Cycloaddition Reactions of an Acetylene-Linked Bis(germaethene)[1,2]

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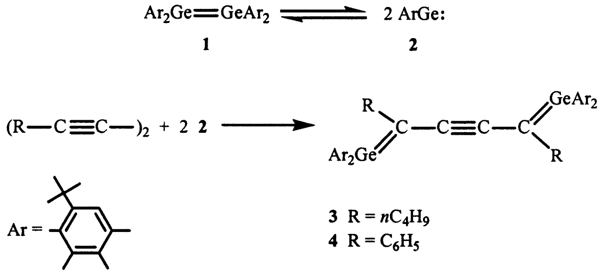
3,5-Di-*tert*-butyl-1,2-benzoquinone reacts with the acetylene-linked bis(germaethene) $Ar_2Ge{=}C(R){-}C{\equiv}C{-}C(R){=}GeAr_2$, $R = C_6H_5$, Ar = 2-*t*Bu-4,5,6-Me_3C_6H (**4**), in a [4+2] fashion to furnish the sterically crowded product **5** of 2-fold cycloaddition to the Ge═C bonds. The reaction of **4** with 1,2-dicyanoethylene proceeds differently, namely, by [2+4] cycloaddition of one of the C≡N bonds to the Ge═C and C≡C bonds, followed by a [2+2] cycloaddition of the remaining Ge═C bond to the newly formed C═C bond to give the bicyclic compound **6**. An unprecedented C−H activation of a *tert*-butyl and an aryl C−H bond leads finally to the hexacyclic compound **8** via the tetracyclic product **7**. Cyanogen gas reacts similarly by [2+4] and [2+2] cycloadditions to furnish the bicyclic compound **9**. In this case, no C−H addition to the endocyclic C═N bond is observed.

Introduction

Since the discovery of thermally stable germaethenes, compounds with a Ge−C double bond, the structures of five representatives have been unambiguously elucidated.[3−7] Common features of these compounds are the short Ge−C double bond lengths of between 1.77 and 1.84 Å and the shielding of the two participating atoms by bulky substituents that effectively prevents further reactions of the multiple bond system. Recently, we allowed the germylene **2**, which is formed in solution from the digermene **1**,[8,9] to react with 1,3-diynes and obtained the acetylene-linked bis(germaethenes) **3** and **4**; the structure of **3** was confirmed by an X-ray crystal structure analysis.[10] The conjugation between the multiple bonds in **3** and **4** is reflected less in the bond lengths but more so in the electronic spectra, in which the absorptions at longest wavelengths experience bathochromic shifts of 100 and 150 nm, respectively, in comparison to those of the yellow or orange germaethenes.

Scheme 1



We now report on the crystal structure of **4** and its cycloaddition reactions, which, in part, follow a very unusual course.

Results and Discussion

The most important features to distinguish between the acetylene-linked bis(germaethenes) **3** and **4** are their colors and, accordingly, their absorptions at longest wavelength in their electronic spectra. While the dark red dialkyl compound **3** shows an absorption at 518 nm, the dark blue diaryl compound **4** exhibits a marked red-shift to furnish an absorption at 595 nm. This suggests that the two phenyl groups are also involved in the conjugation.

Crystals of **4** suitable for X-ray structure analysis (Figure 1) were obtained from a THF solution and contained five molecules of the solvent per molecule of product. The more extensive conjugation of the multiple bonds in **4** as compared to that of **3** has no influence on the bond lengths and angles of the former compound: only slight differences between the two molecules are found. Compound **4**, obtained in almost quantitative yield, reacts differently to the simple germaethenes. Although the latter undergo smooth cycloaddition reactions with phosphaalkynes[11] or with 2,3-dimethylbutadiene,[12,13] compound **4** does not react with these part-

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(1) Compounds of Germanium, Tin, and Lead. Part 38. Part 37: Schäfer, H.; Saak, W.; Weidenbruch, M. *Angew. Chem.* **2000**, *112*, 3847; *Angew. Chem., Int. Ed.* **2000**, *39*, 3703.

(2) Dedicated to Professor Gottfried Huttner on the occasion of his 65th birthday.

