^1J(SNC) 263 Hz, C(7)), 122.9 (ddd, ^1J(CH) 157, ^2J(CH) 4 Hz, ^3J(CH) 8, J(SnC) 41 Hz, C(4)), 126.4 (dd, ^1J(CH) 154, ^3J(CH) 13, J(SnC) 11 Hz, C(6)), 128.7 (dd, ^1J(CH) 159, ^3J(CH) 8, J(SnC) 39 Hz, C(5)), 136.2 (ddd, ^1J(CH) 156, ^2J(CH) 3, ^3J(CH) 8, J(SnC) 40 Hz, C(3)), 138.8 (C(1), 149.8 ppm (C(2)). The aromatic ^{13}C chemical shifts were in good agreement with those calculated from the ^{13}C chemical shifts of toluene corrected for shifts produced in toluene by a trimethylstannyl substituent [28]. Mass spectrum *m/z* (relative intensity): 420 (4) $M^{+\cdot}$, 405 (4), 240 (89), 225 (76), 165 (100), 135 (25). HRMS ($C_{13}H_{24}Sn_2$): found: 419.9903, calc: 419.9919. Found: C, 38.12; H, 5.88; Sn, 55.43. $C_{13}H_{24}Sn_2$ calc: C, 38.38; H, 5.79; Sn, 55.83%.

1,2-Bis(2-trimethylstannylphenyl)ethane (9)

Yield: 2%. For identification, **9** was prepared from **4** [29] and chlorotrimethyl-

stannane, as described for **6**: yield: 93%. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.37 (s, 18H, $^2J(H^{117}Sn/^{119}Sn)$ 52/54 Hz, CH_3), 3.01 (s, 4H, CH_2), 7.21–7.51 ppm (m, 8H, arom.). ^{13}C NMR ($CDCl_3$, 63 MHz): δ −8.0 (q, ^1J(CH) 129, ^1J(SnC) 348 Hz), 40.7 (td, ^1J(CH) 128, ^3J(CH) 9, J (SnC) 27 Hz), 125.6 (dd, ^1J(CH) 160, ^3J(CH) 7, J(SnC) 48 Hz), 127.8 (d, ^1J(CH) 151, J(SnC) 38 Hz), 128.8 (dd, ^1J(CH) 159, ^3J(CH) 7, J(SnC) 42 Hz), 136.2 (dd, ^1J(CH) 159, ^3J(CH) 8, J(SnC) 37 Hz), 141.8, 148.2 ppm. Mass spectrum m/z (relative intensity): 495 (2) $[M-Me]^+$, 330 (10), 315 (100), 179 (25), 178 (23), 165 (47), 135 (27), 120 (20). HRMS ($C_{17}H_{29}Sn_2 = [M - Me]^+$): found 495.0129, calc. 495.0154.

Homophthalic acid (8)

A suspension of 0.6 mmol of unpurified **5** in 8.5 ml THF was added to an excess of dry ice. The mixture immediately became yellow, but turned colourless on warming to room temperature. After quenching with 1 *M* HCl, the product was isolated by extracting the aqueous fraction twice with diethyl ether. The organic layers were combined and dried, and the solvent evaporated. The yield was shown to be 93% by ^{1}H NMR analysis (cyclopentane as internal standard). The crude product was recrystallized from H_2O. Yield (isolated): 60%. M.p. 180°C (lit. m.p. 181°C [30]). ^{1}H NMR (DMSO-d_6/D_2O, 1/1, 90 MHz): δ 4.00 (s, 2H, CH_2), 7.05–7.60 ppm (m, 4H, arom.) [31].

*Reaction of **5** with **12a***

A suspension of 4.08 mmol of **5** in 57 ml THF was added at room temperature to a solution of 4.08 mmol of **12a** in 10 ml of THF. After 24 h stirring saturated NH_4Cl was added and the aqueous fraction extracted twice with diethyl ether. The organic fractions were combined and dried, and the solvent was carefully evaporated. The residue was purified by preparative GLC; the yields were determined by quantitative GLC (FID, hexamethylbenzene as internal standard).

