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SOME APPLICATIONS OF THE METHYLENE DI-GRIGNARD REAGENT FOR THE SYNTHESIS OF MAIN GROUP IV ORGANOMETALLIC COMPOUNDS

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Summary

The di-Grignard reagent methylenedimagnesium dibromide, $CH_2(MgBr)_2$ (**1**), which can be prepared from dibromomethane and magnesium amalgam in diethyl ether/benzene 1/1, has been obtained in a pure form. Treatment of **1** with tetrahydrofuran gave insoluble **5″**, a reagent with the approximate composition $CH_2Mg \cdot CH_2(MgBr)_2$. Both reagents were used for the synthesis of the dimetallomethanes $(Me_3M)_2CH_2$ (M = Si, Ge, Sn) and $(CH_2(HgBr)_2$. Reaction of **1** or **5″** with dichlorodimethylgermane or dichlorodimethylstannane gave the polygermacycloalkanes $((Me_2GeCH_2)_n$; $n = 2,3,4)$ or polystannacycloalkanes $((Me_2SnCH_2)_n$; $n = 3,4)$, respectively, in useful yields (10 to 35%). In the germanium series, there is a pronounced tendency to form the smaller ring systems; in particular, the reaction of **5″** with Me_2GeCl_2 gave 30–35% of 1,1,3,3,-tetramethyl-1,3-digermacyclobutane. In contrast, the corresponding distannacyclobutane was not observed, but the eight-membered species $(Me_2MCH_2)_4$ was formed more readily for M = Sn (9% yield) than for M = Ge (2% yield).

Introduction

The methylene di-Grignard reagent $CH_2(MgBr)_2$ (**1**) was first prepared by Emschwiller [1]. Its synthesis was considerably improved by Cainelli et al. [2], who also demonstrated its use in organic synthesis as a reagent for carbonyl methylenations, where **1** offers an alternative for the Wittig reaction; a few other examples of this application have been reported by Japanese groups [3,4]. The only other organic application of **1** involves its reaction with the oxide and the dibromide of styrene [5]. One of the reasons for the limited use of **1** may be that the reactive carbon–magnesium bond is not compatible with a number of functional groups in the substrate.

With one early exception [6], the potential of **1** in organometallic synthesis has apparently not been explored. This is surprising in so far as use of **1** should in

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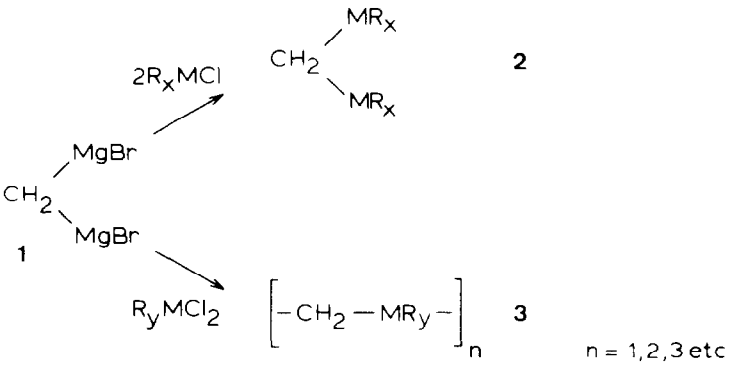
principle provide a route to acyclic (**2**) and cyclic (**3**) organometallic compounds having two metal atoms on the same carbon atom, as illustrated in Scheme 1.

SCHEME 1



Compounds **2** and **3** should be of considerable interest because of their structural features and their reactivity. We have therefore begun a wide-ranging investigation of the use of **1** as shown in Scheme 1. Preliminary results have been reported on the use of **1** for the preparation of titanacyclobutanes and titanacyclobutenes [7] and of some 1,3-metallatitanacyclobutanes [8]. We report here our results with Main Group IV organometallic compounds, in particular those of germanium and tin.

Results and discussion

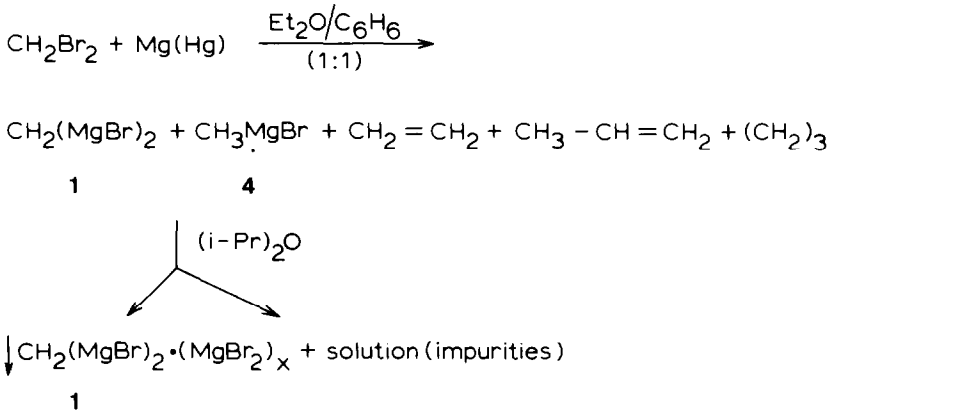
Preparation and stoichiometry of methylenedimagnesium dibromide (1)

The methylene di-Grignard reagent **1** was prepared from dibromomethane and magnesium amalgam in ether/benzene (1/1), essentially by the procedure of Cainelli et al. [2] (see Experimental). Under these conditions, **1** is obtained in reasonable though variable yield (50–60%), along with some methylmagnesium bromide (**4**) and small amounts of ethene, propene (main gaseous component in a closed vessel) and cyclopropane as by-products (Scheme 2). Compound **4** was identified and determined by treatment with chlorotrimethylstannane to give tetramethylstannane; the gaseous hydrocarbons were determined by GCMS.

