SYNTHESIS OF 9,10-DIMETALLATRIPTYCENES CONTAINING GROUP 15 ELEMENTS FROM *ortho*-PHENYLENEMAGNESIUM

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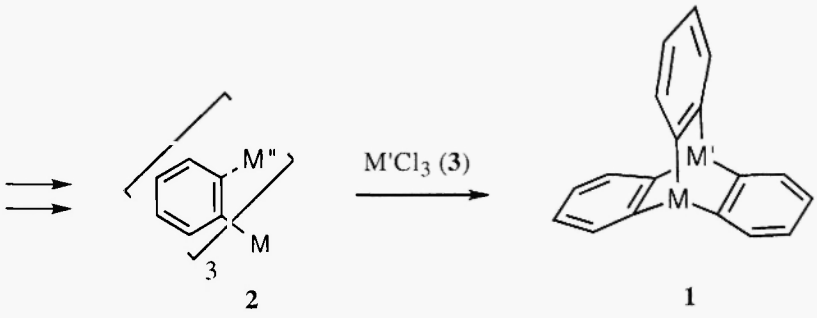
Abstract

The mixed group 14/15 9,10-dimetallatriptycenes RGe(*o*-$C_6H_4)_3$M (**8a**, **9a**, **9b**, and **10a**) were obtained from *ortho*-phenylenemagnesium (**4**) via the tri-Grignard reagents RGe(*o*-$C_6H_4MgCl)_3$ (**6**) and MCl_3 (M = P , As, Sb). The reaction of *ortho*-phenylenezinc (**14**) with $AsCl_3$ opened a new access to 9,10-diarsatriptycene (**7**). An X-ray crystal structure of **9a** and **7** is presented.

Introduction

Several strategies are available for the preparation of 9,10-dimetallatriptycenes (**1**) [1]. One of these proceeds via intermediates of type **2** (M" = Li, MgX, ZnX, etc.) and is particularly useful for the synthesis of triptycenes with two different metals in the bridgehead positions (**1**, M ≠ M'); this is achieved in the final ring closure reaction of **2** to **1** by an appropriate choice of the metal trihalide $M'Cl_3$ (**3**) (Scheme 1).



2 1

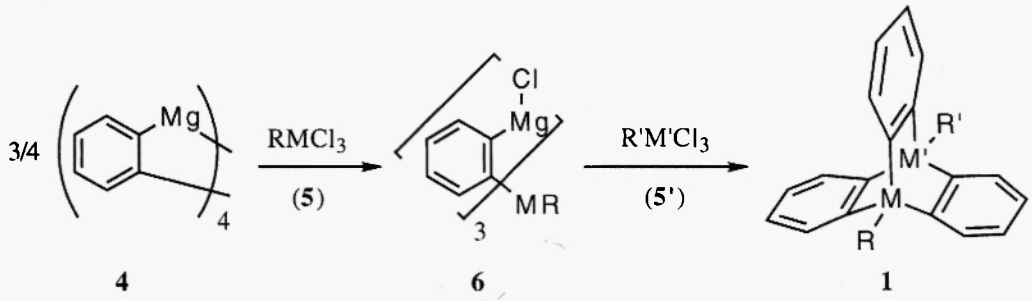
Scheme 1

Starting from *ortho*-phenylenemagnesium (**4**) and group 14 trihalides $RMCl_3$ (**5**), we have recently developed a versatile route towards **1** containing two equal or two different elements of group 14 [2]. It proceeds with amazing selectivity via the in situ formation of tri-Grignard reagents **6** (which correspond to **2** with M = RSi, RGe, RSn; Scheme 2). We here report investigations aimed at extending this approach to triptycenes **1** containing one or two group 15 elements. Although **7** (**1**, M = M' = As), one of the parent compounds of this category, has first been prepared as early as 1927 [3], mixed metal derivatives involving two group 15 elements are less common [1]. Those with heavier elements from two different groups have so far only been reported in the perfluorotriptycene series [4].

Results and Discussion

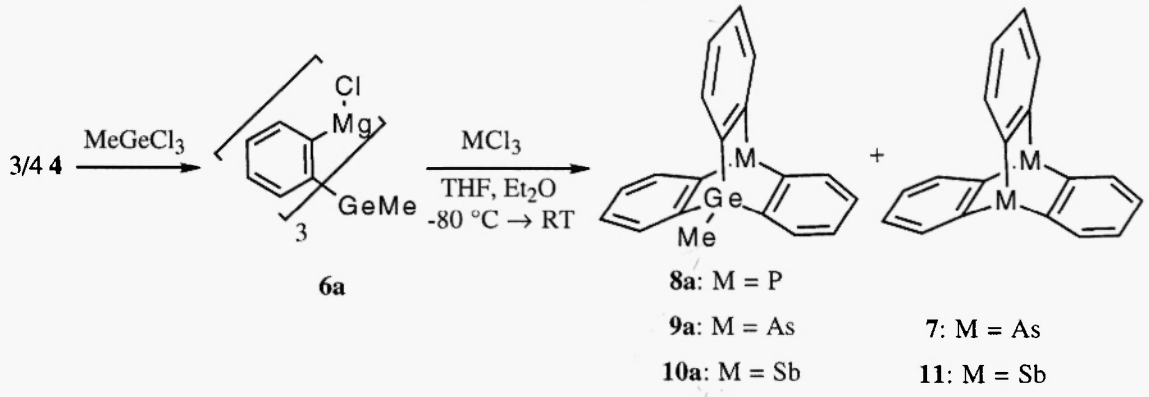
*Reaction of methyltris(2-chloromagnesiophenyl)germanium (**6a**) with PCl_3, $AsCl_3$, and $SbCl_3$*

