Cycloadditions of Diarylgermylenes to a Diazabutadiene [1]

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Abstract. The reaction of tetrakis(2-*tert*-butyl-4,5,6-trimethylphenyl)digermene, which dissociates into the germylene molecules 2 in solution, with 1,4-diisopropyl-1,4-diazabuta-1,3-diene (3) furnishes the [4+1] cycloaddition product of 2 to the nitrogen atoms of 3. Under drastic conditions tetrakis(2,4,6-triisopropylphenyl)digermene also forms the germylene molecules **6** which react with **3** in a similar fashion to afford the corresponding [4+1] cycloadduct. **Keywords**: Germanium; Germylene; Cycloaddition

Although compounds containing Si=Si double bonds are stable towards dissociation into silylene molecules :SiR₂, in the solid state and, mostly, in solution, the behaviour of digermenes $R_2Ge=GeR_2$ is less uniform. For example, the digermene 1 exists in solution almost completely as the germylenes 2 [2, 3]. Reaction of the orange solution of 2 with the 1,4-diazabutadiene 3 at room temperature yielded pale yellow crystals of the [4+1] cycloaddition product 4 in 90 % yield.



First indications for the existence of the cycloadduct 4 were provided by the olefinic protons in the ¹H-NMR spectrum in which the signal of 3 at 7.94 ppm has disappeared and been replaced by a new singlet at 6.01 ppm. The structure of 4 was confirmed by an X-ray crystal structure analysis (Figure 1) which revealed some unusual features. The five-membered ring has an angular sum of 539.7° and is therefore almost planar. Worthy of note are the environments of the nitrogen atoms which, with angular sums of 358.5° and 355.7° are also practically planar with their substituents. In contrast to 1 the structurally related digermene 5 retains its structural integrity in solution and undergoes cleavage into the germylene molecules 6 only under drastic reaction conditions [4]. Treatment of 3 with 5 at room temperature does not result in any detectable reaction. Only after heating for 200 hours in boiling dimethoxyethane (DME) does the colour of the orange solution become lighter and the light yellow crystals of the cycloadduct 7 can be isolated in 33 % yield. A [4+2] adduct of 3 and 5 could not be detected.

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The failure of **3** to react with the digermene **5** is in opposition to the behaviour of disilenes which, when the spatial demands of the substituents on the nitrogen atoms are not too great, can undergo smooth [4+2] cycloadditions [5]. In comparison to the Si=Si double bond the greater length of the Ge=Ge double bond apparently hinders the formation of a [4+2] adduct.



Fig. 1 Molecule of **4** in the crystal (hydrogen atoms omitted; ellipsoids are drawn at 50 % probability). Selected bond lengths/pm and angles/°: C1-C2 132.2(3), C1-N1 140.4(3), C2-N2 141.1(3), N1-Ge 186.8(2), N2-Ge 185.5(2), N1-Ge-N2 88.20(8), C1-N1-Ge 109.4(2), C2-N2-Ge 108.62(14), C2-C1-N1 116.2(2), C1-C2-N2 117.3(2).



Fig. 2 Molecule of 7 in the crystal (hydrogen atoms omitted; ellipsoids are drawn at 50 % probability).

The ¹H- and ¹³C-NMR spectra of **7** show major similarities with those of compound **4**. In addition, the X-ray crystal structure analysis of **7** (Figure 2) shows differences only in the orientation of the two aryl groups. The five-membered ring has an angular sum of 539.8° and is thus almost planar like that of **4**. The environments of the two nitrogen atoms with angular sums of 355.9° und 355.7° are somewhat more pyramidalized as those of the corresponding atoms in **4**.

Compounds 4 and 7 are the first structurally characterized heterocyclic compounds of this type. Although the formation of analogous ring systems by cycloaddition of thermally generated dimethylgermylene to 1,4-diazabutadienes has been reported, the molecules thus obtained were unstable and were characterized merely by their spectroscopic data [6].

Experimental Section

General Procedure. All reactions were carried out in oven-dried glassware under an atmosphere of dry argon.

¹H and ¹³C NMR spectra: Bruker AM 300; mass spectra: Finnigan MAT 212 or MAT 95; elemental analyses: Analytische Laboratorien, D-51789 Lindlar.

2,2-Bis(2-tert-butyl-4,5,6-trimethylphenyl)-1,3-diisopropyl-1,3diaza-2-germacyclopent-4-ene (4): At room temperature a solution of 3 (66 mg, 0.47 mmol) in 20 mL of THF was added dropwise to a solution of 1 (200 mg, 0.238 mmol) in 40 mL of THF and the mixture stirred for 2 d. During this time the colour of the solution changed from orange to pale yellow. The solvent was removed in vacuo and the residue redissolved in 10 mL of *n*-hexane. Cooling to $-30 \,^{\circ}$ C afforded 240 mg (90 % yield) of a pale yellow solid. Recrystallisation from *n*-pentane furnished pale yellow crystals of 4, mp 155 °C.

