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Synthesis of Alkynyl-Substituted 9,10-Dimetallatriptycenes of Group 14 and Their Application in the Preparation of a Novel Class of Organometallic Oligomers

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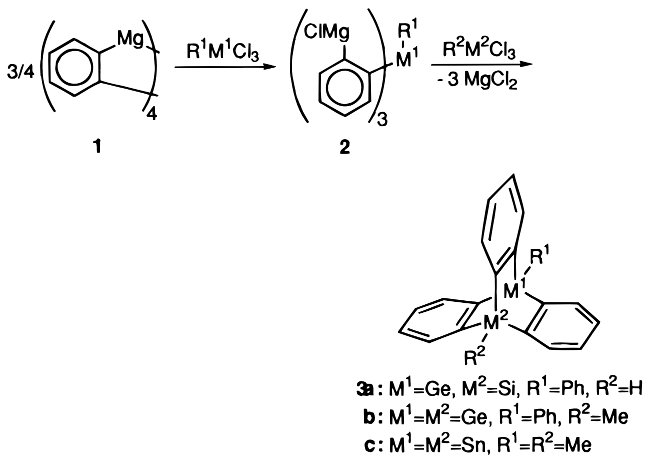
The preparation of ((trimethylsilyl)ethynyl)germanium trichloride (**4**) allowed the synthesis of various alkynyl-substituted 9,10-dimetallatriptycenes via a simple one-pot synthetic procedure. For example, reaction of **4** with *o*-phenylenemagnesium (**1**) gave access to 9,10-$(\mathrm{RC{\equiv}C})_2$-9,10-digermatriptycenes (**5**, R = $\mathrm{SiMe_3}$; **6**, R = H), while reaction of **4** with tris(*o*-(chloromagnesio)phenyl)phenylgermane (**2a**) furnished 9-$(\mathrm{RC{\equiv}C})$-10-phenyl-9,10-digermatriptycenes (**7**, R = $\mathrm{SiMe_3}$; **8**, R = H). The synthetic potential of these compounds in the preparation of rigid organometallic oligomers with conjugated spacers was demonstrated by the oxidative coupling of **8**, which furnished 1,4-bis(9-(10-phenyl-9,10-digermatriptycyl))buta-1,3-diyne (**9**), whose X-ray crystal structure was determined, and the hydrosilylation of **8** with 10-phenyl-10-germa-9-silatriptycene (**3a**), which yielded *trans*-1-(9-(10-phenyl-9,10-digermatriptycyl))-2-(9-(10-phenyl-9-sila-10-germatriptycyl))ethene (**10**).

Introduction

Organometallic polymers in which the metal centers are linked via unsaturated ligands have gained considerable interest due to their possible application in areas such as nonlinear optics[1] and molecular devices such as wires and switches.[2,3]

Our interest in this field of chemistry was raised by a crystallographic study[4] of the substituted 9,10-dimetallatriptycenes **3**[4,5] (obtained via reaction of *o*-phenylenemagnesium (**1**)[6,7] with the corresponding metal trihalides via the intermediate tri-Grignard reagent **2**; see Scheme 1), which indicated that in these compounds the two metal atoms are in closer contact than the sum of their van der Waals radii. It was envisioned that the through-space interaction between these metal atoms and the interaction of filled metal orbitals with vacant p* orbitals of the carbon spacer[8] may be used for the transmission of electrical or optical signals in organometallic polymers.

Scheme 1



In this paper we wish to report the general synthetic approach toward new types of organometallic oligomers containing a group 14 9,10-dimetallatriptycene backbone. Various novel alkynyl-substituted 9,10-digermatriptycenes are described, and their potential for the preparation of organometallic oligomers is demonstrated by the transformation of 9-ethynyl-10-phenyl-9,10-digermatriptycene (**8**) into the dimers 1,4-bis(9-(10-phenyl-9,10-digermatriptycyl))buta-1,3-diyne (**9**) and *trans*-1-(9-(10-phenyl-9,10-digermatriptycyl))-2-(9-(10-phenyl-9-sila-10-germatriptycyl))ethene (**10**). All compounds were characterized by their spectral data and, in the case of **9**, via a single-crystal X-ray structure determination.

Strategic Considerations

The implementation of our one-pot synthetic approach toward substituted 9,10-dimetallatriptycenes (Scheme

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(1) Long, N. J. *Angew. Chem.* **1995**, *107*, 37.

(2) Ward, M. D. *Chem. Ind.* **1996**, 568.

(3) Harriman, A.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1996**, 1707.

(4) Dam, M. A.; de Kanter, F. J. J.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L.; Fornies-Camer, J.; Cardin, C. J. *J. Organomet. Chem.*, in press.

(5) Dam, M. A.; Akkerman, O. S.; de Kanter, F. J. J.; Bickelhaupt, F.; Veldman, N.; Spek, A. L. *Chem. Eur. J.* **1996**, *2*, 1139.

(6) Tinga, M. A. G. M.; Akkerman, O. S.; Bickelhaupt, F.; Horn, E.; Spek, A. L. *J. Am. Chem. Soc.* **1991**, *113*, 3604.

(7) Tinga, M. A. G. M.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Horn, E.; Kooijman, H.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 2808.

(8) Davies, S. J.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Organomet. Chem.* **1991**, *414*, C51.

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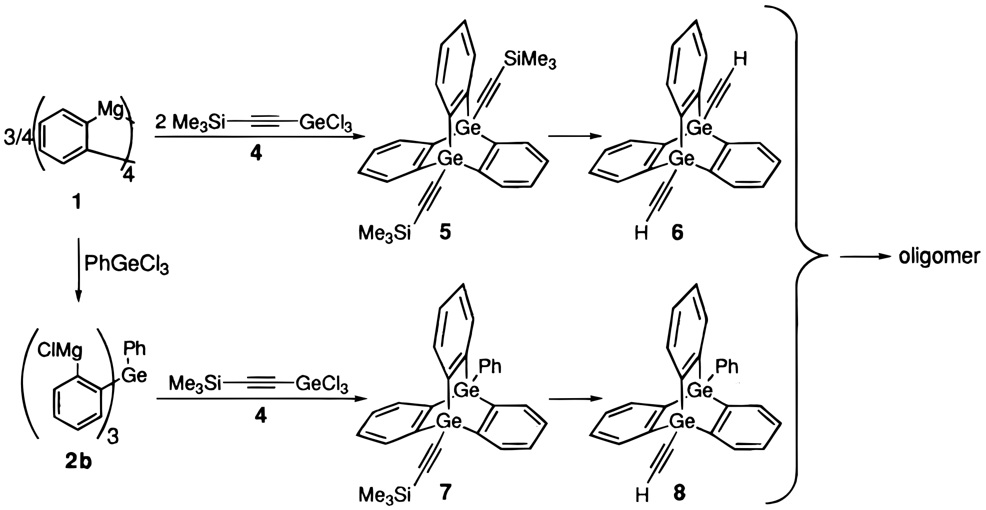
Scheme 2