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10.1021/om020320m CCC: $22.00

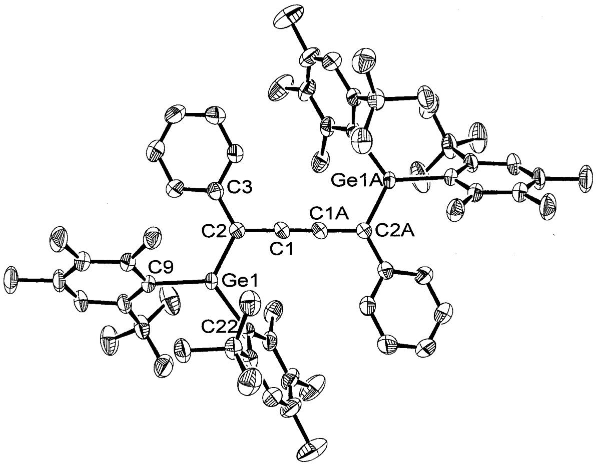
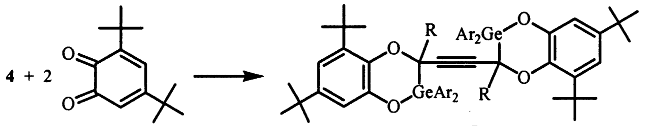


Figure 1. Molecule of **4** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and bond angles (deg): Ge(1)−C(2) = 1.840(4), C(1)−C(2) = 1.428(5), C(1)−C(1a) = 1.205(7), Ge(1)−C(9) = 1.991(3), Ge(1)−C(22) = 1.978(4), C(2)−C(1)−C(1a) = 177.6(3), C(1)−C(2)−Ge(1) = 116.4(3), C(2)−Ge(1)−C(9) = 119.32(16), C(2)−Ge(1)−C(22) = 117.56(15), C(9)−Ge(1)−C(22) = 123.11(14).

Scheme 2



5

ners even under harsher conditions. In contrast, **4** participates in mostly rapid reactions with electron-poor multiple bond systems. For example, its reaction with two molecules of 3,5-di-*tert*-butyl-1,2-benzoquinone proceeds through [4+2] cycloadditions at both Ge−C double bonds to furnish the acetylene-linked product **5**.

The X-ray crystal structure analysis of the cycloadduct **5** (Figure 2) clearly reveals the steric overcrowding of the molecule in the form of longer than usual bond lengths[14] and, in part, by widened bond angles.

While the Ge−C double bonds of **4** behave as ene components toward the diheterodiene, the compound reacts with one of the C−N triple bonds of 1,2-dicyanoethene as a 4π-electron donor to form initially an unsaturated six-membered ring. However, this is not stable on account of the cumulated C−C double bonds and undergoes a spontaneous [2+2] cycloaddition of the second Ge−C double bond to one of the cumulated C−C double bonds to afford the bicyclic compound **6**.

The X-ray crystallographic analysis of **6** (Figure 3) provided an unexpected result: the isomeric compound **7** (Figure 4) was observed in the crystal together with compound **6**. Presumably, the exocyclic acrylonitrile increment of **6** is able to activate a nonpolar C−H bond of a *tert*-butyl methyl group to such an extent that an addition to the N−C double bond occurs to furnish the tetracyclic compound **7**.

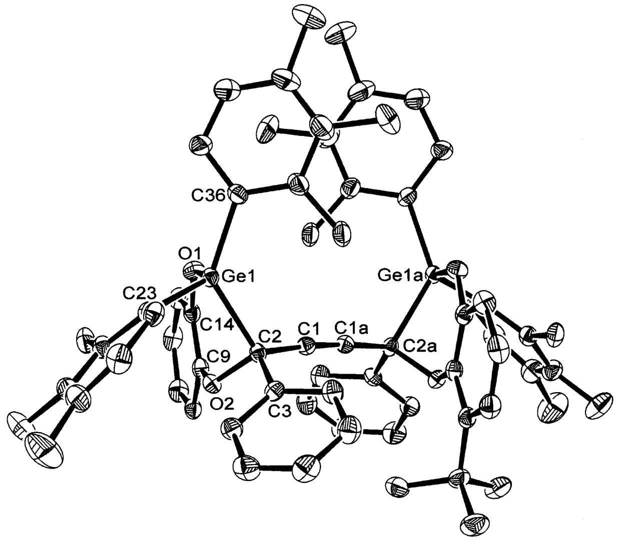


Figure 2. Molecule of **5** in the crystal (hydrogen atoms and *tert*-butyl groups are omitted for clarity). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Ge(1)−C(2) = 2.086(3), C(1)−C(2) = 1.472(4), C(1)−C(1a) = 1.196(5), Ge(1)−C(23) = 2.022(3), Ge(1)−C(36) = 2.010(3), Ge(1)−O(1) = 1.8360(19), C(2)−C(1)−C(1a) = 175.38(19), C(1)−C(2)−Ge(1) = 116.31(19), C(23)−Ge(1)−C(36) = 122.34(11), C(3)−C(2)−O(2) = 104.9(2).

