9,10-Dimetallatriptycenes of Group 14: A Novel Synthetic Approach from *ortho*-Phenylenemagnesium

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Abstract: 9,10-Dimetallatriptycenes of Group 14 are readily accessable by a novel synthetic approach: reaction of *ortho*-phenylenemagnesium (1) with $RMCl_3$ afforded 9,10-dimethyl-9,10-dimetallatriptycenes (3; M = Si, Ge, Sn) or 9,10-dimethyl-9-germa-10-stannatriptycene (11). The reaction can even be tuned to afford unsymmetrically substituted triptycenes such as 9-methyl-10-phenyl-9,10-digermatriptycene (8); in some of these reactions, strong indications were obtained for the intermediacy of tri-Grignard reagents $RM(2\text{-}C_6H_4MgCl)_3$ (5, 10). The new triptycenes were characterised by their spectral data and in the case of 3c (M = Sn) by an X-ray crystal structure determination.

Keywords
Grignard reagents · Group 14 compounds · metallatriptycenes · phenylenemagnesium

Introduction

Triptycene was first synthesized in 1942,[1] and its symmetrical structure and unusual properties have captured the imagination of chemists ever since.[2] Nowadays, derivatives of triptycenes are used, for example, as model compounds to study molecular dynamics in physical chemistry[3] and as resins in polymer chemistry.[4] Though 9,10-dimetallatriptycenes (Fig. 1) are known for Group 15 (e.g., As,[6] Sb,[7] Bi[8]), those of Group 14 have been restricted to four particular cases, all involving two silicon atoms.[9–11]

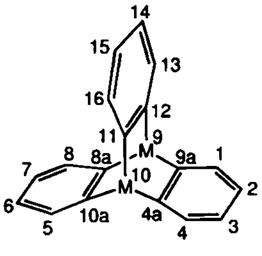
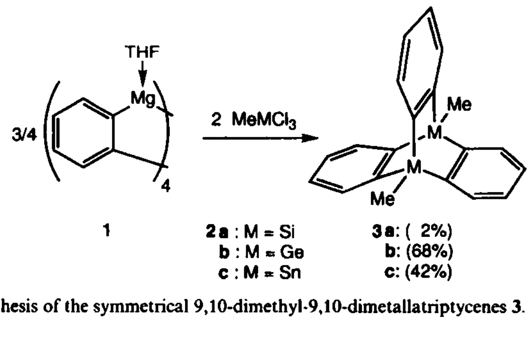


Fig. 1. Numbering of 9,10-dimetallatriptycene (= 9,10-dihydro-9,10-dimetalla-9,10[1',2']-benzenoanthracene) according to IUPAC [5].

In this paper we report a novel synthetic approach to 9,10-dimetallatriptycenes of Group 14, in which *ortho*-phenylenemagnesium (1)[12] serves as a starting material. By this approach different types of 9,10-dimetallatriptycenes are accessible in appreciable yields in simple one-pot procedures.

Results and Discussions

Synthesis: When three equivalents of 1 were treated with two equivalents of the methylmetal trichlorides 2 in THF at −10 °C, the symmetrical 9,10-dimethyl-9,10-dimetallatriptycenes 3 were obtained (Scheme 1). Thus, the disilatriptycene 3a (2%), its digerma analogue 3b (68%) and its distanna analogue 3c (42%) were obtained as novel compounds. The identity of 3 followed from the spectral data and, in the case of 3c, from an X-ray crystal structure determination (vide infra).



Scheme 1. Synthesis of the symmetrical 9,10-dimethyl-9,10-dimetallatriptycenes 3.