Compound **6a** [2a,b] (Scheme 3) was obtained in high yield by the reaction of **4** (3 molar equivalents C_6H_4Mg of (tetrameric!) **4**) with one molar equivalent of methylgermanium trichloride.



Scheme 2

Addition of a metal trichloride **3** of group 15 (M = P, As, Sb) to **6a** was performed at low temperature (-80 °C) because the reactivity of PCl_3, $AsCl_3$, and $SbCl_3$ was found to be much higher than that of their group 14 analogues **5**. After the reaction mixture had been gradually warmed to room temperature, the solvent was evaporated and the residue was extracted with toluene or benzene. Evaporation of the extract gave a solid residue that was filtered over silica with benzene. GC/MS analysis of the eluates showed the presence of the expected mixed group 14/15 triptycenes **8a**, **9a**, and **10**a, respectively.



Scheme 3

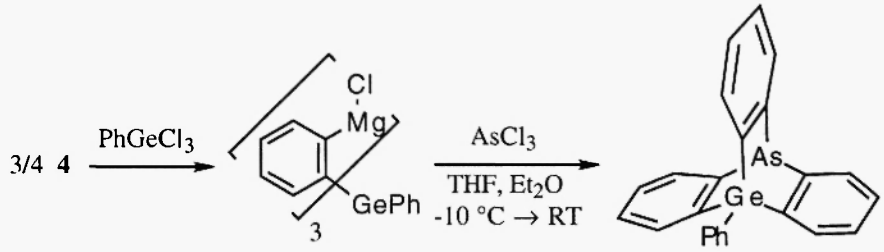
As side-products, $MeGePh_3$ (formed from unreacted **6a** on hydrolysis) and the symmetrical 9,10-dimetallatriptycenes **7** [3] and **11** [5], respectively, were observed. They could be removed by crystallisation, but not by preparative GC (**7**) or by TLC (**11**). The identity of **9a** and **10a** was confirmed by NMR spectroscopic analysis and by a crystal structure determination (vide infra). The phosphorus analogue **8a** has so far not been obtained in pure form. It was detected by GC/MS analysis of the crude reaction mixture, but after column chromatography or preparative TLC, it was not recovered, possibly because it was physically or chemically bonded to silica, or oxidation had occurred under formation of the corresponding oxide which may be insoluble and therefore not detectable by MS or NMR spectroscopy. This aspect clearly needs further investigation.

The formation of the symmetrical side products **7** and **11** is probably due to the extremely fast reaction of MCl_3 with **4** which might have been present as an impurity in the solution of **6a**. Alternative rationalisations involving exchange of metals between intermediates **2** and MCl_3 have been offered for the formation of analogous symmetrical products in the perfluorotriptycene series [4], but they appear less likely, certainly in the case of **7** and **11**.

*Reaction of phenyltris(2-chloromagnesiophenyl)germanium (**6b**) with $AsCl_3$*

In analogy to the procedure described for **9a**, the reaction of **6b** [2] (from 3 equivalents of C_6H_4Mg from **4** with one equivalent of $PhGeCl_3$) with one molar equivalent of $AsCl_3$ at -10 °C gave **9b**. The reaction mixture was allowed to warm to room temperature and furnished a turbid solution; on workup and elution from silica with benzene, it gave a white solid which was identified as pure

10-phenyl-9-arsa-10-germatriptycene **9b** (Scheme 4); the patterns of the ^{1}H and ^{13}C NMR spectra were similar to those of other unsymmetrical triptycenes **1** [2], and the GCMS and HRMS data were in agreement with this interpretation, too. The isolated yield of **9b** was 35%.