Contrary to the report of Cainelli et al. [2], it is our experience that the magnesium content of the amalgam has a marked influence on the yield and purity of **1** (see also ref. [4]). The yield of **4** was greatly lowered (to about 1%) by using dilute magnesium amalgam (0.5% Mg). In order to avoid use of an excessive amount of mercury, a 1% magnesium amalgam is a reasonable compromise for preparative purposes.

The crude **1** obtained in the primary reaction was in general not suitable for direct application to the preparation of organometallic compounds. In particular **4**, which is not very detrimental in the carbonyl methylenation, has to be removed in order to avoid cumbersome purification of reactive organometallic products. For this purpose, the crude reaction mixture containing **1** was evaporated to dryness and the residue washed with diisopropyl ether. This removed all impurities (except magnesium bromide) and left **1** as a white powder which was not soluble in diethyl ether,

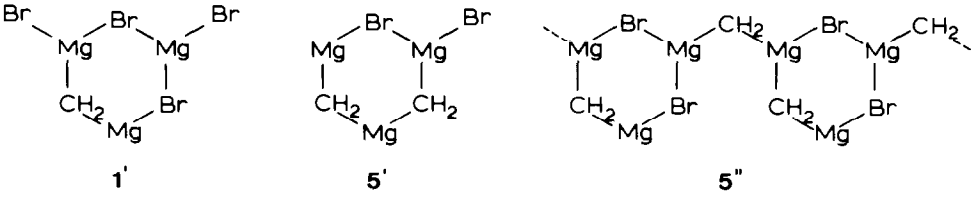
SCHEME 2



but gave a clear stable solution in diethyl ether/benzene (1/1).

We have not yet conducted a systematic investigation of the composition and structure of **1**, but the following observations may be relevant. Compound **1** surprisingly dissolved in the diethyl ether/benzene (1/1) mixture, but hardly at all in pure diethyl ether. In the latter partial disproportionation occurred, giving a solution rich in magnesium bromide and a precipitate (or viscous oil) richer in **1**. The stoichiometry was variable and could be changed by further extraction of magnesium bromide with diethyl ether. Nevertheless, the ratio $\mathbf{1}/MgBr_2$ in the precipitate and of the clear solutions in diethyl ether/benzene tended to be about 1/1, and we take this as an indication of a certain stability of such a complex. A rationalization of this composition is presented in Scheme 3 by structure **1'**, in which the usual

SCHEME 3



tetracoordination of magnesium will be achieved by addition of ether molecules. It is of interest that a 1,2-di-Grignard reagent [9] and a 1,3-di-Grignard reagent [10] also require additional magnesium bromide in order to form soluble low molecular weight species. For convenience we use the simple formula of **1** in the following description of its reactions, but it must be kept in mind that an excess of magnesium bromide was present unless otherwise stated.

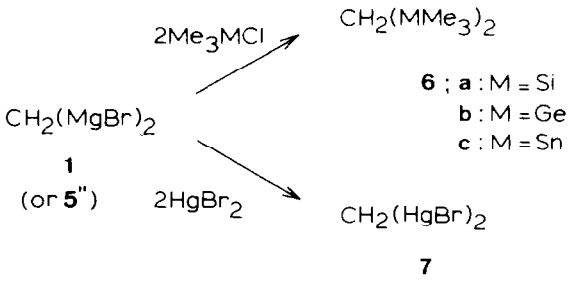
We attempted to prepare methylenemagnesium $(CH_2Mg)_n$ (**5**) from **1**; **5** is the dialkylmagnesium corresponding to the di-Grignard reagent **1**. Ziegler et al. reported the synthesis of **5** by pyrolysis of dimethylmagnesium and described it as a white insoluble powder [11]. We observed that **1** is soluble without decomposition in tetrahydrofuran only in the presence of a large excess of magnesium bromide; in its absence disproportionation occurs. For example, addition of tetrahydrofuran to the

residue obtained by evaporation of the crude, primary reaction mixture containing **1** gave a white, nearly insoluble powder. This powder tenaciously retained magnesium bromide, which was removed only by repeated washing with fresh tetrahydrofuran. At a **5**/**1** ratio of approximately 1/1, the composition stayed relatively constant. Although this stoichiometry does not directly imply the presence of a well-defined stable compound, it can be rationalized in terms of structures like **5'** or **5''** (Scheme 3); once again, for clarity, the solvent molecules coordinated to magnesium have been omitted. As the white powder is highly insoluble and cannot be reconverted into the soluble **1** by addition of magnesium bromide and diethyl ether/benzene (1/1), a polymeric structure such as **5''** is more likely. It should be emphasized that **5''** represents only one of several possible ways in which the components (CH_2, Mg, Br) can be arranged.

