11. A Wagner–Meerwein rearrangement in the cationic moiety of 11 involving migration of the bicyclobutane bridgehead carbon atom to the anionic moiety 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 \[^{[15]}\] with 1,4-naphthoquinone (\(E_r = 75 \text{ kcal mol}^{-1}\) \[^{[16]}\]) at \(-30^\circ\text{C}\) gave the cyclobutane 13 \[^{[17]}\] (17\%). Motivated by the work of Cannell \[^{[11]}\] we also employed 2-benzothiophene (62.6 kcal mol\(^{-1}\) \[^{[14]}\]) at room temperature as well as 2-acyctethylthiophene (64.5 kcal mol\(^{-1}\) \[^{[11]}\]) and 2-acetylfuran (64.9 kcal mol\(^{-1}\) \[^{[11]}\]) at \(-30^\circ\text{C}\) 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\%) \[^{[17]}\]. At \(-30^\circ\text{C}\), excited 1-acyctethylnaphthalene (56.4 kcal mol\(^{-1}\) \[^{[16]}\]) and 1 \[^{[11]}\] 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\%) \[^{[12]}\] (di-methylene rearrangement). Selected physical data for 13–19 are given in Table 1.

We obtained no cycloadduct from I and cyclopent-2-en-1-one (\(E_r = 74 \text{ kcal mol}^{-1}\) \[^{[12a]}\]) in comparison. In conclusion, I, can undergo photochemical cycloadditions, provided that the reaction partner has a triplet energy \(E_T < 65 \text{ kcal mol}^{-1}\).

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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, 120229-64-9; 19, 120229-65-4; (MeCO\(_2\))\(^{-}\), 431-03-8; (PhCO\(_2\))\(^{-}\), 134-81-6; methylenefuryloxoylate, 15206-55-0; 1,4-benzoquinone, 106-51-4; chloranil, 98-0.

3 isomer 2, 120328-37-2; 1,4-naphthoquinone, 130-15-4; 2-benzoylthiophene, 135-00-2; 2-acyctethylfurane, 1192-62-7; 1-acetylnaphthalene, 941-98-0.

[4] Light sources: high-pressure Hg lamp (Hanovia, 450 wavelength); immersion well; radiation with a high energy output, were ca. 0.10 m for a few seconds.
[5] We used I as a solution in hexane, which was diluted with the same or up to two fold volume of benzene (experiments at room temperature) or toluene (experiments at \(-30^\circ\text{C}\)). The solutions, which were saturated with nitrogen before photolysis, were ca. 0.10 m in 1 and 0.05 m in the carbonyl compound.
[7] The isolation was carried out by flash chromatography with petroleum ether/ethyl acetate on SiO\(_2\) (4-8, 17-19) and by preparative gas chromatography with Carbowax 20M on Valaspher \(^{[12]}\) A 2 (2, 3) or silicon SE 30 on Chromosorb \(^{[12]}\) 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.

[8] Analysis by \(\text{H NMR spectroscopy.}\)

Synthesis and Structure of Digerma- and Distannacyclobutenes **

By Adolf Krebs, * Andrea Jacobsen-Bauer, Erhard Haupt, Michael Veith, * and Volker Huch

The first germirenes (germacycloprenenes) were synthesized by reaction of 3,3,6,6-tetramethyl-1-thiacyclohept-4-ene 1 with suitable precursors of dialkyglylene (dialkygermanediyls). \[^{[1]}\] I combines high reactivity of the C-C triple bond with steric shielding of the resulting adduct product, thereby often making possible the synthesis of systems otherwise accessible only with difficulty. \[^{[12]}\] Since, until recently, no addition reactions of stannylene to C-C triple bonds had been described, \[^{[13]}\] we allowed 1 to react with the stabilized diaminoglycerene 2\[^{[4]}\] as well as the diaminostannylene 3\[^{[4]}\] and obtained, in addition to the digermacyclobutene 4, the first distannacyclobutenate 5. Compounds 4 and 5 are both diisopropyl compounds.

Addition of I to the red solution of 3 in various solvents (benzene, THF, n-hexane, diethyl ether) resulted in immediate precipitation of a yellow solid, whose \(^{1}H\) and \(\text{C NMR spectroscopic data in concentrated solution indicate the formation of the 1:2 adduct 5. In dilute solution, however, only the }^{1}H\text{ NMR signals of the starting materials were observed; in the }^{13}C\text{ NMR spectrum of 5, the signal for the sp-hybridized C atom of I was absent. Proof for the presence of an Sn-Sn bond was provided by the }^{119}\text{Sn NMR spectrum, which showed a signal at }\delta = +155 (\text{rel. to Sn(CH}_3)_2\text{; }J^{(119,119}\text{Sn }= 3723 \text{ 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 sp\(^{3}\)-hybridized carbon atoms and two four-fold coordinated germanium or tin atoms, respectively. Whereas 5 is the nearly planar peripheral diazasilastanna four-membered rings are perpendiculat to the completely planar central distannacyclobutene 5 has a C\(^{2}\) 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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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-digermacyclobutene are possible in the case of the dialkyglymelenes.[8] Phosphodistannacyclobutenes, 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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**Highly Reduced Porphyrins**

By Robert Cosmo, Christian Kautz, Klaus Meerholz, Jürgen Heinze,* and Klaus Müllen*

Can an organic σ 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 I of meso-tetrololyloporphyrin 2 can reversibly accept six electrons. The NMR spectra of the intermediate di- and tetra-

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[5] 4: C₁₂H₂₀N₃S₂Sn₂Ge₂, space group P2₁/n, a = 10.761 (9), b = 31.85 (3), c = 12.54 Å (1), β = 114.61° (1), V = 3908 Å³, Z = 4, ρ(ave) = 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.
[6] R = 0.057–5: C₁₂H₂₀N₃S₂Sn₂Ge₂, space group C2, a = 17.135 (9), b = 10.223 Å, c = 14.233 Å, β = 125.63°, v = 2026 Å³, Z = 2, ρ(ave) = 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 depository number CSD-53454, the names of the authors, and the journal citation.