14a. Yield: 58%. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.47 (s, 6H, ^2J(HSi) 7 Hz, CH_3), 2.16 (s, 2H, CH_2), 7.25–7.44 ppm (m, 4H, arom.). ^{13}C NMR ($CDCl_3$, 63 MHz): δ −0.4 (q, ^1J(CH) 120 Hz), 20.2 (t, ^1J(CH) 131 Hz), 126.2 (dd, ^1J(CH) 158, ^3J(CH) 6 Hz), 126.9 (dd, ^1J(CH) 160, ^3J(CH) 7 Hz), 130.39 (d, ^1J(CH) 160 Hz), 130.43 (d, ^1J(CH) 160 Hz), 146.1, 150.7 ppm. ^{29}Si NMR ($CDCl_3$, 50 MHz): δ 9.25 ppm. Mass spectrum m/z (relative intensity): 148 (54) $M^{+\cdot}$, 133 (100).

Dibenzyldimethylsilane. Yield: 12%. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 0.12 (s, 6H, CH_3), 2.24 (s, 4H, CH_2), 7.07–7.52 ppm (m, 10H, arom.). Mass spectrum m/z (relative intensity): 240 (7) $M^{+\cdot}$, 149 (100), 121 (53), 91 (22).

*5,10,11,12-Tetrahydro-5,5,11,11-tetramethyldibenzo[b,g]-1,5-disilocin (**17a**).* Yield: 5%. ^{1}H NMR ($CDCl_3$, 90 MHz): δ −0.11 (s, 6H, CH_3), 0.49 (s, 6H, CH_3), 2.12 (s, 4H, CH_2), 6.87–7.22 (m, 8H, arom.). Mass spectrum m/z (relative intensity): 296 (81) $M^{+\cdot}$, 281 (65), 208 (86), 165 (12), 149 (25), 133 (100), 121 (20), 105 (49), 91 (20), 73 (50).

*5,6,11,12-Tetrahydro-5,5,11,11-tetramethyldibenzo[b,f]-1,5-disilocin (**18a**).* Yield: 5%. ^{1}H NMR ($CDCl_3$, 90 MHz): δ −0.02 (s, 12H, CH_3) 2.17 (s, 4H, CH_2), 6.87–7.22 ppm (m, 8H, arom.). Mass spectrum m/z (relative intensity): 296 (30) $M^{+\cdot}$, 281 (25), 208 (36), 165 (63), 149 (100), 133 (62), 121 (31), 105 (41), 91 (47), 73 (27).

Compound **17a** and **18a** could not be separated by either preparative GLC or TLC (silica).

Reactions of 5 with 12b

A suspension of 1.2 mmol of unpurified **5** in 17 ml of THF was added at room temperature to a solution of 1.2 mmol of **12b** (210 mg) in 5 ml of THF. After 4 h stirring, the mixture was worked up as described for **12a**. Compounds **17b** and **18b** could not separated by preparative GLC or TLC (silica); their ^{1}H NMR spectra were taken from the spectrum of a mixture of the two compounds.

Benzylchlorodimethylgermane. Yield: 6%. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 0.73 (s, 6H, CH_3), 2.74 (s, 2H, CH_2), 7.00–7.40 ppm (m, 5H, arom.). Mass spectrum *m/z* (relative intensity): 230 (25) $M^{+\cdot}$, 139 (100), 91 (66), 89 (12).

5,10,11,12-Tetrahydro-5,5,11,11-tetramethyldibenzo[b,g]-1,5-digermocin (17b). Yield: 16%. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 0.04 (s, 6H, CH_3), 0.44 (s, 6H, CH_3), 2.59 (AB, 4H, δ(A) = 2.62, δ(B) = 2.56, J(AB) 3Hz), 6.80–7.60 pm (m, 8H, arom.). Mass spectrum *m/z* (relative intensity): 388 (5) $M^{+\cdot}$, 373 (37), 269 (84), 195 (10), 179 (100), 178 (49), 151 (25), 119 (20), 89 (26).

5,6,11,12-Tetrahydro-5,5,11,11-tetramethyldibenzo[b,f]-1,5-digermocin (18b). Yield: 20%. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 0.32 (s, 12H, CH_3), 2.31 (s, 4H, CH_2), 6.80–7.60 ppm (m, 8H, arom.). Mass spectrum *m/z* (relative intensity): 388 (4) $M^{+\cdot}$, 373 (44), 269 (100), 195 (11), 179 (98), 178 (50), 119 (25), 89 (28).

