

11. A Wagner–Meerwein rearrangement in the cationic moiety of **11** involving migration of the bicyclobutane bridgehead carbon atom *trans* to the anionic moiety^[3] would then have to occur to give **12**, which would subsequently yield **8**.

In contrast to the reaction with 1,4-benzoquinone, irradiation^[4] of **1**^[5] with 1,4-naphthoquinone ($E_T = 57$ kcal mol⁻¹^[6c]) at -30°C gave the cyclobutane **13**^[7] (17%). Motivated by the work of Cantrell,^[11] we also employed 2-benzoylthiophene (62.6 kcal mol⁻¹^[11b]) at room temperature as well as 2-acetylthiophene (64.5 kcal mol⁻¹^[11b]) and 2-acetylfuran (64.9 kcal mol⁻¹^[11b]) at -30°C and obtained the [2 + 2] cycloadducts **14** (21%), and **15** (27%) as well as the [4 + 2] cycloadduct **16** (19%) together with its diastereomer (6%).^[7] At -30°C , excited 1-acetylnaphthalene (56.4 kcal mol⁻¹^[6a]) and **1**^[5] gave initially the [4 + 2] cycloadduct **17** (25%). Upon further irradiation, however, **17** was converted at a similar rate into **18** (41%) and **19** (9%)^[7] (di- π -methane rearrangement). Selected physical data for **13**–**19** are given in Table 1.

We obtained no cycloadduct from **1** and cyclopent-2-en-1-one ($E_T = 74$ kcal mol⁻¹^[2a]). In conclusion, **1**, too, can undergo photochemical cycloadditions, provided that the reaction partner has a triplet energy $E_T < 65$ kcal mol⁻¹.

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CAS Registry numbers: **1**, 659-85-8; **2**, 120229-54-1; **3** isomer 1, 120229-55-2; **3** isomer 2, 120328-37-2; **4**, 120229-56-3; **5**, 120229-57-4; **6**, 120229-58-5; **7**, 120262-48-8; **8**, 120229-59-6; **13**, 120229-60-9; **14**, 120229-61-0; **15**, 120229-62-1; **16** isomer 1, 120229-63-2; **16** isomer 2, 120328-38-3; **17**, 120229-64-3; **18**, 120262-49-9; **19**, 120220-65-4; (MeCO)₂, 431-03-8; (PhCO)₂, 134-81-6; methylphenylglyoxylate, 15206-55-0; 1,4-benzoquinone, 106-51-4; chloranil, 118-75-2; 1,4-naphthoquinone, 130-15-4; 2-benzoylthiophene, 135-00-2; 2-acetylthiophene, 88-15-3; 2-acetylfuran, 1192-62-7; 1-acetylnaphthalene, 941-98-0.

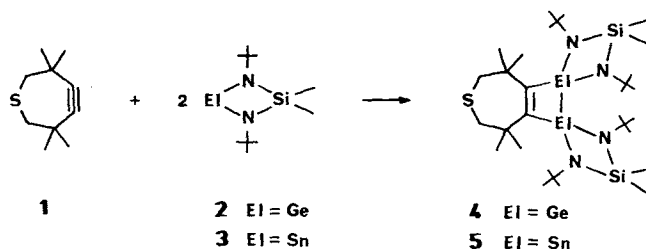
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[4] Light sources: medium-pressure Hg lamp (Hanovia, 450 W) in a Pyrex immersion well; radiation with $\lambda < 400$ nm was filtered out for colored substrates. 1,4-Naphthoquinone and 1-acetylnaphthalene were irradiated in a Rayonet[®] RPR 100 photoreactor with 350-nm and 300-nm light, respectively.
[5] We used **1** as a solution in hexane, which was diluted with the same or up to a fivefold quantity of benzene (experiments at room temperature) or toluene (experiments at -30°C). The solutions, which were saturated with nitrogen before photolysis, were ca. 0.10 M in **1** and 0.05 M in the carbonyl compound.
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[7] The isolation was carried out by flash chromatography with petroleum ether/ethyl acetate on SiO₂ (**4**–**8**, **13**–**15**) or on basic Al₂O₃, activity III (**17**–**19**), and by preparative gas chromatography with Carbowax 20M on Volaspher[®] A2 (**2**, **3**) or silicon SE 30 on Chromosorb[®] W (**16** and diastereomer). Elemental analyses as well as mass, IR, and NMR spectra support the proposed structures. Except for **13**, the configurations were determined from the characteristic magnitudes of the coupling constants or from NOE effects.
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Synthesis and Structure of Digerma- and Distannacyclobutenes**