Dimetallomethanes

The synthetic applicability of **1** and **5''** was first tested for the preparation of the simplest known dimetallomethanes **6** and **7** (Scheme 4). It appears from the

SCHEME 4



extremely slow reaction of **1** with chlorotrimethylsilane that it is even less reactive towards chlorosilanes than normal Grignard reagents; with **5''**, only 55% of bis(trimethylsilyl)methane (**6a**) was formed even after several days. A low reactivity of 1,1-dimetalloalkanes appears to be general [12–14].

In contrast, reaction of chlorotrimethylgermane or chlorotrimethylstannane with **1** or **5''** proceeded rapidly and in high yield to give **6b** [15–18] and **6c** [19–22], respectively. Similarly, bis(bromomercurio)methane (**7**) was obtained in 52% yield from **1** and mercuric bromide. In this latter case, the new method is clearly more convenient than the one recently reported [23].

Polygermacycloalkanes ($Me_2GeCH_2)_n$ (8)

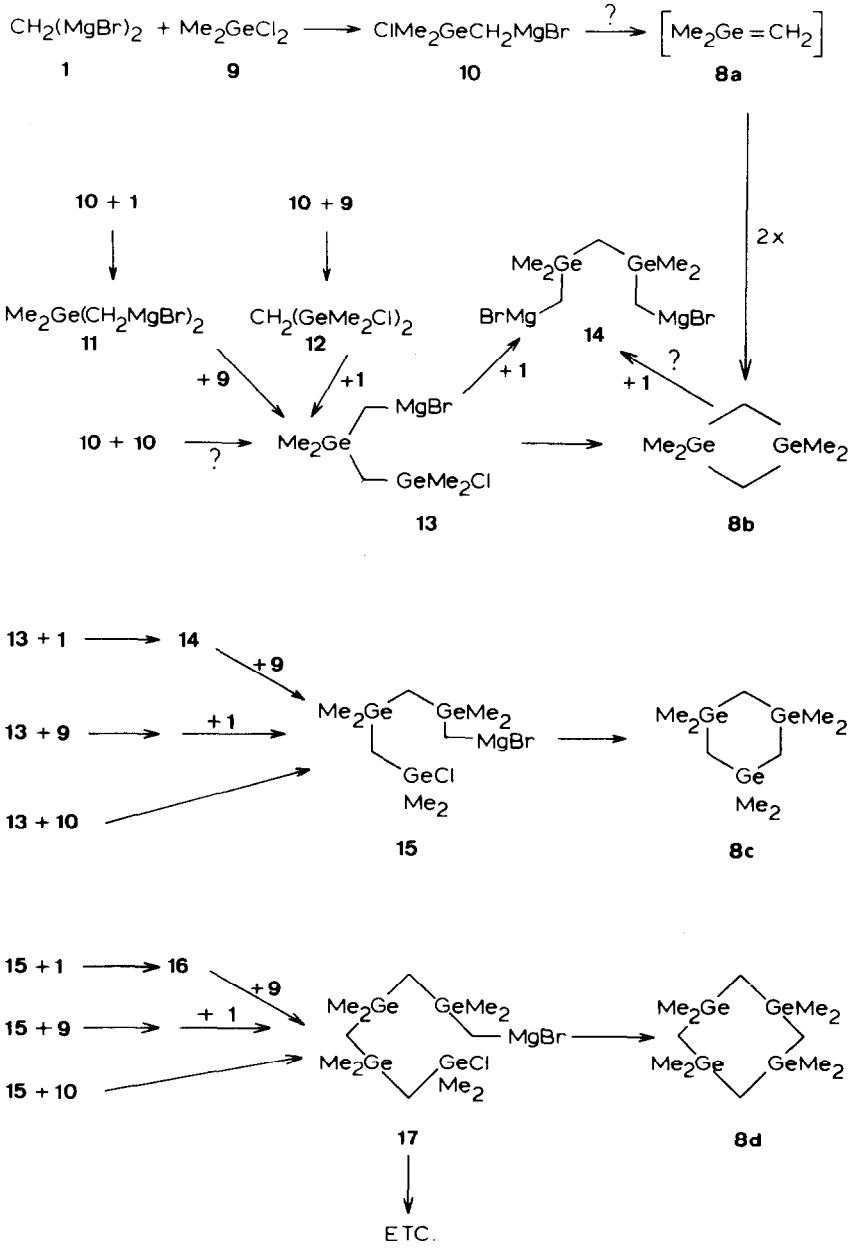
While the attractiveness of the reagents **1** and **5''** for the synthesis of dimetallomethanes (see previous section) may be a matter of personal preference, these reagents are clearly superior for the synthesis of cyclic organometallic compounds such as **3** (Scheme 1).