To test the general applicability of the method, three equivalents of 1 were treated with two equivalents of the phenyl-substituted metal trihalides 4b and 4c (Scheme 2). Unexpectedly, these reactions did not furnish the desired diphenyl-substituted dimetallatriptycenes 6 even after prolonged heating (24 h at 50 °C); on deuterolysis, the $[D_3]$tetraphenylmetal compounds 7b and 7c, respectively, were obtained exclusively. These compounds were also obtained when only one equivalent of 4 was used. In the case of germanium, the quantitative yield of

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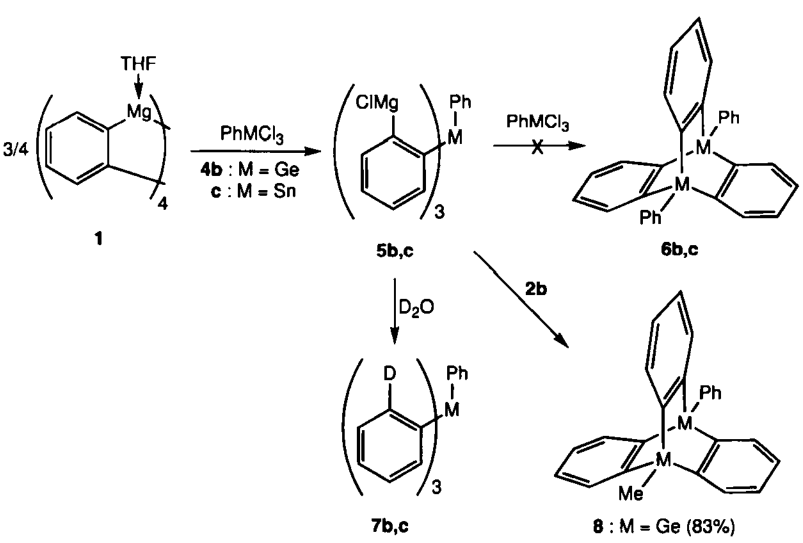


Scheme 2. Reaction of **1** with the phenyl-substituted metal trihalides **4b** and **4c**.

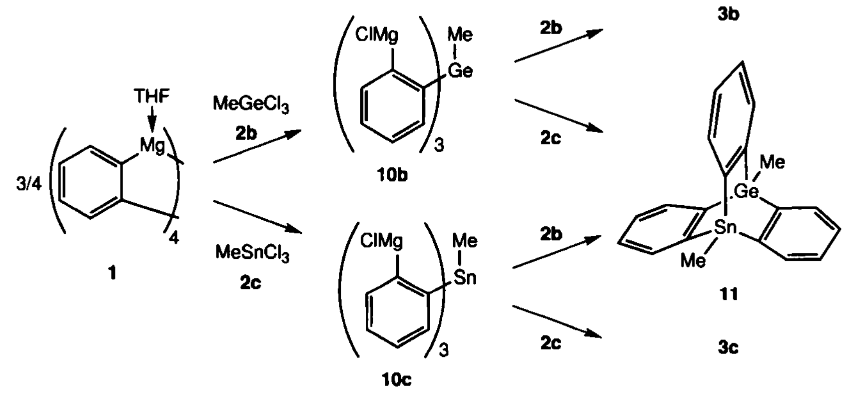
7b, together with the relative ratio Ge:"base":Mg^{2+} of 1.00:2.78:2.94 after hydrolysis, strongly suggest the quantitative formation of the tri-Grignard reagent **5b**. This idea was substantiated by subsequent reaction of **5b** with **2b**: the addition of one equivalent of **4b** to three equivalent of **1**, followed by the addition of one equivalent of **2b**, afforded the unsymmetrically substituted digermatriptycene **8** in 83% isolated yield.

The clean formation of **5b** during the reaction of **4b** with three equivalents of **1** is noteworthy, as reactions of **4b** with aryl Grignard reagents are known to give mixtures of tetraarylgermane and partially arylated germanium halides;[13] only in refluxing toluene has the formation of appreciable amounts of tetraarylgermane been reported.[14] Apparently, the decrease in reactivity of Ge–Cl bonds normally encountered upon successive introduction of organic groups[13, 15] is overcome in our case by an unusual activating effect, as formation of **5b** takes place under mild conditions. In our opinion, this anomalous reactivity might be related to the unique tetrameric structure of **1**, which consists of a tetrahedron of four magnesium atoms bridged by four *ortho*-phenylene units.[12] One can envision that, upon reaction of **4b** with one of the four *ortho*-phenylenemagnesium units of **1**, the remaining part of the organomagnesium cluster, together with the newly created chloromagnesio function, maintain to some extent the original degree of organisation. The close proximity between unreacted *ortho*-phenylenemagnesium units and the remaining Ge–Cl bonds may result in a kinetic activation, which ultimately leads to the quantitative formation of **5b**.