6,11-Dihydro-11,11-dimethyl-5H-dibenzo[b,f]germepin (20b). Yield: 3%; **20b** was prepared independently from **4** [29] and **12b**. To a solution of 0.20 mmol of **4** in 35 ml of THF, a solution of 0.20 mmol **12b** (35.0 mg) in 1 ml THF was added at room temperature. After 1 h stirring, the mixture was worked up as usual; yield: 60%. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 0.59 (s, 6H, CH_3), 3.03 (s, 4H, CH_2), 7.17–7.53 ppm (m, 8H, arom.). Mass spectrum *m/z* (relative intensity): 284 (6) $M^{+\cdot}$, 269 (100), 179 (50), 178 (94), 89 (43) [22].

6,11-Dihydro-5,5-dimethyl-5H-dibenzo[b,e]germepin (21b). Yield: 1%. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 0.42 (s, 6H, CH_3), 2.67 (s, 2H, CH_2), 4.03 (s, 2H, CH_2), 7.10–7.50 ppm (m, 8H, arom.). Mass spectrum *m/z* (relative intensity): 284 $(22)^{+\cdot}$, 269 (52), 195 (100), 179 (42), 178 (42), 165 (41), 91 (88), 89 (48).

6,7-Dihydro-6,6-dimethyl-5H-dibenzo[c,e]germepin (22b). Yield: 1%. **22b** was prepared independently from **23** [32] and **12b**. To a solution of 1.0 mmol of **23** in 17 ml of THF at −78°C was added a solution of 1.0 mmol of **12b** (0.175 g) in 10 ml of THF. The mixture was stirred for 15 min at −78°C then 24 h at room temperature. Work up was as usual; yield: 40%. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 0.23 (s, 6H, CH_3), 1.96 (s, 4H, CH_2), 7.14–7.27 ppm (m, 8H, arom.) ^{13}C NMR ($CDCl_3$, 90 MHz): δ −4.2 (q, ^1J(CH) 126 Hz, 22.5 (td, ^1J(CH) 128, ^3J(CH) 8 Hz), 124.7 (dd, ^1J(CH) 160, ^3J(CH) 8 Hz), 127.2 (dd, ^1J(CH) 155, ^3J(CH) 4 Hz), 127.3 (dd, ^1J(CH) 154, ^3J(CH) 11 Hz), 129.6 (dd, ^1J(CH) 165, ^3J(CH) 2 Hz), 139.3, 140.1 ppm. Mass spectrum *m/z* (relative intensity): 284 (11) $M^{+\cdot}$, 269 (24), 180 (16), 179 (100), 178 (50), 89 (11). HRMS ($C_{16}H_{18}Ge$): found: 284.0623 calc: 284.0620.

When the reaction with pure **5** and **12b** was performed under the conditions described above, the yield of **14b** was shown to be 56% by quantitative GLC. **17b**: Yield: 8%. **18b**: Yield: 16% (hexamethylbenzene as internal standard). Under rigorous exclusion of oxygen and moisture, a mixture of benzylchlorodimethylgermane and **14b** (ratio 1/4) could be isolated by preparative GLC.

*1,2-Dihydro-1,1-dimethyl-1-germabenzocyclobutene (**14b**).* ^{1}H NMR (C_6D_6, 90 MHz): δ 0.63 (s, 6H, CH_3), 2.69 (s, 2H, CH_2), 7.05–7.40 (m, 4H, arom.). Mass spectrum *m/z* (relative intensity): 194(63) $M^{+\cdot}$, 179 (100), 164 (12), 151 (62), 91 (50), 89 (56).

*Reactions of **5** with **12c***

(a) Entry 1, Table 2

A suspension of 1.20 mmol of unpurified **5** in 17 ml of THF was added at room temperature of 1.20 mmol **12c** (265 mg) in 5 ml THF. After 4 h stirring the mixture was worked up as usual. Compounds **17c** and **18c** could not be separated by preparative GLC or TLC; the ^{1}H NMR spectra were taken of a mixture of the two compounds.

*5,10,11,12-Tetrahydro-5,5,11,11-tetramethyldibenzo[b,g]-1,5-distannocin (**17c**).* Yield: 8%. ^{1}H NMR ($CDCl_3$, 90 MHz): δ −0.04 (s, 6H, $^2J(H^{117}Sn/^{119}Sn)$ 50/52 Hz, CH_3), 0.44 (s, 6H, $^2J(H^{117}Sn/^{119}Sn)$ 50/53 Hz, CH_3), 2.62 (AB, 4H, δ(A) 2.67, δ(B) 2.58, J(AB) 4 Hz, CH_2), 6.73–7.56 ppm (m, 8H, arom.). Mass spectrum *m/z* (relative intensity): 480 (16) $M^{+\cdot}$, 465 (62), 330 (15), 315 (100), 225 (27), 210 (15), 180 (13), 135 (77), 91 (7).