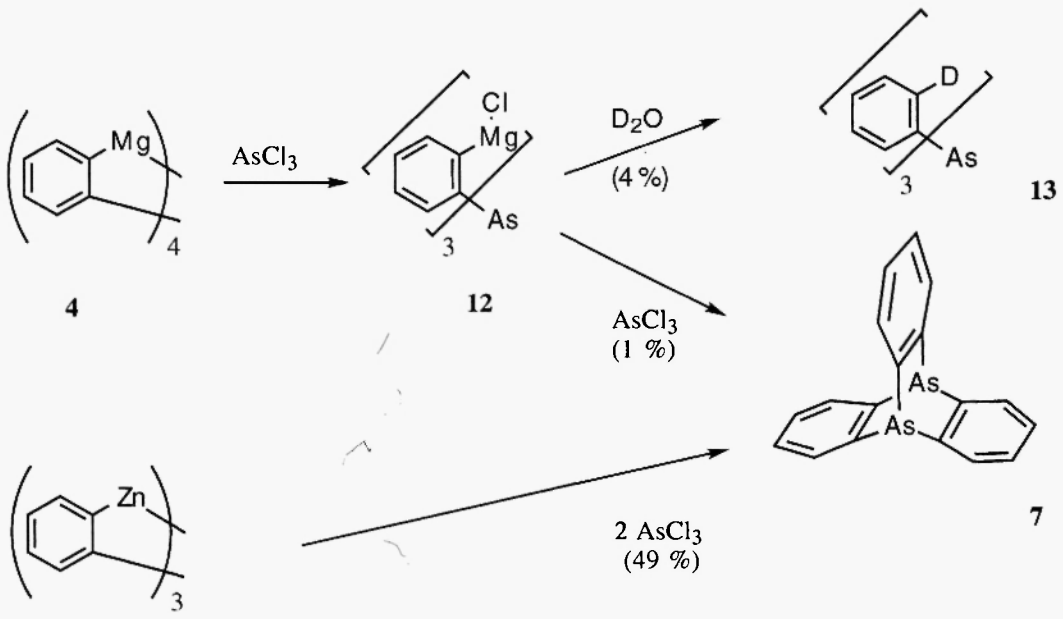


6b **9b**

Scheme 4

*Preparation of 9,10-diarsatriptycene (**7**) from ortho-phenylenezinc (**14**)*

Preparation of the tri-Grignard reagent **12** (Scheme 5) from **4** and $AsCl_3$ in analogy to **6a,b** would be attractive because it would permit another access to mixed metal derivatives of **1**. However, our attempts were so far unsuccessful. Although after deuterolysis of the reaction mixture, the formation of **13** forms evidence for the intermediacy of **12**, the yield of **13** (GCMS: 4 %) was too low to encourage further synthetic applications. The only other identified product was **7** (1 %). In contrast, the reaction of **14** [6], which is the zinc analogue of **4**, with $AsCl_3$ gave **7** in 49 % yield.



Scheme 5

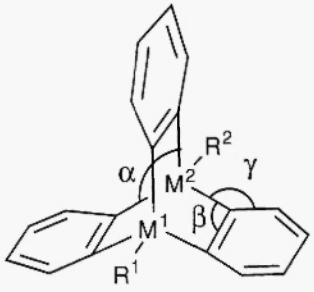
*X-Ray crystal structure determinations of **9a** and **7***

Crystals of **7** and **9a** suitable for a single crystal X-ray structure determination were obtained by slow evaporation of their solution in C_6D_6. These structures are depicted in Figure 1. Compound **7** shows an exact, crystallographic molecular C_2 symmetry in the solid state and an approximate, non-crystallographic D_{3h} symmetry. Compound **9a** expresses a crystallographic C_3 and an approximate C_{3v} symmetry of the molecule in the solid state. Relevant bond distances and angles of **9a**, **7**, and for comparison those of 9-methyl-10-phenyl-9,10-digermatriptycene **15** [2c], are summarized in Table 1.

If one would fix the angles β and γ at the benzene ring of a triptycene (see figure at Table 1) to the ideal unstrained value of 120 °. the angle α at the bridgehead atom M is calculated to be 97.2 ° (for M on a 3-fold axis: α = arccos[-1/8], independent of the M-C distance). Thus in **7**, α is close to the ideal value; this is feasible without much angle strain as the natural hybridisation of arsenic tends to favour smaller angles (AsH_3: 92.0 ° [7], $AsMe_3$: 96.2 ° [8], tri-*p*-tolylarsine: 102 ° [9]. Not surprisingly, the angles β and γ are close to 120 °.

The angles around Ge are wider as germanium would prefer tetrahedral values; this has been discussed in detail for other 9-germatriptycenes [2c]. Accordingly, the angles β and γ deviate more strongly from 120°. On the statistical basis of the given structures **15**, **9a**, and **7**, it cannot be proved whether in the mixed triptycene **9a** the angle α at one metal is influenced by the presence of the other metal. If there is an influence at all, it must be small.

Table 1: Selected bond angles (°) and lengths (Å) of **15**, **9a**, and **7**.