The formation of **5b** and its conversion to **8** offers an opportunity to formulate a general mechanism for the formation of 9,10-dimetallatriptycenes. First, **1** reacts selectively with one equivalent of the organylmetal trihalide to yield a tris(*ortho*-chloromagnesiophenyl)metal compound **5**. This tri-Grignard reagent then reacts with a second equivalent of an organylmetal trihalide. Once *one* of the three Grignard functions of **5** has reacted with *one* metal–halogen bond, the ensuing intramolecular ring closures, eventually leading to the formation of the 9,10-dimetallatriptycene, are favoured by entropy over intermolecular reaction with, for example, another molecule of an organylmetal trihalide, which would lead to the formation of oligomers.

The recognition of the fact that tri-Grignard reagents such as **5** might be general intermediates in dimetallatriptycene formation inspired us to have a closer look at the products of the reaction of three equivalents of **1** with two equivalents of **2a**, which gave such a poor yield of the desired disilatriptycene **3a** (Scheme 1). On deuterolysis of the crude reaction mixture, mainly [D$_3$]methyltriphenylsilane (**9**) and only a small amount of **3a** (**9**:**3a** = 8:1 by GCMS) were formed; **3a** was isolated in the pure form in 2% overall yield. The formation of **9**, which must be originating from the tri-Grignard reagent **10a** (MeSi(2-C$_6$H$_4$MgCl)$_3$; cf. Scheme 3), an analogue of **5**, further supports the postulated intermediacy and remarkable stability of these species; apparently, the less reactive metal–chloride bonds of **2a** are not able to react with **10a**, while those of **2b** and **2c** are sufficiently reactive towards **10b** and **10c**, respectively. The implications of this interesting observation will be the subject of further investigations.

As reactions of **1** with **2b** or **2c** readily afforded the corresponding dimetallatriptycenes, the synthesis of mixed dimetallatriptycene **11** was attempted (Scheme 3). Indeed, **11** could be obtained together with **3b** and **3c** (**11**:**3b**:**3c** = 70:5:25) by treating three equivalents of **1** with a 1:1 mixture of **2b** and **2c**.



Scheme 3. Synthesis of mixed dimetallatriptycene **11**.

At present, the nonstatistical product distribution is not fully understood. A subtle interplay between reactivity and steric crowding may be responsible, and the specific intermediate formation of the tri-Grignard reagents **10b** and **10c** may be important, too. If one assumes the tin derivative **2c** to be more reactive towards **1** than **2b**, a relatively large amount of methyltris(*ortho*-chloromagnesiophenyl)stannane (**10c**) would be formed during the initial stages of the reaction. In the subsequent steps, **10c** and **2b** would then be the most abundant species; they would react to give the mixed triptycene **11**. This process successfully competes with the reaction of **10c** with (the largely consumed) **2c** leading to **3c**.

Crystal structure of 3c: Figure 2 shows the solid-state structure of **3c**. The bonds between the bridgehead tin atoms and the methyl substituents are almost coaxial with the Sn1–Sn1a axis (Sn1–Sn1a = 3.3362(9) Å; Sn1-Sn1a-C1a = Sn1a-Sn1-C1 = 176.25(10)°), while the angles between the (practically planar)

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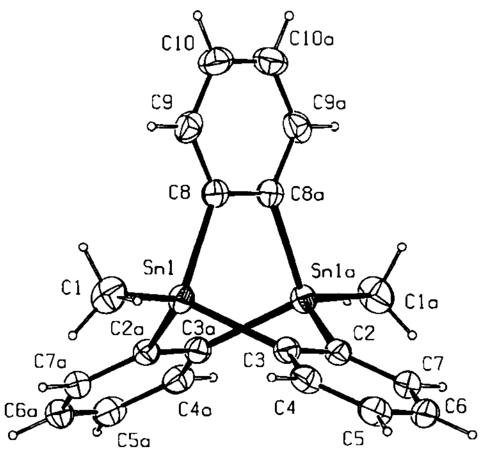