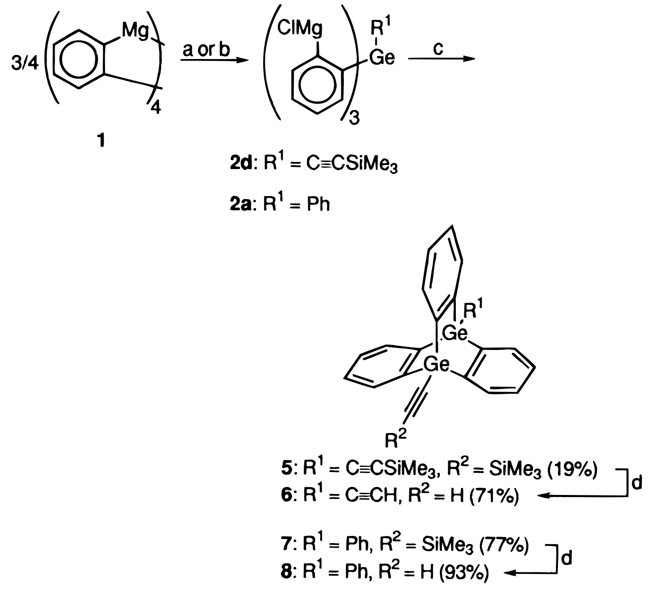


1) in the preparation of organometallic polymers required a synthetic strategy consisting of two steps. The first step encompasses the synthesis of monomers, e.g. 9,10-dimetallatriptycenes containing a suitable substituent at the bridgehead positions, which in the second step are connected to furnish oligomeric structures. The acetylene group was envisioned to be a suitable substituent, as the dimerization and hydrosilylation of substituted acetylenes are well-known,[9−11] and these reactions would furnish a 1,3-butadiyne or a ethene moiety as a conjugating spacer. The introduction of the acetylene function at the bridgehead position of the (monomeric) 9,10-dimetallatriptycene may be achieved in different ways (Scheme 2). One consists of the reaction of 2 equiv of ((trimethylsilyl)ethynyl)germanium trichloride (**4**) with 3 equiv of *o*-phenylenemagnesium (**1**) to furnish 9,10-bis((trimethylsilyl)ethynyl)-9,10-digermatriptycene (**5**), which after desilylation yields 9,10-diethynyl-9,10-digermatriptycene (**6**) as a "repeating unit". Another route is the reaction of 1 equiv of **4** with 1 equiv of tris(*o*-(chloromagnesio)-phenyl)phenylgermane (**2a**; obtained via reaction of 1 molar equiv of $PhGeCl_3$ with three C_6H_4Mg units of **1**),[5] to furnish **7**, which after desilylation may yield 9-ethynyl-10-phenyl-9,10-digermatriptycene (**8**) as a "stopper". The availability of both repeating unit **6** and stopper **8** is essential for the preparation of well-defined oligomeric structures such as dimers and trimers.

Results and Discussion

Synthesis of ((Trimethylsilyl)ethynyl)germanium Trichloride (4). We were able to prepare the novel compound **4** via reaction[12] of trimethylsilylacetylene with $GeCl_4$ and triethylamine in benzene. Workup (filtration and vacuum distillation) furnished a colorless liquid which was identified by ^1H and ^{13}C NMR spectroscopy as pure **4**.

Scheme 3[a]



[a] Conditions: (a) **4**, −10 °C to room temperature (for **2d**). (b) $PhGeCl_3$, −10 °C to room temperature (for **2a**). (c) **4**, −10 °C to room temperature. (d) KOH, H_2O/THF.

Synthesis of "Repeating Unit" 6. The preparation of the dialkynyl-substituted triptycene **5** was performed via a simple one-pot procedure: the tri-Grignard reagent **2d** (generated in situ by reaction of **1** (3 molar equiv of the formally monomeric unit C_6H_4Mg) with **4** (1 molar equiv; Scheme 3) was reacted with 1 equiv of **4** to furnish **5**. However, the yield of **5** was rather poor (≤19%) due to the formation of many byproducts. The formation of these byproducts, probably trimethylsilyl-substituted oligomers and germoxanes, may be explained by a less selective formation of the tri-Grignard intermediate **2d** in comparison to its phenyl analogue **2a**.[4] Although we were able to remove many of the byproducts, we did not obtain **5** in analytically pure form. Removal of the trimethylsilyl groups was easily accomplished via treatment of crude **5** with 2 equiv of aqueous KOH,[13] which gave pure 9,10-diethynyl-9,10-

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(9) Eglinton, G.; McCrae, W. *Adv. Org. Chem.* **1963**, *4*, 225.

(10) Raphael, R. A. *Acetylene Compounds in Organic Synthesis*; Academic Press: New York, 1955.

(11) Lewis, L. N.; Sy, K. G.; Bryant, G. L., Jr.; Donahue, P. E. *Organometallics* **1991**, *10*, 3750.

(12) Efimova, I. V.; Kalganov, B. E.; Kazankova, M. A.; Lutsenko, I. F. *J. Gen. Chem. USSR (Engl. Transl.)* **1984**, *54*, 410.

(13) Takahashi, S.; Koroyama, Y.; Sonogashira, K.; Hagihara, N. *J. Chem. Soc., Chem. Commun.* **1980**, 627.