In the germanium series, only a small number of heterocycles containing germanium as the only heteroatom are known [24]. 1,1,3,3-Tetramethyl-1,3-digermacyclobutane (**8b**) has been prepared in a multistep sequence by Mironov et al. [25]; two other, highly substituted 1,3-digermacyclobutanes have been reported [26,27]. Mironov et al. have also prepared 1,1,3,3,5,5-hexamethyl-1,3,5-trigermacy-

clohexane (**8c**) by the reaction of metallic germanium with dichloromethane at 350°C in the presence of copper, followed by methylation with methylmagnesium chloride [28].

Although in principle, the reaction of **1** with an equimolar amount of dichlorodimethylgermane (**9**) might furnish **8b**, the latter is not the only expected product, since combination of two bifunctional reagents should lead to a complicated mixture

SCHEME 5



of acyclic and cyclic oligomeric or polymeric compounds, some of which are shown in Scheme 5. Nevertheless, we were moderately optimistic because of the previously encountered tendency of germanium to form four-membered rings [29].

From the reaction between **1** and **9** the three cyclic products **8b** (5–12%), **8c** (20–36%, main product) and **8d** (ca. 2%) were identified. Furthermore, a considerable number of smaller peaks were detected by GCMS (usually 1–10%), but these by-products varied in different runs and were not fully identified.

A remarkably different product ratio was observed in the reaction of equivalent amounts of **5''** and **9**. The slurry of **5''** in THF dissolved rapidly on addition of **9**. After hydrolysis, GCMS analysis revealed that **8b** was now the major product (30–35% yield); **8c** (3–12%) and **8d** (ca. 2%) were minor products, and the number and amounts of by-products were smaller than with **1**. We have at present no satisfactory explanation for this marked shift in favour of **8b**. In any case, the difference is not due to attack on **8b** by organomagnesium species present in solution, which would be analogous to the opening of stannacyclobutanes [30], because **8b** was found to be stable in the presence of a one molar excess of **1**.

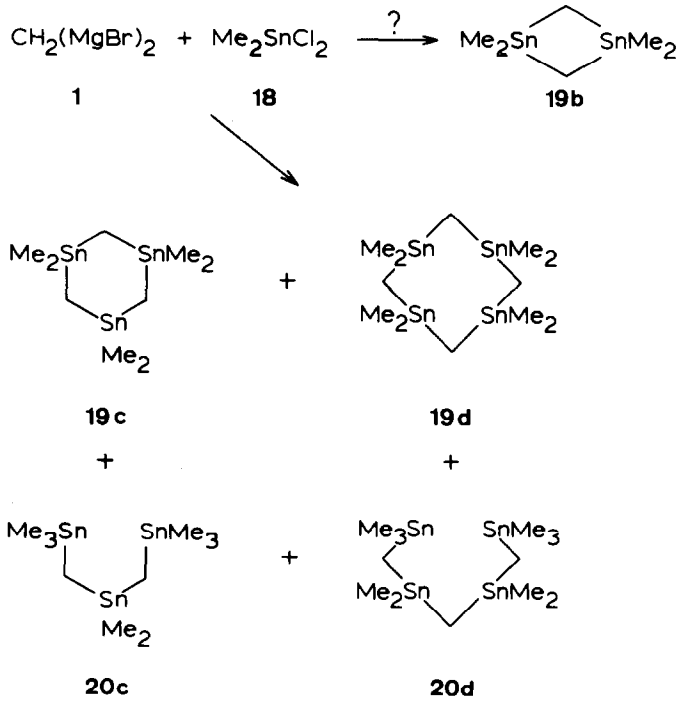
It is noteworthy that the eight-membered ring system **8d** was formed only as a minor by-product (2%). As far as we are aware, **8d** and similar 1,3,5,7-tetragermacyclooctanes have not been reported; however, eight-membered germacycles containing additional heteroatoms such as nitrogen, oxygen, or sulfur are known [24]. The contrast between the low yield of **8d** and the relatively high yield of the four-membered ring species **8b** must therefore be at least in part kinetically determined. In this respect, the situation for germanium is markedly different from that for tin.

*Polystannacycloalkanes ($Me_2SnCH_2)_n$ (**19**)*

We had hoped that the reaction of **1** with dichlorodimethylstannane (**18**) would give 1,1,3,3-tetramethyl-1,3-distannacyclobutane (**19b**), in a reaction analogous to the formation of **8b**, although we expected problems not only because of the potentially complicated course of the reaction, similar to that depicted for germanium in Scheme 5, but also, and more seriously because of the notorious instability of four-membered tin-heterocycles [30]. To our knowledge, the only known 1,3-distannacyclobutane is 1,1,3,3-tetramethyl-2,2,4,4-tetrakis(trimethylsilyl)-1,3-distannacyclobutane, prepared by Seyferth and Lefferts [27]; it is kinetically protected by considerable steric hindrance. Its simpler analogue **19b** would not be sterically protected and could be expected to be highly reactive both thermally and towards nucleophiles [27,30]. The only higher polystannacycloalkane described so far is 1,1,3,3,5,5-hexamethyl-1,3,5-tristannacyclohexane (**19c**) [31,32]. Seyferth and Vick obtained **19c** from (iodomethyl)dimethyltin iodide and magnesium [32]; in this reaction, higher members of the **19** series were apparently also formed according to NMR evidence, but they were not isolated or identified.