Fig. 2. ORTEP plot of **3c** (ellipsoids drawn at 50% propability level; note that the numbering in Fig. 2 is different from the IUPAC numbering in Fig. 1, which is used throughout the rest of the text). Selected bond lengths [Å] and bond angles [°]: Sn1–C1 2.113(4), Sn1–C2a 2.154(2), Sn1–C3 2.153(2), Sn1–C8 2.152(2), C2–C3 1.406(3), C8–C8a 1.404(3); C1-Sn1-C2a 119.88(12), C1-Sn1-C3 115.25 (12), C1-Sn1-C8 114.75(9), C3-Sn1-C2a 102.48(9), C3-Sn1-C8 101.04(8), C8-Sn1-C2a 100.73(9), Sn1-C3-C2 117.85(16), Sn1-C8-C8a 116.60(16), Sn1-C3-C4 122.71(17), Sn1a-C2-C7 125.46(19), Sn1-C8-C9 124.08(18).

ortho-phenylene "propeller vanes" and the Sn1–Sn1a axis are small (1.68(8)–3.51(9)°). Apparently, the last ring closure to furnish the triptycene skeleton introduces substantial ring strain, as the external angles [Sn1-C3-C4 etc. 122.71(17)–125.46(19)°] and the internal angles [Sn1-C3-C2 etc. 115.38(15)–117.85(16)°] at the benzene rings deviate from each other and from 120°. To allow for these structural features, deviation from an ideal tetrahedral environment around the bridgehead tin atoms is required, which is achieved by making the internal angles more acute. This is accompanied by a rehybridization of the orbitals involved in bonding to the *ipso* carbons, as has similarly been observed for the bridgehead atoms of other triptycenes.[11, 16, 17] As a result, the internal angles [C2a-Sn1-C3 etc. 100.73(9)–102.48(9)°] are smaller than 109.5° and the bridgehead-to-"vane" bonds (2.152(2)–2.154(2) Å) are longer than the bridgehead-to-methyl bonds (2.113(4) Å), in contrast to the normal trend expected for bonds involving sp^2 and sp^3 carbons, respectively.

Molecular structure of 3c: The nature of the bonds involving the bridgehead tin atoms in **3c** can also be determined from ^{13}C NMR, as enhanced p character of the bridgehead-to-*ipso* carbon bonds should lead to a decrease in the ^1J(C,Sn) coupling constants compared to those of an unstrained analogue (e.g., methyltriphenyltin). In the same way, the enhanced s character of the bridgehead-to-methyl bonds should lead to an increase in the ^1J(C,Sn) coupling constants compared to those of methyltriphenyltin. From Table 1 it can be seen that, compared to methyltriphenyltin, the expected changes in ^1J(C,Sn) coupling constants are indeed observed for both **3c** and **11**.

Table 1. ^1J(C,Sn) coupling constants for the bridgehead bonds in **3c** and **11** compared to those in an unstrained analogue (^1J(C,^{119}Sn):^1J(C,^{117}Sn)) [Hz].

Compound	C_{ipso}	C_{methyl}
Ph_3SnMe	510.0:487.5	376.1:359.3
3c	488.4:467.1	388.5:371.2
11	475.1:454.0	400.5:382.8