Elemental analysis: Calcd: C 72.48, H 9.66, N 4.97. Found: C 72.36, H 9.34, N 4.72 %.

Spectroscopic data: ¹H NMR: δ 0.76 (d, 6H, ³*J* = 6.4 Hz), 1.23 (d, 6H, ³*J* = 6.8 Hz), 1.63 (s, 18H), 1.81 (s, 6H), 2.13 (s, 6H), 2.30 (s, 6H), 3.55 (m, 2H), 6.01 (s, 2H), 7.39 (s, 2H). – ¹³C NMR: δ 15.85 (C_p), 21.13 (C_p), 23.03 (C_p), 24.48 (C_p), 24.97 (C_p), 33.40 (C_p), 33.75 (C_p), 37.24 (C₁), 48.06 (C_q), 112.18 (C_s), 128.98, 132.99, 136.03, 138.84, 144.09, 150.42. C_p, C_s C_t, and C_q refer

to primary, secondary, tertiary, and quaternary carbon atoms. – MS (CI, isobutene) 564 (M $^+,$ 100 %).

2,2-Bis (2,4,6-triisopropylphenyl-)1,3-diisopropyl-1,3-diaza-2germacyclopent-4-ene (7): Compound **3** (0.23 g, 1.64 mmol) was added to a solution of **5** (0.90 g, 0.94 mmol) in 10 mL of DME and the mixture was heated for 200 h under reflux. During this time the colour of the solution changed from orange to yellow. The volume of the solution was concentrated to 2 mL and cooled at -22 °C. After 12 h 0.40 g (33 % yield) of pale yellow crystals of 7 were isolated, mp 158 - 161 °C.

Elemental analysis: Calcd: C 73.76, H 10.08, N 4.52. Found: C 73.32, H 9.97, N 4.33 %.

Spectroscopic data: ¹**H NMR**: δ 0.41 (d, 6H, ³*J* = 6.4 Hz), 0.92 (d, 6H, ³*J* = 6.4 Hz), 1.15 - 1.18 (m, 12H), 1.25 (d, 6H, ³*J* = 6.4 Hz), 1.31 (d, 6H, ³*J* = 6.4 Hz), 1.38 - 1.45 (m, 12H), 2.73 (sept, 2H), 2.87 (sept, 2H), 3.71 (sept, 2H), 4.57 (sept, 2H), 6.04 (s, 2H), 6.34 (s, 2H), 7.19 (s, 2H). - ¹³**C NMR**: δ 22.72, 23.41, 23.66, 24.06, 24.16, 25.52, 26.83, 31.59, 34.54, 36.85, 47.15, 112.75, 121.96, 122.53, 137.57, 150.38, 151.95, 153.79.

Crystallographic analyses: In each case, the crystal was mounted in an inert oil. Data collection was performed with a STOE IPDS area detector using graphite monochromated Mo K_{α} radiation (71.073 pm). The structures were solved by direct phase determination and refined by full-matrix least-squares techniques against F^2 with the SHELXL-97 program package [7]. Hydrogen atoms were placed in the calculated positions, and all other atoms were refined anisotropically. 4: C₃₄H₅₄GeN₂ (563.38), crystal dimensions $0.35 \times 0.08 \times 0.06 \text{ mm}^3$, temperature 153(2) K, triclinic, space groups $P\bar{1}$, a = 964.24(7), b = 966.61(6), c = 1739.53(12) pm, $\alpha =$ 99.107(8)°, $\beta = 90.187(8)°$, $\gamma = 100.803(8)°$, V = 1571.60(19). 10^6 pm^3 , $d_{\text{calcd}} = 1.191 \text{ g/cm}^3$, Z = 2, $2\theta_{\text{max}} = 52^\circ$; collected reflections 5759, observed reflections 4667; $\mu = 0.998 \text{ mm}^{-1}$. R1 = 0.0310, wR2 (all data) = 0.0731 for 334 parameters, GOF = 0.936. 7: $C_{38}H_{62}GeN_2$ (619.49), crystal dimensions 0.38 \times 0.26 \times 0.25 mm³, temperature 193(2) K, orthorhombic, space group Pna2₁, a = 2065.47(5), b = 1352.84(4), c = 1313.20(6) pm, V = $3669.4(2) \cdot 10^6 \text{ pm}^3$, $d_{\text{calcd}} = 1.121 \text{ g/cm}^3$, Z = 4, $2\theta_{\text{max}} = 52^\circ$; collected reflections 27990, observed reflections 5340; μ = 0.861 mm^{-1} . Flack-x = 0.004(10). R1 = 0.0295, wR2 (all data) = 0.0681 for 370 parameters; GOF = 0.905 [8].

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