*5,6,11,12-Tetrahydro-5,5,11,11,-tetramethyl[b,f]-1,5-distannocin (**18c**).* Yield: 8%. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 0.32 (s, 12H, ^2J ($H^{117}Sn/^{119}Sn$) 50/53 Hz, CH_3), 2.32 (AB, 4H, δ(A) 2.36, δ (B) 2.33, J (AB) 2 Hz, CH_2), 6.73–7.56 ppm (m, 8H, arom.). Mass spectrum *m/z* (relative intensity): 480 (6) $M^{+\cdot}$, 465 (77), 330 (12), 315 (58), 225 (14), 210 (7), 180 (5), 135 (29).

*6,11-Dihydro-11,11-dimethyl-5H-dibenzo[b,f]stannepin (**20c**).* Yield: 2%. **20c** was independently prepared from **4** [29] and **12c** by the procedure described for **20b**; yield: 79%. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 0.40 (s, 6H, $^2J(H^{117}Sn/^{119}SnH)$ 53/56 Hz, CH_3), 3.13 (AB, 4H, δ(A) 3.17, δ (B) 3.13, J(AB) 3 Hz, CH_2), 7.16–7.62 ppm (m, 8H, arom.). Mass spectrum *m/z* (relative intensity): 315 (100) $[M - Me]^+$, 180 (16), 179 (50), 178 (61), 135 (31) [22].

*6,11-Dihydro-5,5-dimethyl-5H-dibenzo[b,e]stannepin (**21c**).* Yield: 1%. Mass spectrum *m/z* (relative intensity): 315 (100) $[M - Me]^+$, 179 (31), 178 (33), 135 (21).

*6,11-Dihydro-6,6-dimethyl-5H-dibenzo[c,e]stannepin (**22c**).* Yield: 1%. **22c** was independently prepared from **23** [32] and **12c** as described for **22b**; yield: 35%. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 0.18 (s, 6H, $^2J(H^{117}Sn/^{119}Sn)$ 50/53 Hz, CH_3), 2.07 (AB, 4H, δ(A) 2.20, δ(B) 1.95, J(AB) 11 Hz, CH_2), 6.73–7.22 (m, 8H, arom.). ^{13}C NMR ($CDCl_3$, 63 MHz): δ −10.3 (q, ^1J (CH) 131, J (SnC) 350 Hz), 17.4 (t, ^1J(CH) 132, J (SnC) 287 Hz), 123.9 (dd, ^1J (CH) 160, ^3J(CH) 8, J (SnC) 16 Hz), 126.5 (dd, ^1J (CH) 151, ^3J (CH) 12, J (SnC) 23 Hz), 127.3 (dd, ^1J (CH) 158, ^3J (CH) 7, J (SnC) 9 Hz), 129.7 (dd, ^1J (CH) 158, ^3J (CH) 7, J (SnC) 9 Hz), 139.7, 140.5 ppm. Mass spectrum *m/z* (relative intensity): 330 (26) $M^{+\cdot}$, 315 (82), 179 (100), 178 (92), 135 (96). HRMS ($C_{16}H_{18}Sn$): found 330.0407, calc. 330.0429.

(b) General procedure for entries 2–10, Table 2

These experiments involved treatment of 0.2 mmol of **5** in 10 ml of THF with 0.2 mmol of **12c** in 3 ml of THF at the indicated temperature (column 2). The mixture was stirred for the indicated temperature and time (column 3), then, with the

exception of entries 2 and 3, treated with a two-fold excess of MeMgBr in diethyl ether (0.185 *M*) and stirred 2 h at room temperature. Subsequently 1 ml of D_2O was added, and the mixture stirred for 1 h. The reaction vessel was opened, and diethyl ether was added followed by saturated aqueous NH_4Cl. The organic fraction was separated and dried, and the solvent carefully evaporated. The residue was analyzed by GC/MS. The yields were established by quantitative GLC (FID hexamethylbenzene as internal standard). The deuterium content was determined from the mass spectra by comparison with those of the nondeuterated analogues.

*1-Chlorodimethylstannylmethyl-2-deuterobenzene (**24**).* Mass spectrum *m/z* (relative intensity): 277 (11) $M^{+\cdot}$, 185 (69), $SnMe_2Cl^+$, 92 (100), $C_7H_6D^+$.