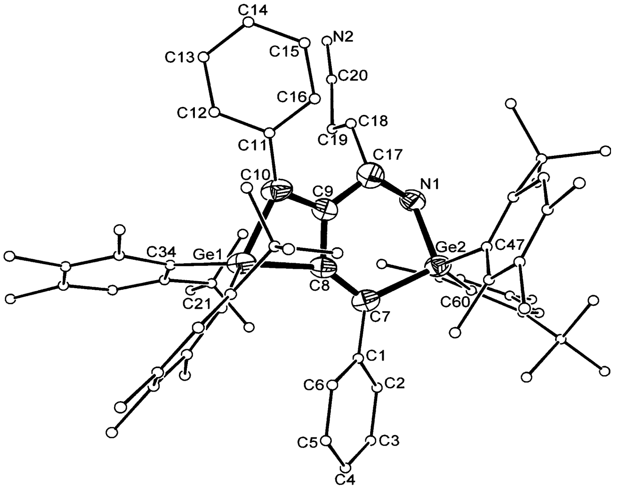


Figure 3. Molecule of **6** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Ge(1)−C(8) = 2.033(4), C(8)−C(9) = 1.475(6), C(9)−C(10) = 1.355(6), C(10)−Ge(1) = 2.010(4), N(1)−C(17) = 1.238(9), C(8)−Ge(1)−C(10) = 69.53(18), C(17)−C(18)−C(19) = 123.5(8), C(18)−C(19)−C(20) = 122.1(9), Ge(2)−N(1)−C(17) = 125.0(4).

A further X-ray crystallographic analysis performed to substantiate the above observation again furnished a surprising result. In addition to **7**, the also isomeric compound **8** was observed. In this case an *ortho*-phenyl C−H bond of low polarity is activated to such an extent that an addition to the C−C double bond of the exocyclic acrylonitrile unit takes place to afford the hexacyclic product **8**. Although such cyanoethylations[15] are not uncommon, they usually require the presence of polar bonds. Each of the three isomers crystallizes with a

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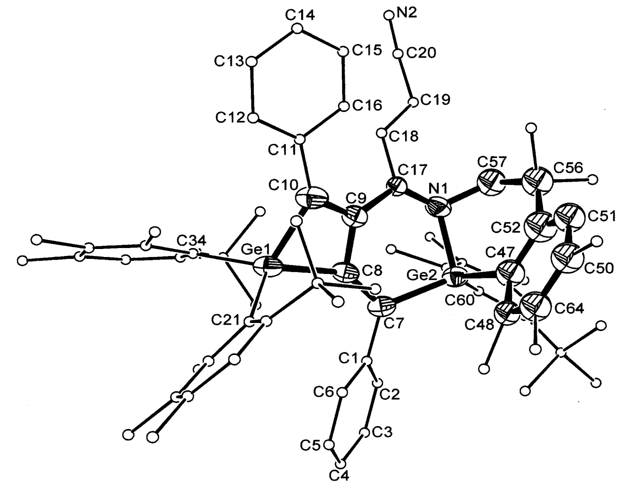


Figure 4. Molecule of **7** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Ge(1)−C(8) = 2.040(3), C(8)−C(9) = 1.469(4), C(9)−C(10) = 1.359(5), C(10)−Ge(1) = 2.004(3), C(19)−C(20) = 1.4703(10), C(20)−N(2) = 1.1503(10), C(8)−Ge(1)−C(10) = 69.43(13), C(17)−C(18)−C(19) = 123.2(16), C(18)−C(19)−C(20) = 122.4(17).