Experimental Procedure

General: All reactions were performed in fully sealed glassware with standard high-vacuum techniques. Reagent **1** was prepared according to the literature [12]. All metal trihalides were purchased from commercial sources. Solvents were predried over NaOH and then dried by distillation from liquid Na/K alloy. Amounts of "base" and Mg^{2+} were determined after hydrolysis of a sample by titration with HCl and EDTA, respectively [18]. NMR spectra were measured at 25 °C on a Bruker AS200 spectrometer (^{1}H NMR: 200.0 MHz; ^{13}C NMR: 50.3 MHz) and on a Bruker MSL400 spectrometer (^{1}H NMR: 400.1 MHz: ^{13}C NMR: 100.6 MHz). ^{13}C,^{1}H COSY and ^{1}H NOE experiments were used for spectral assignment. GCMS analysis were performed on an HP 5890 GC/5970 MS combination, operating at 70 eV and equipped with a Chrompack BP1 (QSGE) 50 m × 0.25 mm column. HRMS measurements were performed on a Finnigan MAT90 mass spectrometer (direct inlet). Yields were determined by isolation after column chromatography unless stated otherwise. All melting points are uncorrected. Elemental analyses were carried out at the Mikroanalytisches Labor Pascher, Remagen, Germany.

Crystallographic data for 3c [19]: $C_{20}H_{18}Sn_2$, $M_r = 495.78$, colourless, transparent (0.25 × 0.38 × 0.38 mm), monoclinic, space group $C2/c$ (no. 15) with $a = 15.150(2)$, $b = 11.422(3)$, $c = 11.1733(11)$ Å, $\beta = 111.890(9)°$, $V = 1194.1(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.836\ \mathrm{g\,cm^{-3}}$, $F(000) = 952$, $\mu(Mo_{K\alpha}) = 27.8\ \mathrm{cm^{-1}}$, 7342 reflections measured, 2061 independent ($2.3 < \theta < 27.5°$, $\Delta\omega = 0.66 + 0.35\tan\theta$, $T = 150$ K, $Mo_{K\alpha}$ radiation, graphite monochromator, $\lambda = 0.71073$ Å) on an Enraf-Nonius CAD4-T diffractometer on rotating anode. Data were corrected for Lp and for a linear decay of 3% of the reference reflections ($\bar{2}\,2\,1$, $\bar{2}\,2\,\bar{1}$, $\bar{4}\,2\,\bar{2}$); empirical absorption correction applied as implemented in PLATON [20] (DIFABS, transmission range 0.431–1.000). The structure was solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92) [21]. Refinement of F^2 was carried out by full-matrix least-squares techniques (SHELXL-93) [22]; no observance criterion was applied during refinement. Final $R1$ value 0.0231, for 1906 reflections with $F_o > 4.0\sigma(F_o)$, $wR2 = 0.0628$ for 2061 data, $w = 1/[\sigma^2(F_o^2 + (0.0319\,P)^2 + 1.4311\,P]$, with $P = (\max(F_o^2,0) + 2F_c^2)/3$, $S = 1.165$, for 101 parameters. Maximum and minimum residual density: 0.43, −0.84 e Å^{-3}. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined riding on their carrier atoms with a fixed isotropic thermal parameter related to the value of the equivalent isotropic thermal parameter of their carrier atoms by a factor of 1.2. Weights were optimized in the final refinement cycles.

9,10-Dihydro-9,10-dimethyl-9,10-disila-9,10[1′,2′]-benzenoanthracene (3a): At −10 °C, **2a** (0.547 mmol in 5.57 mL of toluene) was added over 1 h to **1** (0.821 mmol of monomeric C_6H_4Mg in 18.0 mL of THF). After the mixture had been stirred for 1 h, it was allowed to warm overnight to room temperature. It was then quenched (D_2O/DCl) and extracted with Et_2O (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and the solvent was evaporated in vacuo. The residue, containing a mixture of **9** and **3a** (**9**:**3a** = 8 :1 (GCMS)) was dissolved in benzene and eluted from silica. Yield (after preparative GC): 0.002 g of a white solid (**3a**: 2.4%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.66$ (m, ^3J(H,H) = 7.4 Hz, ^4J(H,H) = 1.1 Hz, 6H; H(1,4,5,8,13,16)), 7.19 (m, ^3J(H,H) = 8.4 Hz, ^3J(H,H) = 7.4 Hz ^4J(H,H) = 1.1 Hz, 6H; H(2,3,6,7,14,15)), 1.16 (s, 6H; H(17,18)); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): $\delta = 145.7$ (brs; C(4a,8a,9a,10a)), 131.3 (dt, ^1J(C,H) = 156.2 Hz, ^3J(C,H) = 3.2 Hz; C(2,3,6,7,14,15)), 127.1 (d, ^1J(C,H) = 159.0 Hz, ^3J(C,H) = 6.5 Hz; C(1,4,5,8,13,16)), −13.4 (q, ^1J(C,H) = 121.4 Hz; C(17,18)); HRMS: $m/z = 314.0947$ (calcd. for $C_{20}H_{18}{}^{28}Si_2$ (M^+): $m/z = 314.0947$).