	15[a]	**9a**	**7**
	$M^1 = M^2 = Ge$	$M^1 = Ge$, $M^2 = As$	$M^1 = M^2 = As$
$\alpha(C_{ipso}\text{-}As\text{-}C_{ipso})$		97.0(4)	94.99(8)-96.17(9)
$\alpha(C_{ipso}\text{-}Ge\text{-}C_{ipso})$	101.0(3)-104.1(3)	101.8(4)	
$\beta(As\text{-}C_{ipso}\text{-}C_{endo})$		121.8(8)	120.74(16)-121.42(14)
$\beta(MeGe\text{-}C_{ipso}\text{-}C_{endo})$	114.5(5)-116.8(5)	114.7(8)	
$\gamma(As\text{-}C_{ipso}\text{-}C_{exo})$		118.2(8)	119.09(17)-119.54(17)
$\gamma(MeGe\text{-}C_{ipso}\text{-}C_{exo})$	124.1(6)-126.1(5)	125.2(9)	
Ge-Me	1.937(7)	1.8790(14)	
$As\text{-}C_{ipso}$		1.970(12)	1.948(2)-1.957(2)
$MeGe\text{-}C_{ipso}$	1.939(7)-1.963(7)	1.946(10)	

[a] R^1 = Me, R^2 = Ph (Ref. 2c).

Structures **15** and **9a** are biased by disorder (**15**) or twinning (**9a**). As a consequence, the differences in Ge-Me distances are not really reliable. Additionally, the bond lengths in the aromatic rings are rather variable with 1.373(11)-1.411(9) Å for **15** and 1.311(17)-1.447(15) Å for **9a**. This bond length variation is also encountered in the well ordered structure of **7**, but to a much smaller extent (1.379(4)-1.401(4) Å); this has been encountered before for compound **1** (M = As, M' = CH) [10].

From **10a**, we were also able to obtain crystals by slow evaporation of its solution in chloroform or toluene. However, the crystal quality was too poor to allow a detailed analysis of the structure by X-ray diffraction. Nevertheless, the general structure could be confirmed.

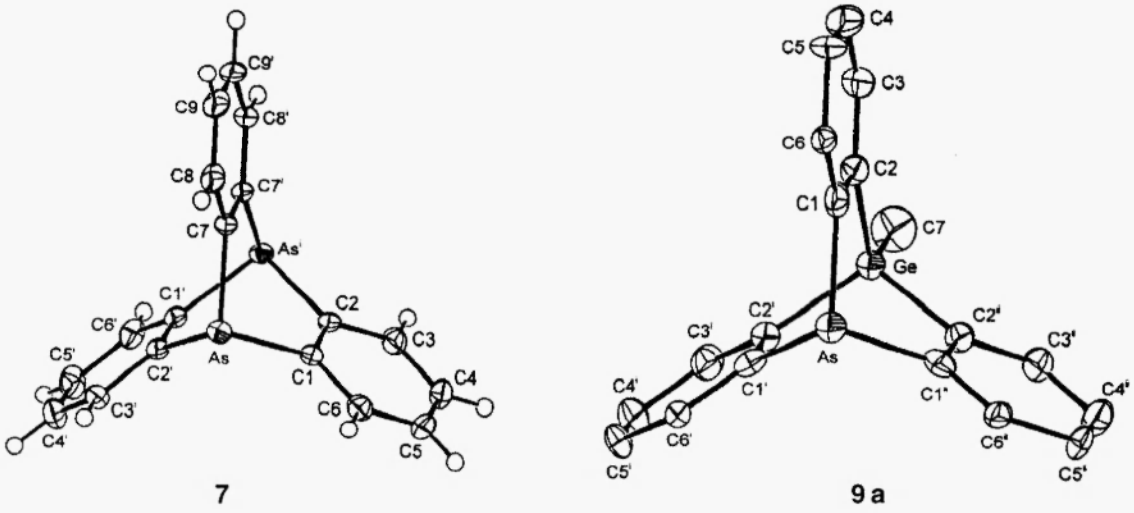


Figure 1: Displacement ellipsoid plots of **7** and **9a** drawn at the 50% probability level. Important distances and angles are presented in Table 1.

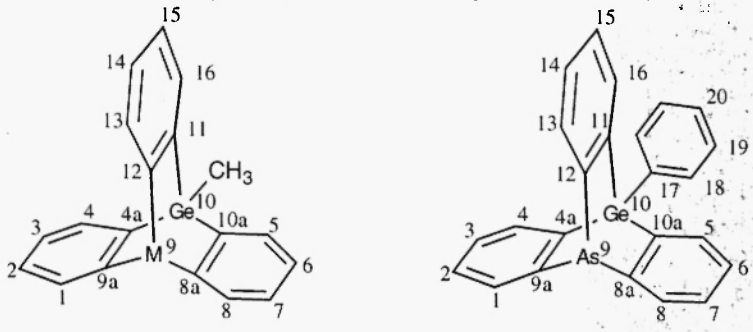
Conclusion

From *ortho*-phenylenemagnesium (**4**) as the primary starting material, mixed group 14/15 9,10-dimetallatriptycenes **8a** - **10a** were obtained via the tri-Grignard reagent **6a** and MCl_3 (M = P, As, Sb, respectively); analogously, **9b** was prepared from **6b** with $AsCl_3$. The reaction of *ortho*-phenylenezinc (**14**) with $AsCl_3$ opened a new access to the long-known 9,10-diarasatriptycene **7**. An X-ray crystal structure determination of **9a** and **7** allowed a comparative structural analysis of the influence of the hybridisation of the bridgehead atom on structure; the smaller natural bond angle of arsenic fit better in the triptycene structure than those of group 14 elements and thus reduce strain in the skeleton.