Scheme 4

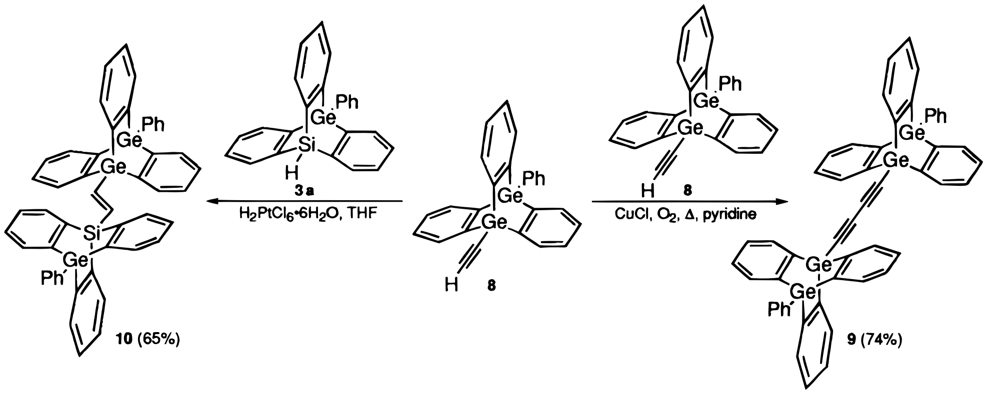

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) of 9·0.5C_6H_5Cl (see Figure 2)

Ge(1)⋯Ge(2)	3.0439(8)	Ge−R^a	1.896(4)
Ge(1a)⋯Ge(2a)	3.0421(7)	Ge(Ph)−C_{ipso}^{a}	1.962(4)
Ge(2)⋯Ge(2a)	7.520(1)	Ge(R)−C_{ipso}^{a}	1.940(4)
Ge(1)⋯Ge(2a)	10.537(2)	C_{ipso}−C_{ipso}^{a}	1.398(6)
Ge(1a)⋯Ge(2)	10.543(2)	−C≡C−	1.189(6)
Ge(1)⋯Ge(1a)	13.543(2)	≡C−C≡	1.383(6)
Ge−Ph^a	1.933(4)		
α_1 (C_{ipso}−Ge(Ph)−C_{ipso})^a	102.8(2)	γ_2 (Ge(R)−C_{ipso}−C)^a	125.0(4)
α_2 (C_{ipso}−Ge(R)−C_{ipso})^a	104.2(2)	Ge(2)−C≡C	174.0(5)
β_1 (Ge(Ph)−C_{ipso}−C_{ipso})^a	115.4(3)	Ge(2a)−C≡C	176.7(5)
β_2 (Ge(R)−C_{ipso}−C_{ipso})^a	114.4(3)	C≡C−C	177.1(6)
γ_1 (Ge(Ph)−C_{ipso}−C)^a	125.3(3)		
Ge(1)−Ge(2)−Ge(2a)−Ge(1a)	14.9(2)		

^{a} Average value.

digermatriptycene (**6**) in an isolated yield of 71%. The identity of the diethynyldigermatriptycenes **5** and **6** followed from comparison of the spectroscopic data (^{1}H and ^{13}C NMR, NOE and CH correlation experiments) with those of known group 14 9,10-dimetallatriptycenes[4,5,14] and, in the case of **6**, from elemental analysis.

Synthesis of "Stopper" 8. The preparation of the trimethylsilyl compound **7** was again performed via our one-pot procedure (Scheme 3): first the tri-Grignard reagent tris(*o*-(chloromagnesio)phenyl)phenylgermane (**2a**) was prepared in situ via reaction of 3 equiv of **1** with 1 equiv of $PhGeCl_3$.[4] Reaction of **2a** with 1 equiv of **4** gave **7** in an isolated yield of 77%. Desilylation of **7** was accomplished with 1 equiv of aqueous KOH, which afforded **8** in an isolated yield of 93%. The identity of ethynyl-digermatriptycenes **7** and **8** followed from elemental analysis and from the spectroscopic data (^{1}H and ^{13}C NMR, NOE and CH correlation experiments).

After having prepared the monomers **6** and **8**, we focused our attention on the application of these compounds in the preparation of organometallic oligomers.

1,4-Bis(9-(10-phenyl-9,10-digermatriptycyl))buta-1,3-diyne (9). Our first attempt to prepare organometallic oligomers was the connection of two molecules of stopper **8** via a Hay coupling[15] (Scheme 4). The reaction was performed by bubbling oxygen through a heated solution of **8** and CuCl (5%) in pyridine. The identification of the white solid obtained after workup was hampered by its poor solubility in common solvents. However, the solubility in bromobenzene was sufficient to allow identification via ^{1}H and ^{13}C NMR spectroscopic analysis, and these data indicated that the reaction had indeed furnished dimer **9** (isolated yield: 74%). Additional proof for the assigned structure came from an X-ray structure determination of a single crystal of **9** which was obtained by crystallization from chlorobenzene (vide infra).

***trans*-1-(9-(10-Phenyl-9,10-digermatriptycyl))-2-(9-(10-phenyl-10-germa-9-silatriptycyl))ethene (10).** Although dimer **9** was obtained in a satisfactory yield, its poor solubility in common solvents foreshadowed practical problems for the preparation of larger oligomers. This low solubility must, at least in part, be due to the high symmetry of this linear molecule. To increase solubility, we attempted to prepare a less symmetrical oligomeric structure via hydrosilylation of **8** with 10-phenyl-10-germa-9-silatriptycene (**3a**)[4] (Schemes 2 and 4). The reaction was performed by stirring a THF solution of **8** and **3a** with a catalytic amount of Speier's catalyst (H_2PtCl_6·$6H_2O$).[11,16] The solubility in $CDCl_3$ of the white solid obtained after workup was sufficient to allow ^{1}H and ^{13}C spectroscopic analysis. The spectra obtained revealed the presence of two unsymmetrical triptycene moieties and a trans-substituted ethene unit (relative ratio 1:1:1). It was therefore concluded that the reaction had indeed furnished *trans*-1-(9-(10-phenyl-9,10-digermatriptycyl))-2-(9-(10-phenyl-10-germa-9-silatriptycyl))ethene (**10**); the isolated yield of **10** was 65%.

Single-Crystal X-ray Structure Determination of Dimer 9. The molecular structure of **9** is depicted in Figure 1. Selected bond lengths, bond angles, and dihedral angles are presented in Table 1, and the crystallographic data for **9** are summarized in Table 2.

In the triclinic unit cell, two adjacent molecules of **9** are arranged in a pairwise fashion together with one molecule of chlorobenzene, which is disordered over an inversion center. From Figure 1 it can be seen that, in each molecule of **9**, one phenyl substituent is disordered over two orientations, represented by C(19)−C(24) and C(19)′−C(24)′, respectively, which are populated in a 1:1 ratio. The two triptycene moieties are connected by a 1,3-butadiyne spacer and are related by a noncrystallographic 2-fold axis perpendicular to C(26)−C(26a). Corresponding values for distances and angles in the other half of the molecule are given in brackets. The

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[14] Takahashi, M.; Hatano, K.; Kawada, Y.; Koga, G.; Tokitoh, N.; Okazaki, R. *J. Chem. Soc., Chem. Commun.* **1993**, 1850.

[15] Hay, A. S. *J. Chem. Soc., Chem. Commun.* **1960**, 1275.

[16] Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.