A molar equivalent of **18** was added to a solution of **1** in ether/benzene; after stirring overnight at room temperature, the reaction mixture was hydrolyzed and analyzed by GLC. Four major reaction products were identified and separated by preparative GLC; **19c** was the main product (33%), followed by its open chain analogue **20c** (15%), its eight-membered ring analogue **19d** (9%) and the open chain analogue of the latter, **20d** (8%) (Scheme 6). We did not detect the formation of the lower homologue **19b**, in spite of attempts to identify it directly or by chemical derivatization; these attempts and alternative attempts to make **19b** will be described

SCHEME 6



elsewhere. We cannot at present exclude the intermediate formation of **19b**, because it may be too unstable to survive under our reaction conditions.

The formation of **19c** and **19d** can be explained in the same way as that of the germanium analogue **8** (Scheme 5). The origin of the acyclic compounds **20c** and **20d** is not obvious; they did not contain deuterium when the reaction mixture was quenched with D_2O.

We have thus a marked difference between germanium and tin with respect to ring formation. Germanium shows a pronounced tendency to form small, especially four-membered, rings (vide supra and [26]). On the other hand, four-membered rings containing tin seem to be less favoured because of thermodynamic and kinetic factors which may both originate in the strain in four-membered tin compounds. Instead, tin forms larger rings more readily. Such a tendency to form large tin-heterocycles was previously encountered in the reaction of **18** with 1,3-dibromomagnesiopropane ($BrMgCH_2CH_2CH_2MgBr$); eight-, twelve- and sixteen-membered rings were formed in a total yield of 70% [30]. There is some evidence that in this latter case a stannacyclobutane may be involved in the formation of the larger rings [33].

Conclusion

The dimagnesiomethane reagents **1** and **5″** may be useful for the synthesis of acyclic and cyclic organometallic compounds containing alternating metal and carbon atoms. This has been demonstrated for germanium and tin, and to a certain

extent for silicon and mercury and will undoubtedly be the case for many other main group or transition metals. With appropriate modifications it is also possible to incorporate different metal atoms into chains or rings [8,34].

Experimental

All reactions involving the organomagnesium reagents **1** and **5''** were performed in a sealed and evacuated glass apparatus [35]. Solvents were distilled from sodium-potassium alloy before use. NMR spectra were recorded on a Bruker WH 90 or WM 250 spectrometer. Mass spectra were recorded on a Finnigan 4000 or a Varian CH5DF mass spectrometer (HRMS); the ions containing germanium or tin atoms showed the expected isotope pattern; when more than one germanium or tin atom is present, only the ions containing exclusively the most abundant isotope (i.e. ^{74}Ge or ^{120}Sn, respectively) are listed, while the relative intensities given represent the sum of the intensities of all isotopic peaks. Elemental analyses were performed by the Instituut voor Toegepaste Chemie TNO, Zeist, The Netherlands under the supervision of Mr. G.J. Rotscheid.

*Methylenedimagnesium dibromide (**1**)*

In our experience, it is advantageous to perform the preparations of magnesium amalgam and of **1** in a sealed and evacuated apparatus [35]; working under nitrogen led to inferior yields, and to solutions of **1** which slowly decomposed.

Magnesium amalgam was prepared by adding magnesium (5 g, 208 mmol) to mercury (30 ml, 408 g) under nitrogen in a 1 l round bottom flask; the reaction started immediately, and the flask was evacuated with a high vacuum pump. After stirring overnight, the reaction was completed by gentle warming and diethyl ether (200 ml) and benzene (200 ml) were added. The flask was connected via a break seal to an ampoule containing dibromomethane (11.4 g, 65.3 mmol) (Fig. 1 [33]) The contents of the flask A were stirred at room temperature, and ampoule B was immersed in an ice/water bath. This caused the ether to distill into B, until a dilute

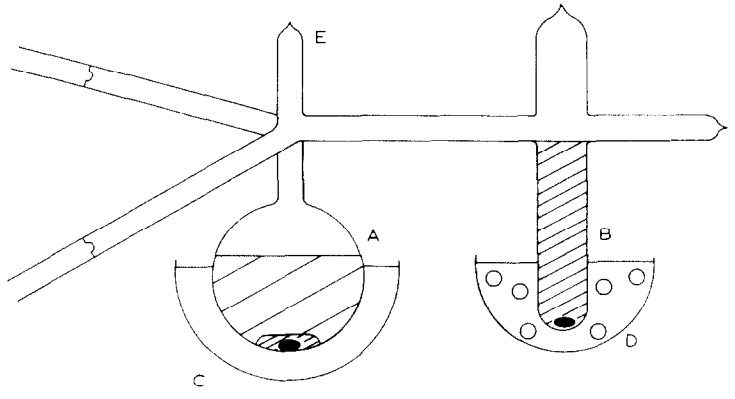


Fig. 1. Glass apparatus for the preparation of **1** [33]. A: 1 l Flask equipped with a magnetic stirring bar, containing magnesium amalgam and diethyl ether/benzene. B: Ampoule containing dibromomethane. C: Heating bath. D: Cooling bath with ice/water mixture. E: Side arms with breakseals.

solution of dibromomethane in ether flowed over onto the amalgam in A; in this way a slow addition of dibromomethane could be maintained. After 24 h an aliquot (taken via one of the side arms E) was hydrolyzed and titrated against HCl and ethylenediaminetetraacetic acid (EDTA); as a control, the yields of **1** and **5** were determined by reaction with chlorotrimethylstannane to give the products **6c** and tetramethylstannane, respectively (vide infra).