Experimental

General Comments

All reactions were performed in fully sealed glassware using high vacuum techniques [11]. All solvents were distilled from Na/K alloy. NMR spectra were measured at 25 °C on a Bruker AS 200 spectrometer (^1H and ^{13}C NMR) or on a Bruker MSL 400 spectrometer (^1H and ^{13}C NMR); the chemical shifts and *J*(H,H) coupling constants were determined by simulation using a gNMR-program [12], from CH correlation spectra, and if necessary from NOE experiments.



9a: M = As; **10a**: M = Sb **9b**

Figure 2. Numbering system of **9a**, **9b**, and **10a**.

The HRMS measurements were performed on a Finnigan MAT 90 mass spectrometer. GC/MS measurements were performed on a HP 5890 GC/5970 MS combination (70 eV, Chrompack BP 1 (QSGE) 50 m x 0.25 mm column). Preparative GC was performed on an Intersmat gas chromatograph GC 120, equipped with a chrompack column (2 m x 4 mm, 10% OV-101 Chromosorb WHP 60/100) and a thermal conductivity detector. Thin Layer Chromatography (TLC)

was performed on a Merck plate (Silicagel 60 F_{254} 20 x 20 cm, layerthickness 2 mm) using *n*-hexane : Et_2O (9 : 1) as the eluent. *ortho*-Phenylenemagnesium (**4**) [13], *ortho*-phenylenezinc (**14**) [6], and the tri-Grignard reagents **6a,b** [2b,c,14] were prepared according to literature. The numbering system for **9a,b** and **10a** is depicted in Figure 2.

*Synthesis of 10-methyl-9,10-dihydro-10-germa-9-phospha-9,10[1',2']-benzenoanthracene (**8a**)*

At -80 °C, phosphorus trichloride in Et_2O (3.00 mL, 0.100 M, 0.30 mmol), was added during 8 h to a solution of **6a** (0.30 mmol) in THF/Et_2O (19.35 mL, 0.0155 M, 0.30 mmol). The reaction mixture was kept for 24 h at -80 °C and regularly shaken, then stirred for 24 h at -20 °C and overnight at RT. The solvent was evaporated and the residue was extracted with benzene (3x10 mL). The combined benzene fractions were evaporated to dryness. GC/MS analysis of the residue showed the presence of **8a** (50%): MS (EI, *m/z*, rel. int. (%)): 348 ($M^{+\cdot}$, $C_{19}H_{15}GeP$, 14), 333 ($[M - CH_3]^+$, 50), 257 ($[M - CH_3 - C_6H_4]^+$, 15), 228 ($[M - CH_3 - C_6H_4 - P]^+$, 4)) and $MeGePh_3$ (50%): MS (EI, *m/z*, rel. int. (%)): 305 ($[M - CH_3]^+$, 100), 227 ($[M - CH_3 - C_6H_5]^+$, 9), 151 ($[M - CH_3 - 2C_6H_5]^+$, 23). Purification attempts were unsuccessful. Part of the product mixture was brought on a silica column and extracted with benzene. Evaporation of the eluate resulted in a white powder that did not contain **8a**, but an unidentified product: MS (EI, m/z, rel. int. (%)): 498 (63), 421 (33), 407 (94), 271 (67), 257 (100). Preparative TLC of this product showed 2 bands which were isolated, powdered and eluted with benzene. On GC/MS analysis, no products were observed.

*Synthesis of 10-methyl-9,10-dihydro-9-arsa-10-germa-9,10[1',2']-benzenoanthracene (**9a**)*

At -80 °C, arsenic trichloride in Et_2O (4.85 mL, 0.0619 M, 0.30 mmol), diluted with THF (10 mL) was added during 4 h to a solution of **6a** in THF/Et_2O (19.35 mL, 0.0155 M, 0.30 mmol). The reaction mixture was kept for 24 h at -80 °C and regularly shaken, then stirred for 24 h at 5 °C and 72 h at RT. The solvent was evaporated and the residue was extracted with toluene (3x10 mL). The combined organic fractions were evaporated to dryness. The residue was dissolved in benzene and eluted over a silica column with benzene. Evaporation of the benzene fractions resulted in a white powder. GC/MS analysis showed the presence of **9a** (95%), 7 (2%), and $MeGePh_3$ (4%). Yield: 88.4 mg (75%). Part of this mixture was purified by preparative GC, traces of **7** (3%) were removed upon crystallisation from $CHCl_3$ or C_6D_6. **9a**: MS (EI, *m/z*, rel. int. (%)): 392 ($M^{+\cdot}$, $C_{19}H_{15}GeAs$, 52), 377 ($[M - CH_3]^+$, 86), 301 ($[M - CH_3 - C_6H_4]^+$, 29), 227 ($[M - CH_3 - 2\,C_6H_4]^+$, 100)). HRMS (EI): calcd. for $[C_{19}H_{15}GeAs]^+$: 391.9601; measured: 391.9584. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.88 (m, ^3J(H,H) = 7.4 Hz, ^4J(H,H) = 1.3 Hz, ^5J(H,H) = 0.5 Hz, 3H; H(1,8,13)), 7.67 (m, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.4 Hz, ^5J(H,H) = 0.5 Hz, 3H; H(4,5,16)), 7.24 (m, ^3J(H,H) = 7.2 Hz, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 1.3 Hz, 3H; H(3,6,15)), 7.21 (m, ^3J(H,H) = 7.4 Hz, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 1.4 Hz, 3H; H(2,7,14)), 1.29 (bs, 3H; CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 146.8 (C(8a,9a,12)), 142.8 (C(4a,10a,11)), 134.3 (C(1,8,13)), 131.4 (C(4,5,16)), 127.7 (C(2,7,14)), 127.6 (C(3,6,15)), -12.8 (CH_3).