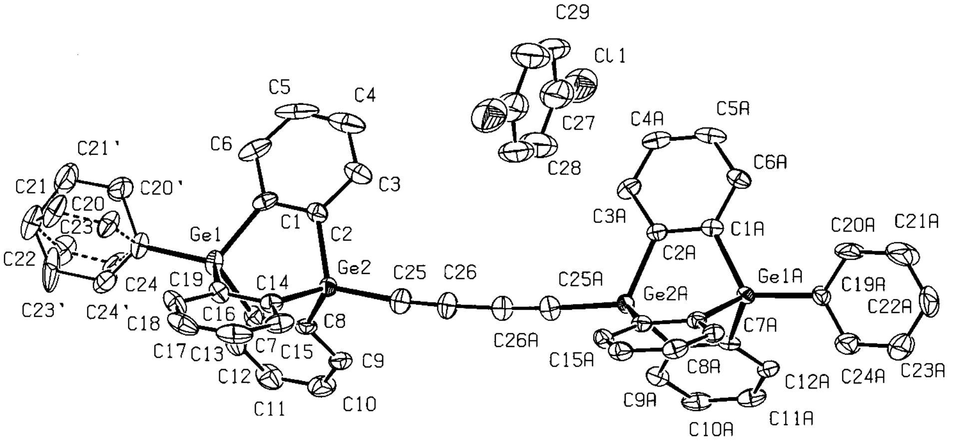
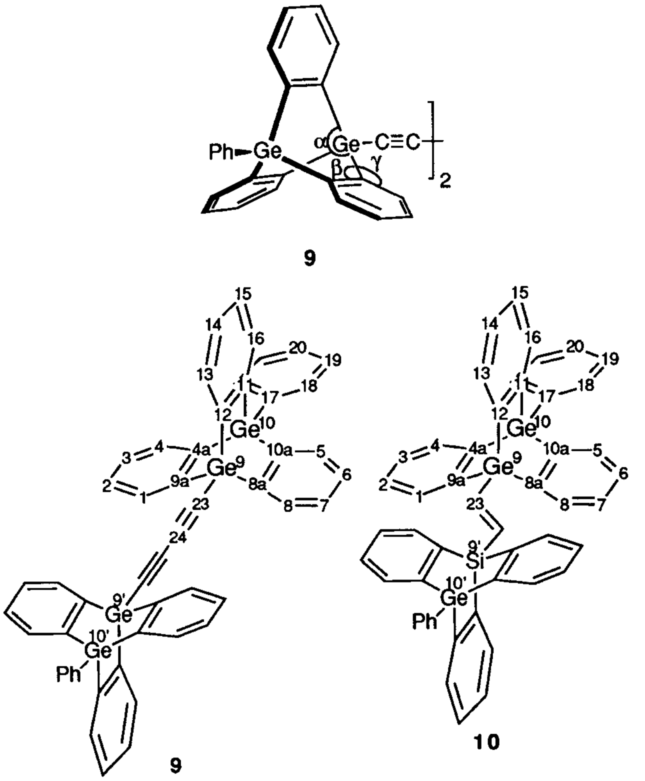


Figure 1. ORTEP plot of **9**·0.5C$_6$H$_5$Cl with ellipsoids drawn at the 50% probability level. Hydrogens are omitted for clarity.

Table 2. Crystal Data and Details of the Structure Determination of 9·0.5C$_6$H$_5$Cl

empirical formula	$C_{52}H_{34}Ge_4 \cdot 0.5C_6H_5Cl$
fw	1005.56
cryst syst	$P\bar{1}$ (No. 2)
a (Å)	8.4807(11)
b (Å)	12.9985(19)
c (Å)	21.141(3)
α (deg)	72.697(12)
β (deg)	80.666(11)
γ (deg)	79.253(11)
V (Å^3)	2171.8(5)
Z	2
D(calc) (g cm^{-3})	1.538
F(000)	1006
μ(Mo Kα) (cm^{-1})	28.1
cryst size (mm)	0.50 × 0.62 × 0.12
temp (K)	150
radiation; λ (Å)	Mo Kα; 0.710 73
θ_{min}, θ_{max}, (deg)	1.0, 27.5
scan (type & range) (deg)	$0.86 + 0.35 \tan \theta$
data set	−11 to 0; −16 to +16; −27 to +27
total of unique no. of data; R(int)	10 624, 9945; 0.075
no. of obsd data ($I > 2.0\sigma(I)$)	7480
transmissn range (empirical)	0.214−0.680
N_{ref}, N_{par}	9945, 579
R, R_w, S^a	0.0503, 0.1332, 1.01
max and av shift/error	0.00, 0.00
min and max resd dens (eÅ^{-3})	−0.98, 0.89

[a] $w = 1/(\sigma^2(F_o^2) + (0.089P)^2 + 2.5065P)$, where $P = (F_o^2 + 2F_c^2)/3$



9

9

10

Figure 2. Schematic representation of **9** and the numbering applied for **9** and **10**.

C−C and C≡C bond lengths of this spacer (1.383(6) and 1.189(6) Å [1.190(6) Å], respectively) are in accordance with those reported for buta-1,3-diyne (1.389(5) and 1.202(7) Å).[17] However, the bond angles around the sp-hybridized C atoms of the spacer deviate from 180° (Ge−C≡C = 174.0(5)° [176.7(5)°], C≡C−C = 177.1(6)° [177.3(6)°]). As a result, the dihedral angle between the central axes of the two triptycene moieties is 14.9(2)°. These triptycene moieties do have the structural features of group 14 9,10-dimetallatriptycenes which have been analyzed and discussed recently.[4] For example, the average "internal" angles at the bridging benzene rings β_n (see Figure 2; β_1 = Ge(Ph)−C$_{ipso}$−C$_{ipso}$, β_2 = Ge(C≡C)−C$_{ipso}$−C$_{ipso}$) are smaller (β_1 = 115.4(3)°, β_2 = 114.(3)°) and the average "external angles" γ_n (γ_1 = Ge(Ph)−C$_{ipso}$−C, γ_2 = Ge(C≡C)−C$_{ipso}$−C) are wider (γ_1 = 125.3(3)°, γ_2 = 125.0(4)°) than the standard angle of 120°, while the average angles α$_n$ (α$_1$ = C$_{ipso}$−Ge(Ph)−C$_{ipso}$, α$_2$ = C$_{ipso}$−Ge(C≡C)−C$_{ipso}$) (α$_1$ = 102.8(2)°, α$_2$ = 104.2(2)°) are more acute than 109.5°. In addition, the two metal atoms within one triptycene moiety are again in much closer contact (Ge(1)···Ge(2) = 3.0439(8) Å [3.0421(7) Å]) than the sum of their van der Waals radii (±4.5 Å).[18] However, in **9** these contacts are rather short in comparison to that in 9-methyl-10-phenyl-9,10-digermatriptycene (**3b**; Ge(1)···Ge(2) = 3.0957(19) Å); they are even shorter than the Si···Ge contact in 10-phenyl-10-germa-9-silatriptycene (**3a**; Si(1)···Ge(2) = 3.0466(5) Å).[4] The short Ge···Ge contacts in **9** may be ascribed to the presence of an acetylene substituent which is more electronegative than a methyl or phenyl substituent. The Ge hybrid orbital used for bonding

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(17) Tanimoto, M.; Kuchitsu, K.; Morino, Y. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 386.