The mixture thus obtained was evaporated to dryness. The gaseous byproducts were determined by GCMS analysis of the distillate (closed vessel!). The residue was washed with diisopropyl ether (ca. 150 ml) and the supernatant solution was decanted; this treatment of the residue was repeated twice. The residue was then dried under vacuum, and a mixture of diethyl ether (200 ml) and benzene (200 ml) was added, to give a clear solution of **1** which was used for the reactions with organometallic halides; it contained additional magnesium bromide, but was free from **4**. The yield of **1**, as determined by titration of a hydrolyzed aliquot with HCl and EDTA, was usually about 50%.

Methylenemagnesium-methylenedimagnesium dibromide (5'')

As described in the previous section, a solution of **1** (ca. 20 mmol; 60% yield; containing ca. 10 mmol extra $MgBr_2$) was prepared from dibromomethane (7.5 g, 43.1 mmol) and magnesium amalgam (5 g Mg in 25 ml Hg) in diethyl/benzene 1/1 (400 ml). The mixture was evaporated to dryness and washed by decantation with 1/1 diethyl ether/toluene which dissolved only very little of the residue, to which tetrahydrofuran (150 ml) was then added. The resulting white precipitate was separated from the clear supernatant solution by decantation. The precipitate was washed twice by redistillation of the decanted tetrahydrofuran. The white residue of **5''** had a ratio of **5/1** of 1/1.13; it was used for the preparation of **6a** and **6b**. A third washing with fresh tetrahydrofuran gave a white residue of **5''** with a **5/1** ratio of 1.95/1; the decanted THF solution had a **1**/$MgBr_2$ ratio of 1/5. It is noteworthy that the concentration of "excess" magnesium bromide was 0.019 *M*, whereas pure magnesium bromide has a solubility in tetrahydrofuran of ca. 0.2 *M*; this means that the "excess" magnesium bromide was not free but bound to **1**, and the magnesium bromide left in the precipitate of **5''** must also chemically be bound.

Bis(trimethylsilyl)methane (6a)

An excess of chlorotrimethylsilane was added with stirring to a slurry of **5''** (0.78 mmol active methylene groups (CH_2Mg)) in THF (6.5 ml); there was no visible reaction. After several days a clear solution had formed, and this was analyzed by GCMS, in addition to **6a** (55%), several unidentified by-products were present. Preparative GC gave pure **6a**; its ^1H NMR and mass spectra were identical with those previously reported [36].

The analogous reaction of chlorotrimethylsilane with **1** gave **6a** in low yield (GCMS).

Bis(trimethylgermyl)methane (6b)

(a) From 1. Chlorotrimethylgermane (1.3 g, 8.5 mmol) was added to the solution of **1** (4 mmol) in diethyl ether/benzene 1/1 (ca. 60 ml). The mixture was stirred for 16 h at room temperature then aqueous NaOH was added with stirring. The organic layer was separated, dried ($MgSO_4$), and filtered, and the solvent was

distilled off carefully (Vigreux column); the residue was analyzed by ^{1}H NMR spectroscopy, and **6b** was isolated by preparative GC. The yield of **6b** was 61% (determined by GC). The ^{1}H NMR [16,17] and mass spectra [17] of **6b** were identical with those previously reported.

(b) From 5''. An excess of chlorotrimethylgermane was added to a slurry of **5''** (1.08 mmol "CH_2Mg") in THF (9 ml). The slurry dissolved within a few minutes to give a clear solution, which was worked up as described under (a). According to quantitative GC, the yield of **6b** was 92%; **6b** was isolated by preparative GC.

Bis(trimethylstannyl)methane (6c)

Chlorotrimethylstannane (4.11 g, 20.6 mmol) was added to a solution of **1** (8.9 mmol) in diethyl ether/benzene 1/1 (51 ml). The mixture was stirred overnight at room temperature and then for 1 h at 40°C. Water was then added and the organic layer was separated, dried ($MgSO_4$), and carefully distilled under reduced pressure to yield **6c** (2.66 g, 7.8 mmol, 87%) as a colourless liquid, b.p. 74–75°C/13 mbar (lit. b.p. 58–60°C/6 mbar [16]. ^{1}H NMR ($CDCl_3$): δ 0.07 (s, $^2J(^1H^{117}Sn/^{119}Sn)$ 50.9/53.3 Hz, 18H, Me), −0.25 ppm (s, $^2J(^1H^{117}Sn/^{119}Sn)$ 57.9/60.3 Hz, 2H, CH_2) [20]. ^{13}C {^{1}H} NMR ($CDCl_3$): δ −7.8 ($^1J(^{117}Sn/^{119}Sn)$ 314/328 Hz, Me), −14.8 ppm ($^1J(^{117}Sn/^{119}Sn)$ 259/271 Hz, CH_2) [21]. Mass spectrum *m/z* (relative intensity): 329(100) $[M - CH_3]^+$, 299(4), 283(1), 269(4), 253(5), 240(2), 165(83), 150(16), 135(30), 121(2), 120(1) [22].