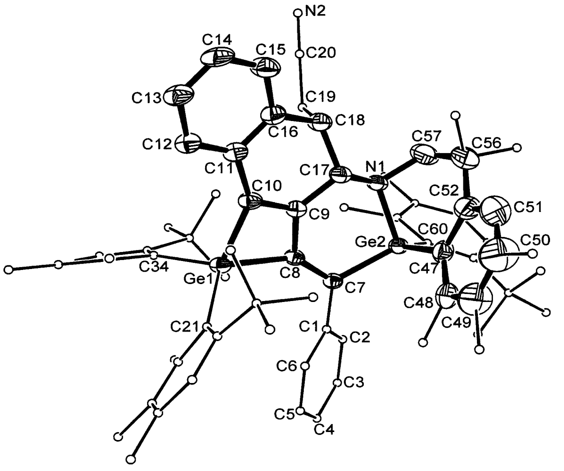


Figure 5. Molecule of **8** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Ge(1)−C(8) = 2.040(3), C(8)−C(9) = 1.469(4), C(9)−C(10) = 1.359(5), C(10)−Ge(1) = 2.004(3), C(10)−C(11) = 1.482(4), C(16)−C(18) = 1.537(5), N(1)−C(57) = 1.471(5), C(8)−Ge(1)−C(10) = 69.43(13), C(16)−C(18)−C(17) = 113.2(4), N(2)−C(20)−C(13) = 179.0(9).

molecule of dicyanoethene and an additional molecule of *n*-hexane that serves merely to stabilize the lattices and does not enter into any interactions with the germanium atoms.

We do not know what the driving force for the 2-fold C−H activation of the predominately nonpolar bonds that leads from the bicyclic compound **6** to the tetracyclic species **7** and finally to the hexacyclic compound **8** is. One possibility could be the steric overcrowding in the molecules **6** and **7**, which forces the C−H bonds to approach the double bonds so closely that new, predominately strain-free six-membered rings form in order to reduce these interactions.

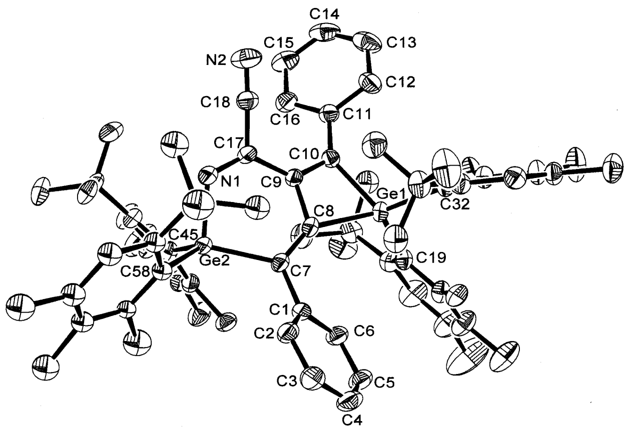
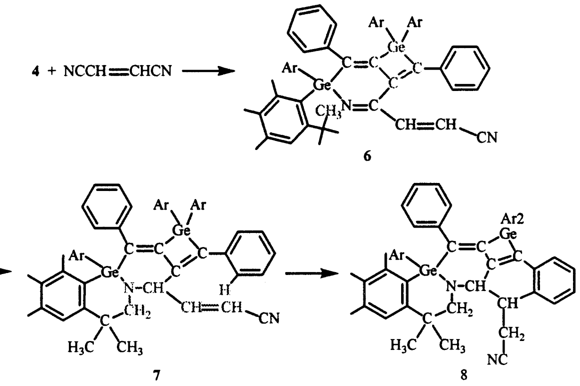


Figure 6. Molecule of **9** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Ge(1)−C(8) = 2.049(3), C(8)−C(9) = 1.489(5), C(9)−C(10) = 1.355(5), C(10)−Ge(1) = 2.015(3), N(1)−C(17) = 1.279(4), N(1)−Ge(2) = 1.910(3), C(18)−N(2) = 1.150(5), C(8)−Ge(1)−C(10) = 69.78(13), C(17)−N(1)−Ge(2) = 119.4(2), N(2)−C(18)−C(17) = 176.6(4).