(18) Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1−83.

with the acetylene ligand will therefore have relatively more p-character, which in turn will leave more s-character for the hybrid orbitals used for bonding to the phenylene ligands. This results in shortening of the bridgehead-to-phenylene bonds and widening of the internal angle α (C_{ipso}−Ge−C_{ipso}) and brings the bridgehead atoms in **9** in closer contact than, for example, in **3b**. The relatively short Ge···Ge contacts in **9** are of interest, as they may additionally facilitate the through-space contribution to the transmission of electrochemical or photochemical transitions along the longitudal axis of this type of organometallic oligomer.

Conclusions

The preparation of the novel compound ((trimethylsilyl)ethynyl)germanium trichloride (**4**) allowed the development of a simple one-pot synthetic approach toward various new alkynyl-substituted 9,10-digermatriptycenes. The synthetic potential of these compounds in the preparation of organometallic oligomers with conjugated spacers was demonstrated by the oxidative coupling of **8**, which furnished **9**, and the hydrosilylation of **8** with **3a**, which yielded **10**. Single-crystal X-ray structure analysis of **9** revealed relatively short Ge···Ge contacts (3.04 Å) which might allow the application of this type of organometallic oligomers in areas such as nonlinear optics and molecular devices such as wires and switches.

Experimental Section

General Methods. All manipulations involving organometallic compounds were performed in fully sealed glassware ("full glass") using standard high-vacuum techniques[19] unless stated otherwise. NMR spectra were measured at 25 °C on a Bruker AC 200 spectrometer (^{1}H NMR, 200.0 MHz; ^{13}C NMR, 50.3 MHz) and on a Bruker MSL 400 spectrometer (^{1}H NMR, 400.1 MHz; ^{13}C NMR, 100.6 MHz). Melting points were measured in a sealed capillary and are uncorrected. Elemental analyses were carried out at the Mikroanalytisches Labor Pascher, Remagen, Germany.

Materials. The commercial reagents $PhGeCl_3$, $GeCl_4$, $H_2PtCl_6 \cdot 6H_2O$, CuCl, EtOAc, Et_3N, $HCCl_3$, pyridine, and (trimethylsilyl)acetylene were used without further purification. HPLC grade benzene, toluene, *n*-hexane, and THF were predried over NaOH and then dried by distillation from liquid Na/K alloy. *o*-Phenylenemagnesium (**1**)[6,7] and 10-phenyl-10-germa-9-silatriptycene (**3a**)[4] were prepared according to the literature. The applied numbering scheme of **9** and **10** is depicted in Figure 2.

((Trimethylsilyl)ethynyl)germanium Trichloride (4). Under an N_2 atmosphere, $GeCl_4$ (4.60 g, 21 mmol) was added over 1 h to a solution of (trimethylsilyl)acetylene (2.06 g, 21 mmol) and triethylamine (2.12 g, 21 mmol) in benzene (15 mL). After additional stirring at 80 °C for 24 h, the mixture was cooled to room temperature to give a red solution and a white precipitate. The red solution was filtered, and the solvent was evaporated in vacuo. The residue was distilled to furnish a colorless liquid (1.45 g, 5.3 mmol, 25%): bp 82 °C (25 mmHg); ^{1}H NMR (C_6D_6, 200 MHz) δ 0.00 (s, $^1J_{CH} = 121.0$ Hz, $^2J_{SiH} = -7.2$ Hz, 9H; $Si(CH_3)_3$); ^{13}C NMR (C_6D_6, 50 MHz) δ 119.1 (s; $C\mathit{C}Si(CH_3)_3$), 100.0 (s; $\mathit{C}CSi(CH_3)_3$), −1.4 (q, $^1J_{CH} = 121.0$ Hz; $CCSi(\mathit{C}H_3)_3$). Anal. Calcd for $C_5H_9GeCl_3Si$: C, 21.75; H, 3.29; Ge, 26.3; Cl, 38.5; Si, 10.2. Found: C, 21.74; H, 3.35; Ge, 26.2; Cl, 38.1; Si, 10.0.