Methylenedimercury dibromide (7)

Mercury(II) bromide (7.33 g, 20 mmol) was added at room temperature to a solution of **1** (10 mmol) in diethyl ether/benzene 2/1; a white precipitate was formed immediately. The mixture was stirred at room temperature for 0.5 h and then under reflux for 10 min, then cooled and decanted from the precipitate. The latter was washed with dilute hydrobromic acid, water, and ethanol, to yield **7** (3.01 g, 52%) as a white powder; this was purified by dissolving it in DMSO and precipitating it out with ethanol. M.p. 261–263°C (lit. m.p. 255°C [23]). ^{1}H NMR (DMSO-d_6): δ 1.51 ppm (s, $^2J(^1H^{199}Hg)$ 165.6 Hz, CH_2). Found C, 2.16; H, 0.38; Hg, 69.72. $CH_2Br_2Hg_2$ calcd.: C, 2.09; H, 0.35; Hg, 69.77%.

Reaction of 1 with dichlorodimethylgermane

Dichlorodimethylgermane (**9**) (271 mg, 1.56 mmol) was added to a solution of **1** (1.56 mmol) in diethyl ether/benzene 1/1 (130 ml). After overnight stirring a saturated aqueous solution of NH_4Cl was added. The organic layer was separated and dried ($MgSO_4$), and the solvent was removed by careful distillation. The residue was analyzed by quantitative ^{1}H NMR spectroscopy and GC; **8b** and **8c** were isolated by preparative GC (10% SE-30 on Chromosorb W, 2 m, diameter $\frac{1}{4}$ inch, 100°C).

1,1,3,3-Tetramethyl-1,3-digermacyclobutane (8b)

Colourless liquid, yield 5% (^{1}H NMR). ^{1}H NMR ($CDCl_3$): δ 0.64 (s, 4H, CH_2), 0.40 ppm (s, 12H, Me). Mass spectrum *m/z* (relative intensity): 236 (29) M^+, 221 (90) $[M - CH_3]^+$, 193(86), 177(8), 163(18), 148(4), 119(55), 105(22), 104(8), 103(3), 102(4), 89(100).

*1,1,3,3,5,5-Hexamethyl-1,3,5-trigermacyclohexane (**8c**)*

Colourless oil, yield 20% (^{1}H NMR). ^{1}H NMR ($CDCl_3$): δ 0.18 (s, 18H, Me), −0.13 ppm (s, 6H, CH_2). Mass spectrum *m/z* (relative intensity): 339(100) [$M - CH_3$]$^+$, 221(4), 193(6), 119(21), 89(7).

In another run, a reaction between **1** (0.2 mmol) and **9** (34.7 mg, 0.2 mmol) in diethyl ether/benzene (20 ml) was carried out as described above for 60 h. Work-up was as usual. Quantitative GCMS analysis gave the following results: **8b** (12% yield), **8c** (36% yield), **8d** (2.3% yield); **8d** was identified by its relative retention time (**8b**/**8c**/**8d** 82/376/724) and mass spectrum *m/z* (relative intensity): 457(65) [$M - 15$]$^+$, 323(30), 219(20), 119(100).

*Reaction of 5″ with **9***

Compound **9** (115 mg, 0.66 mmol) was added at room temperature to a slurry of **5″** (0.66 mmol as CH_2Mg) in THF (6.3 ml). A clear solution was formed rapidly. After 60 h stirring a saturated solution of NH_4Cl was added. Extraction with diethyl ether was followed by separation and drying ($MgSO_4$) of the organic layer. The solvent was removed by careful distillation and the residue analyzed by quantitative GCMS. Besides several peaks with areas corresponding to 1–10%, the following cyclic products were present: **8b** (32%), **8c** (17.5%), **8d** (1.8%).

In another run a reaction between **9**, (957 mg, 5.5 mmol) and **5″** (5.5 mmol as CH_2Mg) in THF (100 ml) was carried out as above, and work-up was as usual. Compounds **8b** (35% yield) and **8c** (ca. 3% yield) were determined by quantitative GCMS; **8d** was not detected. Some of product **8b** was isolated by preparative GC.