Scheme 3



The primary step in the reaction of **4** with cyanogen seems to proceed similarly since the analytical data together with the ^{1}H and ^{13}C NMR spectra are indicative of a 1:1 adduct of the type **6** of the starting materials. However, the reaction proceeds more rapidly and furnishes a pure final product compared to the reaction of **4** with dicyanoethylene. The X-ray crystallographic analysis confirmed the constitution deduced from the NMR data and showed the product to be compound **9**. In analogy to the reaction of **4** with dicyanoethene, this sequence should also start with the [2+4] cycloaddition of one CN group to the C−C triple bond and one of the Ge−C double bonds, followed by the spontaneous [2+2] cycloaddition of the second Ge−C double bond to the newly formed C−C double bond with formation of compound **9**. In contrast to **6**, which undergoes a C−H addition to the endocyclic C=N bond, the bicyclic compound **9** is now the final product of the reaction sequence.

To gain more insight into the unusual rearrangement (Scheme 3), we employed quantum-mechanical methods. The size of the molecules in question prohibit the use of suitable ab initio or density functional theory methods without significant simplifications. Therefore, we decided to apply the semiempirical method PM3, which is the only Hamiltonian with a parametrization for germanium,[16,17] and to verify its reliability.

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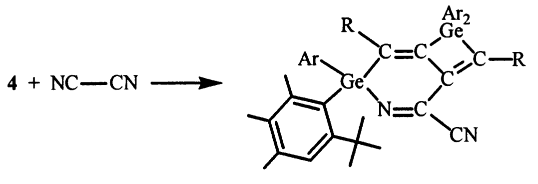
Table 1. Comparison of Selected PM3-Calculated and Observed Bond Lengths (Å)

	4		**6**		**7**		**8**	
	X-ray	PM3	X-ray	PM3	X-ray	PM3	X-ray	PM3
Ge^1-N	1.840	1.787	1.878	1.863	1.878	1.866	1.882	1.874
Ge^1-C^1	1.978	1.885	1.994	1.954	1.994	1.927	1.987	1.939
Ge^1-R^1	1.991	1.900	2.018	1.956	2.018	1.918	2.022	1.922
Ge^1-R^2	1.428	1.396	1.954	1.916	2.100	1.903	1.998	1.906
C^1-C^2	1.205	1.208	1.352	1.317	1.352	1.314	1.353	1.317
C^2-C^3			1.474	1.471	1.474	1.469	1.468	1.457
C^3-C^4			1.425	1.469	1.566	1.497	1.481	1.491
C^4-N			1.236	1.287	1.518	1.485	1.482	1.484
C^2-Ge^2			2.036	2.002	2.036	2.005	2.037	2.022
C^3-Ge^2			2.476	2.479	2.476	2.481	2.480	2.460
C^3-C^5			1.357	1.351	1.357	1.351	1.362	1.355
C^5-Ge^2			2.007	1.994	2.007	1.986	2.002	1.971
Ge^2-R^1			2.020	1.884	2.020	1.885	2.025	1.885

Scheme 4



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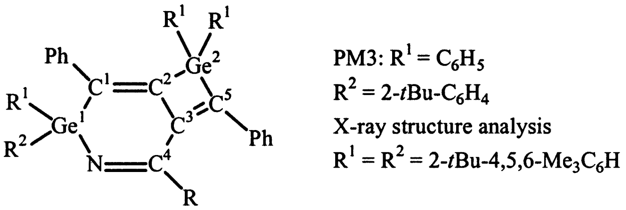
Scheme 5



A comparison of selected bond lengths of the calculated geometries with those of **4** and **6**−**8** is given in Table 1, where the only modification is the use of three phenyl and one 2-*tert*-butylphenyl group in the theoretical study (Scheme 5) instead of the four 2-*tert*-butyl-4,5,6-trimethylphenyl groups (Ar in Scheme 1).

It can be clearly seen that the PM3-derived bond lengths are in good agreement with the experimental data. The only discrepancies are the $Ge-R^1$ distances, which come out slightly too short. This however can be attributed to the smaller phenyl groups used in the calculations so that the steric repulsion is reduced and the Ge−C(phenyl) contacts are more pronounced.

In contrast to the above structural discussion, where experimental data are available to assess the quality of the PM3 calculation, it is necessary to employ ab initio or DFT calculations to get information on the validity of PM3-derived relative energies. For computational efficiency, both R^1 and R^2 were replaced by methyl groups as well as the phenyl substituents at C^1 by hydrogen atoms. The reaction of **4** with NCCH═CHCN to give a primary cycloaddition product and subsequently **6** was investigated with the B3LYP/6-31G(d) method−basis set combination and PM3. The DFT calculation confirmed all structures to have singlet ground states, and the calculated relative energies agree well with the semiempirical results (Table 2).