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The first germirenes (germacyclopropenes) were synthesized by reaction of 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne **1** with suitable precursors of dialkylgermylenes (dialkylgermanediyls);^[1] **1** combines high reactivity of the C–C triple bond with steric shielding of the resulting addition product, thereby often making possible the synthesis of systems otherwise accessible only with difficulty.^[2] Since, until recently, no addition reactions of stannylenes to C–C triple bonds had been described,^[3] we allowed **1** to react with the stabilized diaminogermylene **2**^[4] as well as the diaminostannylene **3**^[4] and obtained, in addition to the digermacyclobutene **4**, the first distannacyclobutene **5**. Compounds **4** and **5** are both dispiro compounds.

Addition of **1** to the red solution of **3** in various solvents (benzene, THF, *n*-hexane, diethyl ether) resulted in immediate precipitation of a yellow solid, whose ¹H and ¹³C NMR spectroscopic data in concentrated solution indicate the formation of the 1:2 adduct **5**. In dilute solution, however, only the ¹H NMR signals of the starting materials were observed; in the ¹³C NMR spectrum of **5**, the signal for the sp-hybridized C atom of **1** was absent. Proof for the presence of an Sn–Sn bond was provided by the ¹¹⁹Sn NMR spectrum, which showed a signal at $\delta = +155$ (rel. to Sn(CH₃)₄; $J(^{119}\text{Sn}, ^{117}\text{Sn}) = 3723$ Hz). Compound **4** was synthesized in a similar way from **1** and **2**.



The results of the X-ray structure analyses of **4** and **5** are given in Figure 1. They confirm the structure derived for **5** in solution. In both cases, there is a central four-membered ring containing two sp²-hybridized carbon atoms and two four-fold coordinated germanium or tin atoms, respectively. Whereas in **5** the nearly planar peripheral diazasilastanna four-membered rings are perpendicular to the completely planar central distannacyclobutene (**5** has a C₂ axis in the crystal, the thiacycloheptene unit being disordered; only one of the two variants is shown in Fig. 1), the diazasilagerma four-membered rings in **4**, which are also planar, are twisted

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[**] Cyclic Diazastannylenes, Part 29. Part 28: M. Veith, V. Huch, R. Lisowsky, P. Hobein, *Z. Anorg. Allg. Chem.*, in press.

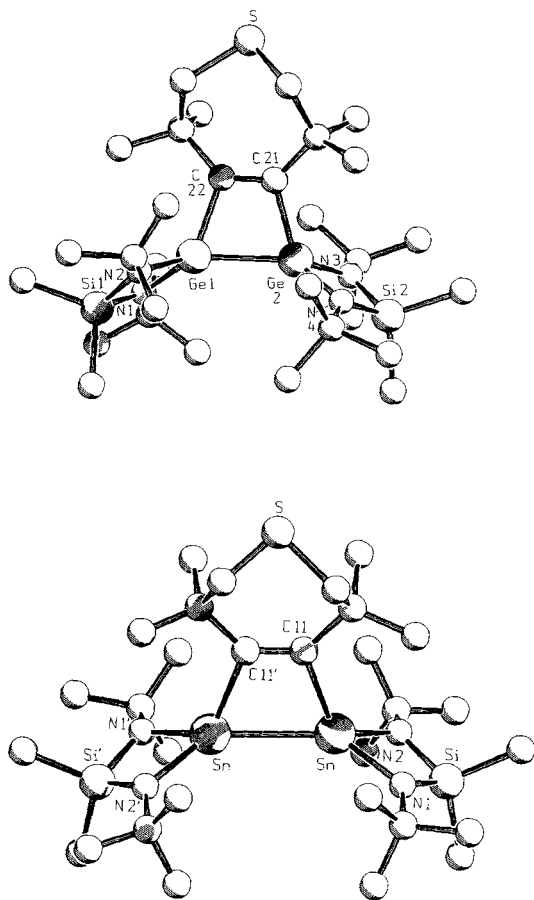
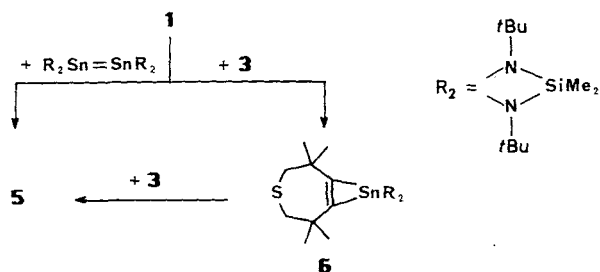