9-((Trimethylsilyl)ethynyl)-10-phenyl-9,10-dihydro-9,10-digerma-9,10[1′,2′]-benzenoanthracene (7). At −10 °C, $PhGeCl_3$ (3.56 mmol in 33.0 mL of toluene) was added over 4 h to **1** (10.68 mmol of the formal monomeric unit C_6H_4Mg in 169.8 mL of THF). After additional stirring for 1.5 h at −10 °C and for 2 h at 5 °C, the mixture was warmed to room temperature overnight and then was cooled to −10 °C, and **4** (3.56 mmol in 121.9 mL of toluene) was added over 5 h. After additional stirring for 2 h at −10 °C and for 1.5 h at 5 °C, the mixture was stirred at room temperature for 18 h. The mixture was quenched (H_2O/HCl), the solvent was evaporated in vacuo, and the residue was extracted with toluene (3 × 15 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and the solvent was evaporated in vacuo. The residue was dissolved in *n*-hexane and transferred to a silica column. The column was washed with *n*-hexane; then the product was eluted from the column with benzene. The benzene eluate was evaporated to dryness to give a white solid (1.51 g, 2.74 mmol, 77%): mp 217 °C; ^{1}H NMR (400 MHz, $CDCl_3$)[20] δ 8.13 (m, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.2$ Hz, $^5J_{HH} = 0.8$ Hz, 2H; H(18,22)), 7.89 (m, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 1.3$ Hz, $^5J_{HH} = 0.7$ Hz, 3H; H(4,5,16)), 7.69 (m, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.3$ Hz, $^5J_{HH} = 0.7$ Hz, 3H; H(1,8,13)), 7.67 (m, $^3J_{HH} = 7.6$ Hz, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 1.2$ Hz, $^5J_{HH} = 0.8$ Hz, 2H; H(19,21)), 7.64 (m, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 1.2$ Hz, 1H; H(20)), 7.27 (m, $^3J_{HH} = 7.5$ Hz, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 1.3$ Hz, 3H; H(3,6,15)), 7.22 (m, $^3J_{HH} = 7.5$ Hz, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.3$ Hz, 3H; H(2,7,14)), 0.43 (s, $^2J_{SiH} = 7.1$ Hz, 9H; H(25,26,27)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5 (bs; C(8a,9a,12)), 144.2 (bs; C(4a,10a,11)), 136.2 (dt, $^1J_{CH} = 159.5$ Hz, $^3J_{CH} = 7.2$ Hz; C(18,22)), 132.2 (dd, $^1J_{CH} = 159.5$ Hz, $^3J_{CH} = 8.5$ Hz; C(1,8,13)), 132.1 (dd, $^1J_{CH} = 161.2$ Hz, $^3J_{CH} = 7.5$ Hz; C(4,5,16)), 130.2 (dt, $^1J_{CH} = 160.5$ Hz, $^3J_{CH} = 7.4$ Hz; C(20)), 129.4 (s; C(17)), 129.06 (dd, $^1J_{CH} = 159.1$ Hz, $^3J_{CH} = 5.6$ Hz; C(19,21)), 127.7 (dd, $^1J_{CH} = 159.2$ Hz, $^3J_{CH} = 6.9$ Hz; C(2,7,14)), 127.6 (dd, $^1J_{CH} = 159.3$ Hz, $^3J_{CH} = 7.1$ Hz; C(3,6,15)), 122.5 (s; C(23)), 98.3 (s; C(24)), 0.1 (q, $^1J_{CH} = 120.4$ Hz; C(25,26,27)). Anal. Calcd for $C_{29}H_{26}Ge_2Si$: C, 63.58; H, 4.79. Found: C, 63.19; H, 4.75.

9-Ethynyl-10-phenyl-9,10-dihydro-9,10-digerma-9,10-[1′,2′]-benzenoanthracene (8). A solution of KOH (0.046 g, 1 mmol) in H_2O (1 mL) was added to a solution of **7** (0.265 g, 0.485 mmol) in THF (2 mL). The resulting mixture was stirred for 1 h and extracted with toluene (2 × 1 mL). The combined organic layers were dried ($MgSO_4$), filtered and the solvent was evaporated in vacuo to give a white solid (0.217 g, 0.451 mmol, 93%): mp 202 °C; ^{1}H NMR (400 MHz, $CDCl_3$)[20] δ 8.13 (m, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.3$ Hz, $^5J_{HH} = 0.8$ Hz, 2H; H(18,22)), 7.91 (m, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 1.3$ Hz, $^5J_{HH} = 0.7$ Hz, 3H; H(4,5,16)), 7.70 (m, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.3$ Hz, $^5J_{HH} = 0.7$ Hz, 3H; H(1,8,13)), 7.67 (m, $^3J_{HH} = 7.6$ Hz, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.3$ Hz, $^5J_{HH} = 0.8$ Hz 2H; H(19,21)), 7.65 (m, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.3$ Hz, 1H; H(20)), 7.28 (m, $^3J_{HH} = 7.4$ Hz, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 1.3$ Hz, 3H; H(3,6,15)), 7.24 (m, $^3J_{HH} = 7.4$ Hz, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.3$ Hz, 3H; H(2,7,14)), 3.00 (s; H(24)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5 (bs; C(8a,9a,12)), 143.9 (bs; C(4a,10a,11)), 136.2 (dt, $^1J_{CH} = 159.9$ Hz, $^3J_{CH} = 7.7$ Hz; C(18,22)), 132.4 (dd, $^1J_{CH} = 159.0$ Hz, $^3J_{CH} = 7.2$ Hz; C(1,8,13)), 132.1 (dd, $^1J_{CH} = 161.0$ Hz, $^3J_{CH} = 6.9$ Hz; C(4,5,16)), 130.3 (dt, $^1J_{CH} = 160.4$ Hz, $^3J_{CH} = 7.8$ Hz; C(20)), 129.3 (s; C(17)), 129.1 (dd, $^1J_{CH} = 160.4$ Hz, $^3J_{CH} = 7.8$ Hz; C(19,21)), 127.9 (dd, $^1J_{CH} = 159.3$ Hz, $^3J_{CH} = 7.8$ Hz; C(2,7,14)), 127.8 (dd, $^1J_{CH} = 159.6$ Hz, $^3J_{CH} = 7.5$ Hz; C(3,6,15)), 100.0 (d, $^1J_{CH} = 242.1$ Hz; C(24)), 76.8 (d, $^2J_{CH} = 43.8$ Hz; C(23)). Anal. Calcd for $C_{26}H_{18}Ge_2$: C, 65.66; H, 3.82. Found: C, 65.29; H, 3.87.

9,10-Bis((trimethylsilyl)ethynyl)-9,10-dihydro-9,10-digerma-9,10[1′,2′]-benzenoanthracene (5). At −10 °C, **4**

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(19) Vreugdenhil, A. D.; Blomberg, C. *Recl. Trav. Chim. Pays-Bas* **1963**, *82*, 453.

(20) Chemical shifts and $^xJ_{HH}$ coupling constants followed from simulations with the gNMR program[21,22] and, if necessary, from NOE and CH correlation experiments; for the numbering system, see Figure 2.

(0.21 mmol in 7.3 mL of toluene) was added over 2 h to **1** (0.64 mmol of the formal monomeric unit C_6H_4Mg in 10.0 mL of THF). After additional stirring for 1.5 h at −10 °C and for 2 h at 5 °C, the mixture was warmed to room temperature overnight and then cooled to −10 °C, and **4** (0.21 mmol in 2.6 mL of toluene) was added over 1 h. After additional stirring for 2 h at −10 °C and for 1.5 h at 5 °C, the mixture was warmed to room temperature overnight. The mixture was quenched (H_2O/HCl), the solvent was evaporated in vacuo, and the residue was extracted with toluene (3 × 15 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and the solvent was evaporated in vacuo. The residue was dissolved in benzene, the solution was eluted from silica, and the eluate was evaporated to dryness to furnish a white solid (0.022 g, 0.040 mmol, 19%): ^{1}H NMR (400 MHz, $CDCl_3$)[20] δ 7.81 (m, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 1.3$ Hz, $^5J_{HH} = 0.7$ Hz, 6H; H(1,4,5,8,13,16)), 7.26 (m, $^3J_{HH} = 7.6$ Hz, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 1.3$ Hz, 6H; H(2,3,6,7,14,15)), 0.39 (s, 18H; H(20,21,22,26,27,28)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0 (bs; C(4a,8a,9a,10a,11,12)), 131.9 (dt, $^1J_{CH} = 159.8$ Hz; C(1,4,5,8,13,16)), 127.9 (ddd, $^1J_{CH} = 159.0$ Hz, $^2J_{CH} = 1.8$ Hz, $^3J_{CH} = 6.9$ Hz; C(2,3,6,7,14,15)), 122.6 (s; C(17,23)), 97.6 (s; C18,24)), 0.0 (q, $^1J_{CH} = 120.0$ Hz; C(20,21,22,26,27,28)). Attempts to obtain an analytically pure sample of **4** suitable for elemental analysis were unsuccessful.