Table 2. Comparison of Calculated Relative Energies (kcal mol^{-1}) for the Model Reaction (see text for details)

	PM3	B3LYP/6-31G(d)
4 + NCCH═CHCN	0.0	0.0
primary product	−30.8	−35.4
6	−68.4	−83.5

From the above results, we can conclude that PM3 appears to be suitable for the study of the systems presented in this work, and it therefore is used to investigate the complete sequence leading to the unexpected product **8** (Scheme 3). The same restrictions as for the geometry comparison apply. The first step is the [2+4] cycloaddition of a CN group to the CC triple bond of **4** with a barrier of about 20 kcal mol^{-1}. This primary product then undergoes a spontaneous [2+2] cycloaddition to the isoenergetic structure **6**, for which no transition state could be localized. From a thermodynamical point of view, the sequence is favorable, since structure **8** is the most stable molecule. It is 78 kcal mol^{-1} lower in energy than the starting molecules (**7**, −58 kcal mol^{-1}; **6**, −51 kcal mol^{-1}). Of particular interest in the light of the unexpected C−H activations are the two transition states connecting **6** to **7** and **7** to **8**, respectively. The activation energy required for the step from the bicyclic compound **6** to the tetracyclic **7** is calculated to be around 90 kcal mol^{-1}, which is slightly lower than the barrier for the C−H addition of ethane to *N*-ethylidenemethanamine (102 kcal mol^{-1}).[18] The second C−H reaction possesses an activation energy of less than 50 kcal mol^{-1}, so that it will proceed much more readily. The model character of the calculation however does not fully account for the enormous steric strain in the molecules **6**−**8**, so that the derived activation barriers may be estimated as too high.

Experimental Section

General Procedures. All manipulations were carried out in oven-dried glassware under an atmosphere of dry argon. The ^1H and ^{13}C NMR spectra were obtained on a Bruker ARX 500 spectrometer using C_6D_6 as solvent. Elemental analyses were performed by Analytische Laboratorien, D-51789 Lindlar, Germany. Compound **4** was prepared according to the literature procedure.[10] Single crystals of **4** were grown from THF at room temperature.

5,7-Di-*tert*-butyl-2,2-bis(6-*tert*-butyl-2,3,4-trimethylphenyl)-3-{[5,7-di-*tert*-butyl-2,2-bis(6-*tert*-butyl-2,3,4-trimethylphenyl)-3-phenyl-2,3-dihydro-1,4,2-benzodioxagermin-3-yl]ethynyl}-3-phenyl-2,3-dihydro-1,4,2-benzodioxagermine (5). To a solution of the bisgermaethene **4** (ca. 0.35 mmol), prepared from the digermene **1** (0.302 g, 0.36 mmol) and 1,4-diphenylbuta-1,3-diyne (0.071 g, 0.35 mmol) in toluene (40 mL), was added 5,7-di-*tert*-butyl-1,2-benzoquinone (0.155 g, 0.70 mmol) with stirring. The color of the solution changed immediately from dark blue to colorless. The solution was concentrated to a volume of 20 mL and cooled to −20 °C for several days to furnish 0.380 g (84% yield) of a colorless solid of **5**: mp 275−277 °C; ^1H NMR δ 0.38 (s, 6 H, CH_3), 0.63 (s, 9 H, *t*Bu), 0.85 (s, 6 H, CH_3), 0.88 (s, 9 H, *t*Bu), 0.90 (s, 6 H, CH_3), 1.22 (s, 36 H, *t*Bu), 1.56 (s, 9 H, *t*Bu), 1.73 (s, 9 H, *t*Bu), 1.98 (s, 3 H, CH_3), 2.04 (s, 3 H, CH_3), 2.08 (s, 3 H, CH_3), 2.10 (s, 3 H, CH_3), 2.57 (s, 3 H, CH_3), 2.71 (s, 3 H, CH_3), 6.93−7.45 (m, 18 H, Ar-H). Owing to the low solubility of **5**, a ^{13}C NMR spectrum could not be obtained. Anal. Calcd for $C_{96}H_{126}Ge_2O_4$: C, 77.43; H, 8.53. Found: C, 77.61; H, 8.48. Single crystals suitable for X-ray diffraction analysis were obtained from benzene at room temperature.