9,10-Dihydro-9,10-dimethyl-9,10-digerma-9,10[1′,2′]-benzenoanthracene (3b): Prepared from **2b** (0.438 mmol in 4.47 mL of Et_2O) and **1** (0.657 mmol of monomeric C_6H_4Mg in 20.1 mL of THF) as described for **3a**. Yield: 0.060 g of a white solid (**3b**: 68%), m.p. > 330 °C. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.62$ (m, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.2 Hz, 6H; H(1,4,5,8,13,16)), 7.19 (m, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.2 Hz, 6H; H(2,3,6,7,14,15)), 1.26 (s, 6H; H(17,18)); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): $\delta = 145.8$ (s; C(4a,8a,9a,10a,11,12)), 131.1 (d, ^1J(C,H) = 156.0 Hz; C(2,3,6,7,14,15)), 127.1 (d, ^1J(C,H) = 157.3 Hz; C(1,4,5,8,13,16)), −13,8 (q, ^1J(C,H) = 128.5 Hz; C(17,18)); HRMS: $m/z = 403.9845$ (calcd. for $C_{20}H_{18}{}^{72}Ge^{74}Ge$ (M^+): $m/z = 403.9838$); elemental analysis: calcd. for $C_{20}H_{18}Ge_2$ (403.6): C 59.53, H 4.50; found: C 59.63. H 4.41.

9,10-Dihydro-9,10-dimethyl-9,10-distanna-9,10[1′,2′]-benzenoanthracene (3c): Prepared from **2c** (0.430 mmol in 6.32 mL of benzene) and **1** (0.645 mmol of monomeric C_6H_4Mg in 19.7 mL of THF) as described for **3a**. Yield: 0.045 g of a white solid (**3c**: 42%), m.p. > 340 °C. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.65$ (m, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 1.0 Hz, 6H; H(1,4,5,8,13,16)), 7.19 (m, ^3J(H,H) = 8.0 Hz, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 1.0 Hz, 6H; H(2,3,6,7,14,15)), 1.05 (s, ^2J(H,^{119}Sn) = 61.1 Hz, ^2J(H,^{117}Sn) = 58.6 Hz, 6H; H(17,18)); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): $\delta = 150.6$ (s, ^1J(C,^{119}Sn) = 488.4 Hz, ^1J(C,^{117}Sn) = 467.1 Hz, ^2J(C,Sn) = 31.2 Hz, C(4a,8a,9a,10a,11,12)), 135.0 (d, ^1J(C,H) = 156.0 Hz, ^3J(C,Sn) = 45.0 Hz; C(2,3,6,7,14,15)), 127.6 (d, ^1J(C,H) = 161.2 Hz, ^3J(C,Sn) = 49.9 Hz, ^4J(C,Sn) = 11.1 Hz; C(1,4,5,8,13,16)), −16.6 (q, ^1J(C,H) = 132.8 Hz, ^1J(C,^{119}Sn) = 388.5 Hz,

^{1}J(C,^{117}Sn) = 371.2 Hz, ^{4}J(C,Sn) = 16.3 Hz; C(17,18)); HRMS: m/z = 477.9228 (calcd. for $C_{19}H_{15}{}^{117}Sn^{118}Sn$ (M^{+} – CH_3): m/z = 477.9222); elemental analysis: calcd. for $C_{20}H_{18}Sn_2$ (495.8): C 48.46, H 3.66; found: C 48.55, H 3.68.