*Synthesis of 10-methyi-9,10-dihydro-10-germa-9-stiba-9,10[1',2']-benzenoanthracene (**10a**)*

At -80 °C, antimony trichloride in THF (4.85 mL, 0.0654 M, 0.32 mmol), was added during 4 h to a solution of **6a** in THF/Et_2O (19.35 mL, 0.0155 M, 0.30 mmol). The reaction mixture was kept for 4 h at -80 °C and regularly shaken, then stirred for 2 h at -20 °C and overnight at RT. The solvent was evaporated and the residue was extracted with benzene (3x10 mL). The combined organic fractions were evaporated to dryness. The residue was dissolved in benzene and eluted over a silica column with benzene. Evaporation of the benzene fractions resulted in a slightly yellow powder. GC/MS analysis showed the presence of **10a** (80%), **11** (19%), and $MeGePh_3$ (1%). Yield: 88.9 mg (68%). Part of this mixture was purified by TLC. The upper band was isolated, powdered, and extracted with $CHCl_3$. Removal of the solvent in vacuo, gave a powder containing **10a** and **11** (95 : 5). Pure **10a** was obtained by crystallisation from toluene or $CDCl_3$. **10a**: MS (EI, *m/z*, rel. int. (%)): 438 ($M^{+\cdot}$, $C_{19}H_{15}GeSb$, 90), 423 ($[M - CH_3]^+$, 28), 347 ($[M - CH_3 - C_6H_4]^+$,7), 317 ($[M - Sb]^+$, 17), 273 ($[C_{12}H_8Sb]^+$, 83), 241 ($[M - C_6H_4 - Sb]^+$, 46), 228 ($[M - CH_3 - C_6H_4 - Sb]^+$, 100)), 197 (27), 152 (69). HRMS (EI): Calcd. for $[C_{19}H_{15}GeSb]^{+\cdot}$: 437.9423; measured: 437.9423. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.91 (m, ^3J(H,H) = 7.4 Hz, ^4J(H,H) = 1.3 Hz, ^5J(H,H) = 0.6 Hz, 3H; H(1,8,13)), 7.74 (m, ^3J(H,H) = 7.3 Hz, ^4J(H,H) = 1.4 Hz, ^5J(H,H) = 0.6 Hz, 3H; H(4,5,16)), 7.26 (m, ^3J(H,H) = 7.3 Hz, ^3J(H,H) = 7.3 Hz, ^4J(H,H) = 1.3 Hz, 3H; H(2,7,14)), 7.19 (m, ^3J(H,H) = 7.3 Hz, ^3J(H,H) = 7.4 Hz, ^4J(H,H) = 1.4 Hz, 3H; H(3,6,15)), 1.27 (bs, 3H; CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 146.1 (C(8a,9a,12)), 142.8 (C(4a,10a,11)), 137.0 (C(1,8,13)), 131.5 (C(4,5,16)), 128.2 (C(3,6,15)), 127.9 (C(2,7,14)), -11.2 (CH_3). **11**: MS (EI, *m/z*, rel. int. (%)): 472 ($M^{+\cdot}$, $C_{18}H_{12}Sb_2$, 42), 349 ($[M - Sb]^{+\cdot}$, 24), 273 ($[M - Sb - C_6H_4]^+$, 50), 228 (100), 197 ($[M - Sb - 2C_6H_4]^+$, 17)), 152 (68). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 8.09 (m, ^3J(H,H) = 7.3 Hz, ^4J(H,H) = 1.4 Hz, ^5J(H,H) = 0.6 Hz, 6H, H(1,4,5,8,13,16)), 7.23 (m, ^3J(H,H) = 7.5 Hz, 6H, H(2,3,6,7,14,15)). ^{13}C NMR$\{^1H\}$ (100.6 MHz, $CDCl_3$): δ = 149.0 (C(4a,8a,9a,10a,11,12)), 136.6 (C(1,4,5,8,13,16)), 128.7 (C(2,3,6,7,14,15)).