*Benzylchlorodimethylstannane (**24** − H).* ^1H NMR ($CDCl_3$, 90 MHz): δ 0.70 (s, 6H, ^2J ($H^{117}Sn/^{119}Sn$) 51/53 Hz, CH_3), 2.70 (s, 4H, CH_2), 7.05–7.35 (m, 5H, arom.). Mass spectrum *m/z* (relative intensity): 276 (11) $M^{+\cdot}$, 185 (65), $[SnMe_2Cl]^+$, 91 (100), $C_7H_7^+$.

*1-Deutero-2-trimethylstannylmethylbenzene (**25**).* Mass spectrum *m/z* (relative intensity): 257 (8) $M^{+\cdot}$, 242 (8), $[M - Me]^+$, 165 (100), $SnMe_3^+$, 92 (78), $C_7H_6D^+$.

*Benzyltrimethylstannane (**25** − H).* ^1H NMR ($CDCl_3$, 90 MHz): δ 0.05 (s, 9H, ^2J ($H^{117}Sn/^{119}Sn$) 51/54 Hz, CH_3), 2.32 (s, 2H, ^2J(HSn) 62 Hz), 6.91–7.36 ppm (m, 5H, arom.) [33]. Mass spectrum *m/z* (relative intensity): 256 (8) $M^{+\cdot}$, 241 (10), $[M - Me]^+$, 165(100), $SnMe_3^+$, 91 (86), C_7H_7.

*1-Deuteromethyl-2-trimethylstannylbenzene (**26**).* Mass spectrum *m/z* (relative intensity): 242 (100) $[M - Me]^+$, 212 (36), $[M - 3Me]^+$, 135 (18), $SnMe^+$, 92 (30), $C_7H_6D^+$.

*1-Methyl-2-trimethylstannylbenzene (**26** − H).* ^1H NMR ($CDCl_3$, 90 MHz): δ 0.30 (s, 9H, ^2J ($H^{117}Sn/^{119}Sn$) 52/54 Hz, CH_3), 2.40 (s, 3H, CH_3), 7.03–7.53 ppm (m, 4H, arom.). Mass spectrum *m/z* (relative intensity): 241 (100), $[M - Me]^+$, 211 (37), [*M* − 3Me], 135 (18), $SnMe^+$, 91 (33), $C_7H_7^+$ [34].

*Di(2-deuterobenzyl)dimethylstannane (**27**).* Mass spectrum *m/z* (relative intensity): 334 (3) $M^{+\cdot}$, 242 (50), $[M - C_7H_6D]^+$, 135 (23), 92 (100), $C_7H_6D^+$.

*Dibenzyldimethylstannane (**27** − H).* ^1H NMR ($CDCl_3$, 90 MHz): δ 0.07 (s, 6H, ^2J($H^{117}Sn/^{119}Sn$) 51/53 Hz, CH_3), 2.35 (s, 4H, CH_2), 7.05–7.38 (m, 10H, arom.). Mass spectrum *m/z* (relative intensity): 332 (2) $M^{+\cdot}$, 241 (43), $[M - C_7H_7]^+$, 135 (18), $SnMe^+$, 91 (100), $C_7H_7^+$.

*2-Deuterobenzyl-(2-trimethylstannylbenzyl)dimethylstannane and 2-deuterobenzyldimethyl-(2-trimethylstannylmethyl)phenylstannane (**28**).* Mass spectra *m/z* (relative intensity): **28a**: 482 (3) $[M - Me]^+$, 405 (68) $[M - C_7H_6D]^+$, 240 (28), 225 (71), 210 (14), 165 (100) Me_3Sn^+, 135 (30) $MeSn^+$, 92(90) $[C_7H_6D]^+$; **28b**: 405 (21) $[M - C_7H_6D]^+$, 315(6), 225(40), 165(100) Me_3Sn^+, 135(10) $MeSn^+$, 92(88) $[C_6H_6D]^+$. Undeuterated analogues, mass spectra *m/z* (relative intensity): **28a** − H, 481(1) $[M - Me]^+$, 405(47) $[M - C_7H_7]^+$, 204(38), 225(66), 210(6), 65(100) Me_3Sn^+, 135(25) $MeSn^+$, 91(98) $[C_7H_7]^+$; **28b** − H, 405(21) $[M - C_7H_7]^+$, 315(10), 225(46), 165(100) $MeSn^+$, 135(13) $MeSn^+$, 91(90) $[C_7H_7)^+$.

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