Tris(*ortho*-chloromagnesiophenyl)methylgermane (5b): At –10 °C, **4b** (0.836 mmol in 7.65 mL of toluene) was added over 1 h to **1** (2.508 mmol of monomeric C_6H_4Mg in 55.0 mL of THF). After additional stirring for 1 h, the mixture was warmed overnight to room temperature.

Tris(*ortho*-deuterophenyl)methylgermane (7b): D_2O was used to quench 9.18 mL of the solution of **5b** thus obtained, and the resulting mixture was washed with H_2O (4 × 5 mL). After extraction with Et_2O (2 × 5 mL), the combined aqueous layers were subjected to acid/base titration and EDTA titration: $OH^-:Mg^{2+}$ = 0.331:0.350 mmol. The combined organic layers were dried ($MgSO_4$) and filtered, and the solvent was evaporated in vacuo. The residue was dissolved in benzene and eluted from silica. Yield: 0.0458 g of a white solid (**7b**: 0.119 mmol, 100%). MS (70 eV): m/z (%): 385 (2.3) [M^{+}] (>95% D_3 from cluster analysis).

9,10-Dihydro-9-methyl-10-phenyl-9,10-digerma-9,10[1′,2′]benzenoanthracene (8): At –10 °C, **2b** (0.52 mmol in 5.31 mL of Et_2O) was added over 1 h to **5b** (0.52 mmol in 40.2 mL of THF). The reaction mixture was worked up as described for **3a**. Yield: 0.200 g of a white solid (**8**: 83%), m.p. 226 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (m, ^{3}J(H,H) = 7.4 Hz, ^{4}J(H,H) = 1.3 Hz, 2H; H(19)), 7.61 (m, ^{3}J(H,H) = 7.4 Hz, ^{4}J(H,H) = 1.3 Hz, ^{5}J(H,H) = 0.7 Hz, 3H; H(4,5,16)), 7.58 (m, ^{3}J(H,H) = 7.3 Hz, ^{4}J(H,H) = 1.3 Hz, ^{5}J(H,H) = 0.7 Hz, 3H; H(1,8,13)), 7.55 (m, ^{3}J(H,H) = 7.4 Hz, ^{3}J(H,H) = 7.5 Hz, 2H; H(20)), 7.52 (m, ^{3}J(H,H) = 7.5 Hz, ^{4}J(H,H) = 1.3 Hz, 1H; H(21)), 7.12 (m, ^{3}J(H,H) = 7.6 Hz, ^{3}J(H,H) = 7.3 Hz, ^{4}J(H,H) = 1.3 Hz, 3H; H(2,7,14)), 7.09 (m, ^{3}J(H,H) = 7.4 Hz, ^{3}J(H,H) = 7.6 Hz, ^{4}J(H,H) = 1.3 Hz, 3H; H(3,6,15)), 1.20 (s, 3H; H(17)); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 146.1 (brt; C(8a,9a,12)), 145.4 (d, ^{2}J(C,H) = 2.3 Hz, ^{3}J(C,H) = 7.2 Hz; C(4a,10a,11)), 136.3 (ddt, ^{1}J(C,H) = 159.9 Hz, ^{2}J(C,H) = 2.2 Hz, ^{3}J(C,H) = 6.9 Hz; C(19)), 132.3 (ddd, ^{1}J(C,H) = 158.9 Hz, ^{2}J(C,H) = 2.2 Hz, ^{3}J(C,H) = 7.0 Hz; C(4,5,16)), 131.5 (ddd, ^{1}J(C,H) = 158.9 Hz, ^{2}J(C,H) = 1.5 Hz, ^{3}J(C,H) = 7.0 Hz; C(1,8,13)), 130.2 (brs; C(18)), 130.0 (dt, ^{1}J(C,H) = 160.5 Hz, ^{3}J(C,H) = 7.0 Hz; C(21)), 129.0 (ddd, ^{1}J(C,H) = 155.4 Hz, ^{2}J(C,H) = 1.1 Hz, ^{3}J(C,H) = 7.5 Hz; C(20)), 127.3 (dd, ^{1}J(C,H) = 159.0 Hz, ^{3}J(C,H) = 6.8 Hz; C(2,3,6,7,14,15)), –13.6 (q, ^{1}J(C,H) = 128.6 Hz; C(17)); HRMS: m/z = 462.0023 (calcd. for $C_{25}H_{20}{}^{72}Ge^{74}Ge$ (M^{+}): m/z = 462.0025); elemental analysis: calcd. for $C_{25}H_{20}Ge_2$ (465.6): C 64.49, H 4.33; found: C 64.80, H 4.36.