Fig. 1. Molecular structures of **4** (top) and **5** (bottom). Important bond lengths [Å] and angles [°] in the dimetallacyclobutenes: **4**: Ge1-Ge2 2.459 (1), Ge1-C22 2.030 (7), Ge2-C21 2.028 (6), C21-C22 = 1.34 (1); C22-Ge1-Ge2 73.3 (1), Ge2-C21-C22 105.0 (1). **5**: Sn-Sn' 2.803 (1), Sn-C11 2.27 (1), C11-C11' 1.31 (2); C11-Sn-Sn' 70.7 (2), Sn-C11-C11' 109.3 (3) [5].

away from orthogonal positions with respect to the slightly puckered digermacyclobutene. This twisting is due to the sterically demanding *tert*-butyl groups on the nitrogen atoms of the two peripheral rings. Compound **5** is not twisted because the Sn-Sn distance is 0.344 Å longer, thereby reducing this steric interaction.

Whereas the bond lengths and angles of the central ring of **4** are in the expected range, the C=C bond in **5** is quite short (1.31 Å versus the expected value of 1.34 Å) and the Sn-C bonds are very long (2.27 Å versus the expected value of 2.17 Å).^[6] For comparison, in the stannirene synthesized by Sita et al.,^[3] the bond lengths are $d(\text{C}=\text{C}) = 1.34$ Å and $d(\text{Sn}-\text{C}) = 2.14$ Å. The Sn-C bond is thus very weak, which would also explain the dissociation to the starting compounds observed in solution.

Compound **5** could have formed either via the stannirene **6** and subsequent insertion of **3** or by a [2 + 2] cycloaddition



of **1** and a dimer of **3** having an Sn-Sn double bond; since such dimers of **3** are not known^[7] whereas a stannirene has already been isolated,^[3] we believe that the pathway via **6** is more likely. Both pathways to the 1,2-digermacyclobutenes are possible in the case of the dialkylgermylenes.^[8] Phosphadistannacyclobutenes, however, are probably formed by [2 + 2] cycloaddition.^[9]

Experimental Procedure

4, **5**: Compound **1** (0.78 g, 4.68 mmol) was added dropwise under argon to **2** (1.28 g, 4.68 mmol) or **3** (1.5 g, 4.68 mmol) in 5 mL of dry benzene at +10 °C over 5 min, resulting in the formation of yellow crystals. After purification (**4**, recrystallization from benzene; **5**, sublimation at 40–50 °C/10⁻³ torr), 1.43 g of **4** (86%) or 1.05 g of **5** (56%) was obtained.

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[5] **4**: C₃₀H₆₄N₄SSi₂Ge₂, space group P2₁/n, a = 10.761 (9), b = 31.85 (3), c = 12.54 (1) Å, β = 114.61 (7)°, V = 3908 Å³, Z = 4, ρ_{calcd.} = 1.197 g cm⁻³, μ(MoKα) = 16.25 cm⁻¹, 4634 unique reflections, 1047 classified as not observed (F ≤ 3σ(F)). Reflection/parameter ratio = 15. R = 0.057. **5**: C₃₀H₆₄N₄SSi₂Sn₂, space group C2, a = 17.135 (9), b = 10.223 (5), c = 14.233 (7) Å, β = 125.63 (4)°, V = 2026 Å³, Z = 2, ρ_{calcd.} = 1.305 g cm⁻³, μ(MoKα) = 12.52 cm⁻¹, 1410 unique reflections, 14 classified as not observed (F ≤ 3σ(F)). Reflection/parameter ratio = 8.2. R = 0.044. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depositary number CSD-53 454, the names of the authors, and the journal citation.

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Highly Reduced Porphyrins**

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Can an organic π system be used to store charge by successive addition of electrons and is the storage capacity increased on going to higher analogues containing several redox centers? We have examined this question for the first time for porphyrins^[1] and have found that the zinc complex **1** of *meso*-tetratolylporphyrin **2** can reversibly accept six electrons. The NMR spectra of the intermediate di- and tetra-

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