*Reaction of **1** with dichlorodimethylstannane*

Dichlorodimethylstannane (**18**) (1.11 g, 5 mmol) was added to a solution of **1** (5 mmol) in diethyl ether/benzene 1/1 (81 ml). The mixture was stirred overnight, then saturated aqueous NH_4Cl was added. The organic layer was separated, washed with $NaHCO_3$ solution and brine, and dried ($MgSO_4$), and the solvent was removed by careful distillation. The residue (0.76 g, 93% yield if calculated as $(Me_2SnCH_2)_n$ (**19**)) was investigated by ^{1}H NMR and GC. GC on SE-30 (10% SE-30 on Chromosorb W, 2 m, diameter $\frac{1}{4}$ inch, linear increase from 130–220°C with a rate of 10°C per minute) gave two main peaks, which were collected. However, GC of these fractions on Carbowax (20% Carbowax on Chromosorb W, 2 m, diameter $\frac{1}{4}$ inch, linear increase from 130–200°C with a rate of 10°C per minute) separated **19c** from **20c** and **19d** from **20d**, respectively. The yields were calculated from the relative peak areas, and based on 93% total yield (vide supra).

Compound **19c** gave data essentially identical with those previously reported [32], except that the literature data for both the ^{1}H NMR and the mass spectrum reveal that they were recorded with samples which contained considerable amounts (presumably close to 50%) of **20c**; as the samples had been obtained by GC on silicone rubber, the separation of **19c** from **20c** may have been incomplete.

*1,1,3,3,5,5-Hexamethyl-1,3,5-tristannacyclohexane (**19c**)*

Colourless crystals, m.p. 32–34°C, lit. m.p. 34–37°C [31], 33–34°C [32]. ^{1}H NMR ($CDCl_3$): δ 0.13 (s, $^2J(H^{117}Sn/^{119}Sn)$ 50.6/53.0 Hz, 18H, Me), −0.28 ppm (s, $^2J(H^{117}Sn/^{119}Sn)$ 54.6/57.2 Hz, 6H, CH_2). ^{13}C {^{1}H} NMR ($CDCl_3$): δ −6.3 ($^1J(^{13}C^{117}Sn/^{119}Sn)$ 303/317 Hz, Me), −14.6 ppm ($^1J(^{13}C^{117}Sn/^{119}Sn)$ 250/260

Hz, CH_2). Mass spectrum m/z (relative intensity): 477(100) $[M-CH_3]^+$, 447(4), 297(11) 165(8), 135 (7). High resolution MS $[M-CH_3]^+$: Found 476.8722; C_8H_{21}-$^{120}Sn_3$ calcd. 476.8705. 1,1,3,3,5,5,7,7-Octamethyl-1,3,5,7-tetrastannacyclooctane (**19d**). Colourless crystals, m.p. 114–115°C. ^1H NMR ($CDCl_3$): δ 0.12 (s, $^2J(^1H^{117}Sn/^{119}Sn)$ 50.2/52.5 Hz, 24H, Me), −0.24 ppm (s, $^2J(^1H^{117}Sn/^{119}Sn)$ 55.5/58.1 Hz, 8H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ − 6.02 ($^1J(^{13}C^{117}Sn/^{119}Sn)$ 305/319 Hz, Me), −12.3 ppm ($^1J(^{13}C^{117}Sn/^{119}Sn)$ 251/263 Hz, CH_2). Mass spectrum m/z (relative intensity): 641(100) $[M-CH_3]^+$, 477(7), 461(87), 313(6), 283(12), 165(29), 135(11). High resolution MS $[M-CH_3]^+$: Found 640.8389; $C_{11}H_{29}Sn_4$ calcd. 640.8358 (calculated with the approximation that the Sn_4 cluster of 480 AMU had the following composition: $^{120}Sn_4$ (65%), $^{118}Sn^{120}Sn_2{}^{122}Sn$ (11.7%), $^{116}Sn^{120}Sn_2{}^{124}Sn$ (11.7%), $^{118}Sn_2{}^{120}Sn^{124}Sn$ (11.7%)).

The structures of the acyclic polystannanes **20c** and **20d** were tentatively assigned by ^1H NMR data, for **20c**, by the $[M-15]^+$ ions. Bis(trimethylstannylmethyl)dimethylstannane (**20c**). ^1H NMR ($CDCl_3$, 250 MHz): δ 0.08 (s, $^2J(^1H^{117}Sn/^{119}Sn)$ 50.8/53.3 Hz, 18H, $SnMe_3$), 0.07 (s, $^2J(^1H^{117}Sn/^{119}Sn)$ ca. 50/52.5 Hz (from the 90 MHz spectrum), 6H, $SnMe_2$), −0.24 ppm (s, $^2J(^1H^{117}Sn/^{119}Sn)$ 57.3/60.0 Hz, 4H, CH_2). Mass spectrum m/z (relative intensity) 493(23) $[M-CH_3]^+$, 313(100), 165(58), 150(24), 135(23). Bis((trimethylstannylmethyl)dimethylstannyl)methane (**20d**). ^1H NMR ($CDCl_3$, 250 MHz): δ 0.08 (s, 18H, $SnMe_3$), 0.07 (s, 12H, $SnMe_2$), −0.22 (s, 2H, central CH_2), −0.23 ppm (s, 4H, external CH_2); the tin satellites could not be observed because of partial overlap of signals. The mass spectrum was not recorded.

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