9,10-Diethynyl-9,10-dihydro-9,10-digerma-9,10[1′,2′]-benzenoanthracene (6). Compound **6** was prepared from a solution of KOH (0.023 g, 0.5 mmol) in H_2O (0.5 mL) and a solution of **5** (0.009 g, ≤0.016 mmol) in THF (1 mL) as described for **8**. The crude product obtained after column chromatography (0.008 g) was subjected to preparative TLC (silica gel 60 F_{254}, *n*-hexane/EtOAc (80:20), R_f 0.66) to furnish a white solid (0.005 g, 0.011 mmol, 71%): ^{1}H NMR (400 MHz, $CDCl_3$)[20] δ 7.83 (m, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 1.2$ Hz, $^5J_{HH} = 0.7$ Hz, 6H; H(1,4,5,8,13,16)), 7.28 (m, $^3J_{HH} = 7.6$ Hz, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 1.2$ Hz, 6H; H(2,3,6,7,14,15)), 2.99 (s, 2H; H(18,20)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9 (bs, $^2J_{CH} = 2.6$ Hz, $^3J_{CH} = 7.9$ Hz, $^3J_{CH} = 7.4$ Hz, $^4J_{CH} = -1.5$ Hz; C(4a,8a,9a,10a,11,12)), 132.2 (m, $^1J_{CH} = 161.3$ Hz, $^2J_{CH} = 1.6$ Hz, $^3J_{CH} = 7.2$ Hz, $^4J_{CH} = -1.4$ Hz; C(1,4,5,8,13,16)), 128.5 (m, $^1J_{CH} = 158.9$ Hz, $^2J_{CH} = 1.6$ Hz, $^2J_{CH} = 1.1$ Hz, $^3J_{CH} = 7.1$ Hz; C(2,3,6,7,14,15)), 100.6 (d, $^1J_{CH} = 239.8$ Hz; C(18,20)), 76.1 (d, $^2J_{CH} = 44.0$ Hz; C(17,19)). Anal. Calcd for $C_{22}H_{14}Ge_2$: C, 62.39; H, 3.33. Found: C, 61.63; H, 3.74.

1,4-Bis(9-(10-phenyl-9,10-digermatriptycyl))buta-1,3-diyne (9). A solution of CuCl (0.0017 g, 0.017 mmol) and **8** (0.1593 g, 0.330 mmol) in pyridine (15 mL) was stirred for 1 h at 80 °C while pure O_2 was bubbled through the solution. A clear green-blue solution and a fine white precipitate were obtained. The solution was removed by decantation, and the precipitate was washed with pyridine (2 × 5 mL), toluene (2 × 5 mL), and *n*-hexane (2 × 5 mL). The undissolved residue was dried in vacuo to give a white solid (0.116 g, 0.122 mmol, 74%): mp >280 °C; ^{1}H NMR (400 MHz, C_6D_5Br)[20] δ 8.19 (m, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.3$ Hz, $^5J_{HH} = 0.6$ Hz, 6H; H(4,5,16)), 8.12 (m, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.4$ Hz, $^4J_{HH} = 1.2$ Hz, $^5J_{HH} = 0.7$ Hz, 4H; H(18,22)), 7.79 (m, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.2$ Hz, $^5J_{HH} = 0.6$ Hz, 6H; H(1,8,13)), 7.64 (m, $^3J_{HH} = 7.6$ Hz, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.3$ Hz, $^5J_{HH} = 0.7$ Hz, 4H; H(19,21)), 7.62 (m, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.2$ Hz, 2H; H(20)), 7.31 (m, $^3J_{HH} = 7.4$ Hz, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.2$ Hz, 6H; H(3,6,15)), 7.24 (m, $^3J_{HH} = 7.4$ Hz, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.3$ Hz, 6H; H(2,7,14)); ^{13}C NMR (100 MHz, C_6D_5Br) δ 144.6 (bs; C(8a,9a,12)), 143.7 (bs; C(4a,10a,11)), 136.4 (dt, $^1J_{CH} = 159.9$ Hz, $^3J_{CH} = 7.1$ Hz; C(18,22)), 132.8 (dd, $^1J_{CH} = 159.6$ Hz, $^3J_{CH} = 7.1$ Hz; C(1,8,13)), 132.6 (dd, $^1J_{CH} = 161.0$ Hz, $^3J_{CH} = 7.3$ Hz; C(4,5,16)), 130.6 (dt, $^1J_{CH} = 160.5$ Hz, $^3J_{CH} = 7.4$ Hz; C(20)), 129.4 (dd, $^1J_{CH} = 160.3$ Hz, $^3J_{CH} = 6.8$ Hz; C(19,21)), 129.1 (s; C(17)), 128.3(dd, $^1J_{CH} = 158.8$ Hz, $^3J_{CH} = 8.4$ Hz; C(2,7,14)), 128.2 (dd, $^1J_{CH} = 161.0$ Hz, $^3J_{CH} = 6.8$ Hz; C(3,6,15)), 94.9 (s; C(23)), 75.8 (s; C(24)). Anal. Calcd for $C_{52}H_{34}Ge_4$: C, 65.80; H, 3.61; Ge, 30.6. Found: C, 65.04; H, 3.81; Ge, 30.1. Single crystals of **9** suitable for X-ray structure determination were obtained from a concentrated chlorobenzene solution via slow evaporation of the solvent.