*Synthesis of 10-phenyl-9,10-dihydro-9-arsa-10-germa-9,10[1',2']-benzenoanthracene (**9b**)*

At -10°C, $AsCl_3$ (0.323 mmol in 6.55 mL of Et_2O) was added during 1 h to a solution of **6b** (0.323 mmol in 20.0 mL of THF). After the mixture had been stirred for 1.5 h, it was allowed to warm to room temperature overnight. The solvent was evaporated in vacuo and the residue was

extracted with toluene (3 x 10 mL). The combined organic layers were filtered over a glass fritte and the obtained clear solution was evaporated to dryness. The residue was dissolved in benzene and eluted from silica. The eluate was evaporated to dryness to furnish 0.051 g of a white solid which was identified by ^{1}H and ^{13}C NMR spectroscopy as pure **9b**. Yield: 0.112 mmol (35%). **9b**: HRMS: calcd. for $C_{24}H_{17}{}^{70}GeAs$ ($M^{+\cdot}$): 449.9789; measured: 449.9795. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.97 (m, ^3J(H,H) = 7.4 Hz, ^4J(H,H) = 1.5 Hz, ^4J(H,H) = 1.3 Hz, ^5J(H,H) = 0.7 Hz, 2H; H(18)), 7.94 (m, ^3J(H,H) = 7.4 Hz, ^4J(H,H) = 1.2 Hz, ^5J(H,H) = 0.7 Hz, 3H; H(4,5,16)), 7.73 (m, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.4 Hz, ^5J(H,H) = 0.7 Hz, 3H; H(1,8,13)), 7.34 (m, ^3J(H,H) = 7.6 Hz, ^3J(H,H) = 7.4 Hz, ^4J(H,H) = 1.3 Hz, ^5J(H,H) = 0.7 Hz, 2H; H(19)), 7.34 (m, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 1.3 Hz, 1H; H(20)), 7.32 (m, ^3J(H,H) = 7.6 Hz, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 1.3 Hz, ^5J(H,H) = 0.7 Hz, 2H; H(19)), 6.99 (m, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.2 Hz, 3H; H(2,7,14)), 6.99 (m, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 7.4 Hz, ^4J(H,H) = 1.4 Hz, 3H; H(3,6,15)); ^{13}C NMR (100 MHz, C_6D_6): δ = 147.5 (m; C(8a,9a,12)), 142.6 (m; C(4a,10a,11)), 136.3 (dm, ^1J(C,H) = 159.7 Hz; C(18)), 135.0 (dt, ^1J(C,H) = 157.9 Hz, ^3J(C,H) = 5.1 Hz; C(4,5,11)), 132.8 (dt, ^1J(C,H) = 157.8 Hz, ^3J(C,H) = 3.9 Hz; C(1,8,13)), 130.7 (s; C(17)), 130.3 (dt, ^1J(C,H) = 160.0 Hz, ^3J(C,H) = 7.2 Hz; C(20)), 129.4 (dm, ^1J(C,H) = 163.5 Hz; C(19)), 128.2 (dt, ^1J(C,H) = 159.6 Hz, ^3J(C,H) = 5.8 Hz; C(2,3,6,7,14,15)).

*Reaction of of **4** with arsenic trichloride*

Into a cooled solution (-80 °C) of **4** in THF (16.66 mL, 0.054 M, 0.90 mmol), $AsCl_3$ in Et_2O (5.26 mL, 0.057 M, 0.30 mmol) was condensed and the reaction mixture was stirred for 5 h at -80 °C, 3 h at -20 °C and 72 h at 5 °C. To an aliquot (2.51 mL), D_2O and hexamethylbenzene (3.6 mg, 0.023 mmol) were added and subsequently extracted with Et_2O, washed (water and brine) and the combined organic layers were dried ($MgSO_4$). GC/MS analysis showed the presence of **7** (1%) and **13** (Ph_3As-d_3, 4%, 80% D_3). **7**: MS (EI, *m/z*, rel. int. (%)): 378 ($M^{+\cdot}$, 100), 228 ([M - C_6H_5As]$^+$, 66), 151 ([C_6H_4As]$^+$, 83)). **13**: MS (EI, *m/z*, rel. int. (%)): 309 ($M^{+\cdot}$, 37), 308 (6), 229 (30), 153 (100), 78 (17).