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[18] Koch, R. Unpublished results.

Table 3. Crystallographic Data for 4, 5, 6/7,[a] 7/8,[a] and 9

	4	**5**	**6/7**	**7/8**	**9**
empirical formula	$C_{68}H_{86}Ge_2$·5 THF	$C_{96}H_{126}Ge_2O_4$·2C_6H_6	$C_{72}H_{88}Ge_2N_2$·$C_4H_2N_2$·C_6H_{14}	$C_{72}H_{88}Ge_2N_2$·$C_4H_2N_2$·C_6H_{14}	$C_{70}H_{86}Ge_2N_2$·C_6H_{14}
fw	1409.07	1645.36	1290.87	1290.87	1186.76
a (Å)	19.2928(10)	19.4916(3)	20.5379(9)	20.5938(8)	11.5069(5)
b (Å)	9.5428(3)	19.4916(39	17.6749(5)	17.5927(5)	16.0706(8)
c (Å)	23.0232(10)	50.1999(12)	21.9050(9)	21.9977(8)	19.6696(14)
α (deg)	90	90	90	90	75.763(7)
β (deg)	110.350(5)	90	109.883(5)	110.377(4)	79.852(7)
γ (deg)	90	90	90	90	75.474(5)
V ($Å^3$)	3974.2(3)	19072.1(16)	7477.6(5)	7471.0(5)	3387.4(3)
Z	2	8	4	4	2
d (calcd) (g cm^{-3})	1.178	1.146	1.147	1.148	1.164
cryst size (mm)	0.34 × 0.31 × 0.22	0.40 × 0.31 × 0.30	0.25 × 0.13 × 0.10	0.50 × 0.26 × 0.19	0.31 × 0.23 × 0.17
cryst syst	monoclinic	tetragonal	monoclinic	monoclinic	triclinic
space group	$P2/n$	$I4_1/a$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
$2\theta_{max}$ (deg)	52	52	52	52	52
no. of rflns measd	28 840	71 021	60 080	60 330	40 991
no. of unique rflns	7562	9255	14 290	14 287	12 115
lin abs coeff (mm^{-1})	0.806	0.680	0.848	0.848	0.929
no. of params	438	478	641	736	683
R ($I > 2\sigma(I)$)	0.0597	0.0487	0.0584	0.0483	0.0479
wR_2 (all data)	0.1679	0.1286	0.1560	0.1352	0.1188
GOF (F^2)	0.953	0.977	0.866	0.898	0.924

[a] For explanations, see text.

(*Z*)-3-[4,4,7,7-Tetrakis(6-*tert*-butyl-2,3,4-trimethylphenyl)-5,8-diphenyl-3-aza-4,7-digermabicyclo[4.2.0]octa-1(8),2,5-trien-2-yl]-2-propennitril (6), **(*E*)-3-[10,10,12-Tris(6-*tert*-butyl-3,4,5-trimethylphenyl)-1,2,3,5,5-pentamethyl-9,11-diphenyl-5,8,10,12-tetrahydro-6*H*-germeto[2′,3′:4,5][1,2]azagermino[2,1-*a*][2,1]benzazagermin-8-yl]-2-propennitril (7), and [5,7,7-Tris(6-*tert*-butyl-2,3,4-trimethylphenyl)-2,3,4,15,15-pentamethyl-6-phenyl-5,7,12,12a,14,15-hexahydro[1,2]azagermino[1,2-*a*]benzo[*g*]germeto[2,3,4-*de*][1,2]benzazagermin-12-yl]acetonitrile (8).** To a suspension of **1** (0.68 g, 0.80 mmol) in *n*-hexane (80 mL) was added 1,4-diphenylbuta-1,3-diyne (0.163 g, 0.8 mmol), and the mixture was stirred for 4 days at room temperature. After this time dicyanoethylene (0.126 g, 1.6 mmol) was added and the stirring continued for 2 days. After filtration, the solution was concentrated to a volume of 40 mL and cooled at −20 °C. After several months, orange crystals (0.410 g, 51% yield) of the isomers **6**−**8** were isolated: mp > 175 °C. Since a separation of the isomers was not possible, reasonable spectral data could not be obtained. Anal. Calcd for $C_{72}H_{88}Ge_2N_2$·NCCHCHCN: C, 75.77; H, 7.53; N, 4.65. Found: C, 75.77; H, 7.75; N, 4.46. Single crystals suitable for X-ray diffraction analysis were grown from *n*-hexane at room temperature.