9,10-Dihydro-9,10-dimethyl-9-germa-10-stanna-9,10[1′,2′]-benzenoanthracene (11): Prepared from a mixture of **2b** (0.228 mmol in 2.56 mL of Et_2O) and **2c** (0.228 mmol in 2.17 mL of THF) and **1** (0.684 mmol of monomeric C_6H_4Mg in 15.0 mL of THF) as described for **3a**. Yield: 0.038 g (35%) of a white solid (mixture of **11**, **3b** and **3c**, relative ratio (GCMS): **11**:**3b**:**3c** = 70:5:25). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (m, ^{3}J(H,H) = 7.6 Hz, ^{4}J(H,H) = 1.2 Hz, 3H; H(4,5,16)), 7.54 (m, ^{3}J(H,H) = 7.5 Hz, ^{4}J(H,H) = 1.0 Hz, 3H; H(1,8,13)), 7.10 (m, ^{3}J(H,H) = 8.3 Hz, ^{3}J(H,H) = 7.5 Hz, ^{4}J(H,H) = 1.2 Hz, 3H; H(2,7,14)), 7.09 (m, ^{3}J(H,H) = 8.3 Hz, ^{3}J(H,H) = 7.6 Hz, ^{4}J(H,H) = 1.0 Hz, 3H; H(3,6,15)), 1.16 (s, 3H; H(17), 1.02 (s, ^{2}J(H,^{119}Sn) = 63.7 Hz, ^{2}J(H,^{117}Sn) = 60.8 Hz, 3H; H(18)); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 148.8 (s, ^{1}J(C,^{119}Sn) = 475.1 Hz, ^{1}J(C,^{117}Sn) = 454.0 Hz, C(8a,9a,12)), 147.4 (s, ^{2}J(C,Sn) = 23.5 Hz; C(4a,10a,11)), 134.6 (dd, ^{1}J(C,H) = 158.6 Hz, ^{3}J(C,H) = 6.0 Hz, ^{2}J(C,^{119}Sn) = 42.5 Hz, ^{2}J(C,^{117}Sn) = 40.6 Hz, C(1,8,13)), 131.8 (dd, ^{1}J(C,H) = 158.3 Hz, ^{3}J(C,H) = 5.9 Hz, ^{3}J(C,^{119}Sn) = 41.8 Hz, ^{3}J(C,^{117}Sn) = 40.1 Hz, C(4,5,16)), 127.5 (dd, ^{1}J(C,H) = 165.8 Hz, ^{3}J(C,H) = 8.1 Hz, ^{4}J(C,Sn) = 10.6 Hz, C(3,6,15)), 127.4 (dd, ^{1}J(C,H) = 158.2 Hz, ^{3}J(C,H) = 9.0 Hz, ^{3}J(C,^{119}Sn) = 50.85 Hz, ^{3}J(C,^{117}Sn) = 48.6 Hz, C(2,7,14)), –12.4 (q, ^{1}J(C,H) = 128.1 Hz, ^{4}J(C,Sn) = 10.7 Hz; C(17)), –16.9 (q, ^{1}J(C,H) = 133.1 Hz, ^{1}J(C,^{119}Sn) = 400.5 Hz, ^{1}J(C,^{117}Sn) = 382.8 Hz; C(18)); HRMS: m/z = 432.9404 (calcd. for $C_{19}H_{15}{}^{72}Ge^{118}Sn$ (M^{+} – CH_3): m/z = 432.9409.

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