*Reaction of **4** with arsenic trichloride (NMR experiment)*

To a frozen solution (-196 °C, liquid nitrogen) of **4** (0.15 mmol) in THF-d_8 (0.4 mL) in an NMR tube, $AsCl_3$ (0.05 mmol) was condensed. The NMR tube was homogenised very shortly at RT (vortex), on which, immediately, a precipitate formed. ^{1}H NMR spectroscopy at -60 °C showed the presence of **7** (30%), **4** (70%), and an unidentified product (**A**). **4**: ^{1}H NMR (400.1 MHz, THF-d_8): δ = 7.72 (m, 2 H), 6.79 (m, 2 H). **7**: ^{1}H NMR (400.1 MHz, THF-d_8): δ = 8.03 (m, ^3J(H,H) = 7.0 Hz, ^4J(H,H) = 1.5 Hz, ^5J(H,H) = 1.0 Hz,6H, H(1,4,5,8,13,16)), 6.87 (m, ^3J(H,H) = 7.0 Hz, ^3J(H,H) = 7.4 Hz, ^4J(H,H) = 1.5 Hz, ^5J(H,H) = 1.0 Hz, 6H, H(2,3,6,7,14,15). (**A**): ^{1}H NMR (400.1 MHz, THF-d_8): δ = 7.39 (d, J(H,H) = 8 Hz, 1H), 7.02 (m, 2H), 6.64 (t, J(H,H) = 8 Hz, 6H).

*Synthesis of 9,10-dihydro-9,10-diarsa-9,10[1',2']-benzenoanthracene (**7**)*

On a frozen solution (-196 °C, liquid N_2) of **14** (0.30 mmol) in THF (2.80 mL), $AsCl_3$ (0.10 mmol) in Et_2O (1.62 mL) was condensed. After stirring for 24 h at -90 °C, overnight at 5 °C, and 4 h RT, the reaction mixture was recooled to -196 °C and a second equivalent of $AsCl_3$ was condensed thereupon. At -80 °C, the molten mixture was stirred for 24 h, overnight at 5 °C and 8 h at RT. After removal of the volatiles, the remaining residue was extracted with benzene (3 x 20 mL), and the combined organic layers were washed with HCl (5%) and water and dried ($MgSO_4$). After evaporation of the solvent (*in vacuo*) a slightly yellow powder resulted that was sublimed during 3 h under vacuum (175 °C, 0.01 atm.). Yield: 49% (18.4 mg). A crystal suitable for an X-ray determination was obtained upon recrystallisation from C_6D_6. MS (EI, *m/z*, rel. int. (%)): 378 ($M^{+\cdot}$, 100), 228 ([M - C_6H_5As]$^+$, 66), 151 ([C_6H_4As]$^{+\cdot}$, 83)). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$): δ = 146.1 (C(4a,8a,9a,10a,11,12)), 133.7 (C(1,4,5,8,13,16)), 128.2 (C(2,3,6,7,14,15).

X-Ray crystal structure determinations

Intensities were measured on an Enraf-Nonius CAD4T diffractometer with rotating anode (Mo-K_α, λ = 0.71073 A) at a temperature of 150 K. The data reduction was performed with the program HELENA [15]. The structures were solved with automated Patterson methods (DIRDIF-97 [16]). The refinement was done with the program SHELXL-97 [17] against F^2 of all reflections. Non hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were refined as rigid groups. The drawings, structure calculations, and checking for higher symmetry was performed with the program PLATON [18]. Further details of the crystal structure determinations can be obtained by contacting the author A.L.S.

*Compound **7***

$C_{18}H_{12}As_2$, M_r = 378.12 g mol^{-1}, colourless needle, 0.25 x 0.38 x 1.00 mm^3, monoclinic, C2/c, a = 15.0329(15) Å, b = 8.3598(6) Å, c = 13.2391(13) A, β = 120.461(11)°, V = 1434.1(2) Å^3, Z = 4, ρ = 1.751 g cm^{-3}, 3408 measured reflections, (sin θ/λ)$_{max}$ = 0.65 Å^{-1}. Absorption correction based on psi-scans (μ = 4.65 mm^{-1}, 0.76-0.97 transmission). 1643 unique reflections (R_{int} = 0.045). 91 parameters, no restraints. R (I > 2σ(I)): R_1 = 0.0250, wR2 = 0.0596. R (all data): R1 = 0.0306, wR2 = 0.0616. S = 1.121. Dρ$_{fin}$ (min./max.) –0.94/0.50 e/Å^3.

*Compound **9a***

$C_{19}H_{15}AsGe$, M_r = 390.82 g mol^{-1}, colourless block, 0.2 x 0.2 x 0.2 mm^3, trigonal, $R\bar{3}$, a = b =

12.1425(2) Å, c = 18.3142(2) Å, V = 2338.49(6) Å^3, Z = 6, ρ = 1.665 g cm^{-3}, 7351 measured reflections, $(\sin\theta/\lambda)_{max}$ = 0.59 Å^{-1}. An absorption correction was not considered necessary. 919 unique reflections (R_{int} = 0.057). The crystal appeared to be merohedrically twinned with {0001} as a twin plane (dolomite type twinning). The twin ratio refined to 0.49(1):0.51(1). 62 parameters, 3 restraints. R (I > 2σ(I)): R1 = 0.0596, wR2 = 0.1898. R (all data): R1 = 0.0605, wR2 = 0.1907. S = 1.205. $D\rho_{fin}$ (min./max.) –2.35/3.08 e/Å^3.

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