4,4,7,7-Tetrakis(6-*tert*-butyl-2,3,4-trimethylphenyl)-5,8-diphenyl-3-aza-4,7-digermabicyclo[4.2.0]octa-1(8),2,5-triene-2-carbonitrile (9). Cyanogen was prepared according to the literature procedure from potassium cyanide and copper(II) sulfate.[19] At −70 °C, an excess of anhydrous cyanogen (2.6 g, 50 mmol) was condensed onto a suspension of **4** (ca. 1.7 mmol) in *n*-hexane (80 mL), which had been freshly prepared from **1** (1.44 g, 1.7 mmol) and 1,4-diphenylbuta-1,3-diyne (0.344 g, 1.7 mmol). The mixture was allowed to come to room temperature. During this time the color of the mixture changed from dark blue to greenish yellow. After filtration the solution was concentrated to a volume of 40 mL and left to crystallize at 20 °C for 2 days to yield 1.07 g (57% yield) of yellow crystals of **9**, mp 208−211 °C; ^{1}H NMR δ 0.86 (s, 3 H, CH_3), 0.88 (s, 9 H, CH_3), 1.22 (s, 3 H, CH_3), 1.23 (s, 3 H, CH_3), 1.36 (s, 3 H, CH_3), 1.48 (s, 9 H, *t*Bu), 1.50 (s, 3 H, CH_3), 1.53 (s, 3 H, CH_3), 1.56 (s, 3 H, CH_3), 1.61 (s, 3 H, CH_3), 1.65 (s, 3 H, CH_3), 2.06 (s, 9 H, *t*Bu), 2.11 (s, 9 H, *t*Bu), 2.13 (s, 9 H, *t*Bu), 6.94−7.40 (m, 14 H, Ar-H); ^{13}C NMR δ 14.28, 15.36, 15.91, 20.87, 20.99, 21.08, 22.99, 26.26, 27.19, 31.90, 32.61, 32.91, 33.57, 33.95, 34.12, 37.33, 114.79, 126.79, 127.80, 128.95, 133.09, 136.52, 136.73, 141.26, 141.78, 152.67, 153.14, 161.87, 164.37, 167.78, 176.39. Anal. Calcd for $C_{70}H_{86}Ge_2N_2$: C, 76.39; H, 7.88; N, 2.55. Found: C, 76.09; H, 8.08; N, 2.66.

Crystallographic Analyses. Crystal and numerical data of structure determinations are given in Table 3. In each case the crystal was mounted in an inert oil. Data collection was performed with a Stoe IPDS area detector at 193(2) K using graphite-monochromated Mo Kα radiation (0.71073 Å). The structures were solved by direct phase determination and refined by full-matrix least-squares techniques against F^2 with the SHELXL-97 program system.[20] Hydrogen atoms were placed in the calculated positions, and the other atoms were refined anisotropically. The carbon atoms C11−C16 and C18−C20 as well as the nitrogen atom N2 of **6** and **7** were refined isotropically. The solvent molecules of **6**/**7** and **7**,**8** are disordered and were refined on two positions with occupancy factors of 0.5 each. The carbon atoms C58−C70 of **9** are disordered and were refined on two positions with occupancy factors of 0.5 each. The data have been deposited with the Cambridge Crystallographic Data Centre: CCDC-182 236 (**4**), CCDC-182 233 (**5**), CCDC-182 235 (**6**, **7**), CCDC-182 234 (**7**, **8**), and CCDC-182 724 (**9**).

Computational Details. All geometries were optimized with the semiempirical method PM3 employing the program

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package MOPAC 2002.[21] Local minima and transition states were verified through calculation of the number of imaginary frequencies. The additional DFT calculations at the hybrid functional Becke3LYP[22,23] level of theory (within both the restricted and the unrestricted framework of the Hartree–Fock theory) with the 6-31G(d) basis set were performed with the program package Gaussian 98[24] and, again, the nature of the obtained geometries was verified.

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Supporting Information Available: Listing of atomic coordinates, anisotropic displacement parameters, and bond lengths and angles for **4**, **5**, **6/7**, **7/8**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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