***trans*-1-(9-(10-Phenyl-9,10-digermatriptycyl))-2-(9-(10-phenyl-10-germa-9-silatriptycyl))ethene (10).** Over 5 min, air was bubbled through a solution of **8** (0.1754 g, 0.369 mmol) and **3a** (0.1503 g, 0.368 mmol) in THF (5 mL), after which a catalytic amount of $H_2PtCl_6{\cdot}6H_2O$ (0.005 g, 0.01 mmol) was added. The reaction mixture was stirred at room temperature for 18 h to furnish a clear brown solution and a white precipitate. The solution was decanted, the residue was washed with THF (1 × 5 mL), and the solvent was evaporated in vacuo. The residue was dissolved in $CHCl_3$ and eluted from silica, and the eluate was evaporated to dryness. The residue was washed with benzene (1 × 20 mL), after which it was dried in vacuo to furnish a white solid (0.212 g, 0.240 mmol, 65%): mp >280 °C; ^{1}H NMR (400 MHz, $CDCl_3$)[20] δ 8.38 (d, $^3J_{HH} = 23.3$ Hz, 1H; H(23 or 23′)), 8.20 (m, 4H; H(18,22,18′,22′)), 8.17 (d, $^3J_{HH} = 23.3$ Hz, 1H; H(23′ or 23)), 8.08 (dm, $^3J_{HH} = 7.0$ Hz, 3H; H(4,5,16 or 4′,5′,16′)), 8.01 (dm, $^3J_{HH} = 6.8$ Hz, 3H; H(4′,5′,16′ or 4,5,16)), 7.81 (dm, $^3J_{HH} = 7.0$ Hz, 3H; H(1,8,13 or 1′,8′,13′)), 7.80 (dm, $^3J_{HH} = 7.1$ Hz, 3H; H(1′,8′,13′ or 1,8,13)), 7.70 (m, 6H; H(19,20,21,19′,20′,21′)), 7.32 (m, 6H; H(3,6,15,3′,6′,15′)), 7.28 (m, 6H; H(2,7,14,2′,7′,14′)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4 (dt, $^2J_{CH} = 3.5$ Hz, $^3J_{CH} = 7.7$ Hz; C(4a,10a,11 or 8a,9a,12 or 4a′,10a′,11′ or 8a′,9a′,12′)), 146.1 (d, $^1J_{CH} = 142.8$ Hz; C(23 or 23′)), 145.5 (dt, $^2J_{CH} = 3.2$ Hz, $^3J_{CH} = 6.6$ Hz; C(4a,10a,11 or 8a,9a,12 or 4a′,10a′,11′ or 8a′,9a′,12′)), 145.2 (bt, $^3J_{CH} = 7.1$ Hz; C(4a,10a,11 or 8a,9a,12 or 4a′,10a′,11′ or 8a′,9a′,12′)), 143.7 (d, $^1J_{CH} = 142.8$ Hz; C(23′ or 23)), 141.6 (dt, $^2J_{CH} = 4.7$ Hz, $^3J_{CH} = 6.8$ Hz; C(4a,10a,11 or 8a,9a,12 or 4a′,10a′,11′ or 8a′,9a′,12′)), 136.2 (dm, $^1J_{CH} = 159.2$ Hz; C(18,22 or 18′,22′)), 136.1 (dm, $^1J_{CH} = 159.1$ Hz; C(18′,22′ or 18,22)), 132.7 (dd, $^1J_{CH} = 158.1$ Hz, $^3J_{CH} = 7.2$ Hz; C(4,5,16 or 4′,5′,16′)), 132.6 (dd, $^1J_{CH} = 159.3$ Hz, $^3J_{CH} = 7.3$ Hz; C(1,8,13 or 1′,8′,13′)), 132.0 (dd, $^1J_{CH} = 159.4$ Hz, $^3J_{CH} = 7.6$ Hz; C(1′,8′,13′ or 1,8,13)), 131.8 (dd, $^1J_{CH} = 162.4$ Hz, $^3J_{CH} = 6.6$ Hz; C(4′,5′,16′ or 4,5,16)), 130.1 (dt, $^1J_{CH} = 153.9$ Hz; C(20 or 20′)), 130.1 (dt, $^1J_{CH} = 153.0$ Hz; C(20′ or 20)), 129.7 (s; C(17 or 17′)), 129.4 (s; C(17′ or 17)), 129.0 (dd, $^1J_{CH} = 162.8$ Hz; C(19,21 or 19′,21′)), 129.0 (dd, $^1J_{CH} = 160.1$ Hz; C(19′,21′ or 19,21)), 127.5 (dd, $^1J_{CH} = 159.3$ Hz, $^3J_{CH} = 6.6$ Hz; C(3,6,15,2,7,14,2′,7′,14′)), 127.3 (dd, $^1J_{CH} = 159.9$ Hz, $^3J_{CH} = 6.3$ Hz; C(3′,6′,15′)). Anal. Calcd for $C_{50}H_{36}Ge_3Si$: C, 68.03; H, 4.11; Ge, 24.7; Si, 3.2. Found: C, 67.84; H, 4.09; Ge, 23.8; Si, 3.1.

X-ray Crystallographic Data for Dimer 9. X-ray data were collected on an Enraf-Nonius CAD4T/rotating anode diffractometer[23] for a colorless transparent crystal mounted with the inert oil technique and transferred into the cold nitrogen stream. Numerical details have been collected in Table 2.

Accurate cell dimensions were derived from setting angles of 25 SET4[24] reflections. The unit cell was checked for possible higher metrical symmetry.[25] The reflection data were corrected for absorption using the DELABS procedure as implemented in PLATON.[26] The structure was solved by direct methods (SHELXS97[27]) and refined on F^2 using SHELXL97.[28]

One of the terminal phenyl moieties is disordered over two orientations and was refined with a disorder model. In addition a disorder model for a chlorobenzene molecule of crystallization was used. Hydrogen atoms were taken into

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(21) Budzelaar, P. H. M. gNMR; Ivorysoft, Amsterdam, The Netherlands, 1992.

(22) Castellano, S.; Bothner-By, A. A. *J. Chem. Phys.* **1964**, *41*, 3863.

(23) Enraf-Nonius CAD-4 Software, Version 5; Enraf Nonius, Delft, The Netherlands, 1989.

(24) De Boer, J. L.; Duisenberg, A. J. M. *Acta Crystallogr.* **1984**, *A40*, C-410.

(25) LePage, Y. *J. Appl. Crystallogr.* **1987**, *20*, 264.

(26) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C-34.

account at calculated positions riding on their carrier atoms. All geometric calculations and the ORTEP illustration were done with PLATON.[26]

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Supporting Information Available: Tables giving atomic coordinates, thermal parameters, and bond distances and angles for **9** (16 pages). Ordering information is given on any current masthead page.

OM980073F

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(27) Sheldrick, G. M. SHELXS97, Program for Crystal Structure Solution; University of Göttingen, Göttingen, Germany, 1997.

(28) Sheldrick, G. M. SHELXL97, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.