Via this reaction, we surprisingly directly obtained not only 1 but, in addition, two isomers, which we assign\textsuperscript{[9]} to the unexpectedly stable syn,syn,anti- and syn,anti,anti-conformations 9 and 10\textsuperscript{[10]} (Fig. 1) on the basis of their \textit{1}H-NMR spectra and their thermal rearrangement to give 1.

![Fig. 1. anti- and syn-Arrangements (selected) in 1, 9, and 10.](image)

Upon heating of the products of the phenyllithium cyclization to 350°C, a syn–anti rearrangement takes place. As expected, the optical stability of the new molecular propeller 1, which is important for practical applications\textsuperscript{[11]} is considerable; it is even higher than that of the helicenes 1 even sustains heating at 310°C for several minutes—conditions that lead to the racemization of the helicenes as well as of 2. This is plausible since the inversion of a phenylene group in the anti-position is coupled with that of each of the other five, in contrast to the independent ring inversion in 2.

By analogous synthetic strategy, other helices, with high optical rotation and stability, might be accessible\textsuperscript{[12]}. The dehydrogenation product of 1, a diphenanthrovalene, is also of interest due to its polycyclic aromatic structure.

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CAS Registry numbers:
(\pm)•1: 95216-91-4; (\pm)•1: 95340-76-4; (-)•1: 95340-77-5; 3: 35286-92-1: 4:
74844-03-4: 5: 95216-92-5: 6: 95216-93-6: 7: 95216-94-7: 8: 95216-95-8: (\pm)•9:
95340-78-6; (\pm)•10: 95342-08-8.

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6. Name according to IUPAC nomenclature:
Decacycl(37.3.1.1\textsuperscript{11,12})\textsuperscript{18,21,25(19)}\textsuperscript{22.12129.1~210.02''.0'}octatetraconta-
(42)\textsuperscript{2,4(48),5,7,11(47),12,14,16,18(46),19,21,23(45),26,28,30,32(44),35,35,39(43),40-henicosaene.
7. M.p. [°C]: 5: 206: 6: 64: 7: liquid, R. value=0.39 (CHCl\textsubscript{3}/acetone 9:1): 8:
6: 66: 9: rearrangement to 1 above ca. 300: 10: rearrangement to 1 above ca. 300.
8. Examination of molecular models plausibly explains the lack of formation of the all-syn conformer, in which a sterically less-favorable arrangement of the six peripheral benzene rings should be present.
9. Elemental analyses and spectra of the new compounds are in agreement with the structures given. The weighing of small amounts of 1 poses some difficulties owing to its strong electrical charge. The optical rotation of the (―)–enantiomer is of the same order of magnitude as that of the (\pm)–enantiomer.

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**"Stereochemical Activity" of a Lone Pair of Electrons on Low Valent Elements of the 4th Main Group:**
(\textit{Ge}N\textit{Bu})\textsubscript{4}·2\textit{AlCl}\textsubscript{3} and (\textit{Sn}N\textit{Bu})\textsubscript{4}·2\textit{AlCl}\textsubscript{3}\textsuperscript{[**]}

By Michael Veith* and Walter Frank

Dedicated to Professor Gerhard Fritz on the occasion of his 65th birthday

The "stereochemical activity" of a lone pair of electrons on heavy main group elements has often been discussed

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\[\text{[**]}\] Prof. Dr. M. Veith, Dipl.-Chem. W. Frank
Institut für Anorganische Chemie der Universität
D-6600 Saarbrücken (FRG)

with resort to bond theory and structural and chemical aspects for evidence of the existence or non-existence of such an activity. In the case of molecular compounds of divalent elements of the fourth main group (especially of Ge<sup>11</sup> and Sn<sup>11</sup>), primarily the existence of transition-metal complexes of the type X<sub>n</sub>M = EY<sub>y</sub> [1] or [X<sub>n</sub>M = EY<sub>y</sub>] [2] (E = Ge, Sn) has been taken as supporting evidence for these elements being able to function as bases by virtue of the lone pair of electrons; however, the particular electronic structure of the transition metal was ignored (back-bonding etc., cf. also carbene complexes) [3]. Even though a whole series of acid-base adducts such as (Cp)<sub>2</sub>Sn = AlX<sub>3</sub> [4] (Cp = cyclopentadienyl, X = halogen) and X<sub>2</sub>Sn = BF<sub>3</sub> [5] have been reported, neither the exact structures are known, nor is the formulation of the compounds as adducts confirmed. According to most recent structure investigations even the species (η<sup>2</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Sn = BF<sub>3</sub> designated as adduct must be described as [(BF<sub>3</sub>]<sup>2</sup>[(μ-η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Sn(μ-η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)]<sup>2</sup> (ή). [4]. By reaction of the cubane-like compounds (GeNtBu)<sub>4</sub> [5] and (SnNtBu)<sub>4</sub> [6] with aluminum trichloride we have now succeeded in preparing adducts which contain Ge-Al and Sn-Al bonds, respectively. By varying the molar ratio of the reaction partners we have tried to prepare the adducts (tBuNGe)<sub>4</sub> (AlCl<sub>3</sub>), with x = 1-4; however, on crystallization only those adducts with x = 2 could be isolated.

(tBuNEt)<sub>x</sub> + AlCl<sub>3</sub> $\xrightarrow{\Delta \text{coconut}}$ (tBu-NEt)<sub>x</sub>·2AlCl<sub>3</sub>

1, E1 = Ge; 2, E1 = Sn

The <sup>1</sup>H-NMR spectra of the reaction solutions surprisingly contain (see molecular structure in Fig. 1) only one singlet, whose chemical shift depends upon the ratio of the reaction partners (when x = 2, 1: δ = 1.30 (s); 2: δ = 1.32 (s), 60 MHz, 28°C, toluene) [6]. This finding could be explained in terms of the presence of various adducts and a rapid exchange of the AlCl<sub>3</sub> groups in solution. An X-ray structure analysis of single crystals of 2 confirmed the adduct structure. 1 and 2 are relatively unstable; they decompose into the starting components, slowly in solution and rapidly under reduced pressure (in the mass spectrometer).

The structure analysis of 2 (Fig. 1) proves for the first time that low-valency elements such as Sn<sup>11</sup> can function as donors in Lewis acid-base adducts. The Sn-Al bond length corresponds exactly to that expected from the atomic radii [7]; the aluminum atoms coordinate in a distorted tetrahedral fashion, with the Cl-Al-Cl angle of 113.9° (mean) lying in the range typical for AlCl<sub>3</sub> adducts [8]. On comparing the structure of 2 with the structure of the uncoordinated (SnNtBu)<sub>4</sub> [9] the following differences emerge: a) the distance between the fourfold coordinated tin atoms in 2 is reduced (Sn···Sn = 236.2 pm), while the other intramolecular distances all remain, within the standard deviations, the same. b) As a direct consequence of this closing-up, the N-Sn-N angles in the four membered ring N2-Sn1-N3-Sn2 (84° in 2 compared to 80° in (SnNtBu)<sub>4</sub>) are widened and the Sn-N-Sn angles compressed. A very superficial interpretation of this effect could lead to the conclusion that the distance between the respective tin atoms becomes smaller by withdrawal of the electron density of the lone electron pairs. The adducts 1 and 2 support the hypothesis that the (tBuNEt)<sub>4</sub> molecules (E = Ge, Sn) may better be described as cage molecules with oriented bonding [9]. But it is still unclear why only the adducts with two AlCl<sub>3</sub> moieties crystallize and not also those with another Al:Sn ratio.

**Experimental:**

Newly sublimed aluminum trichloride (0.152 g, 1.44 mmol) was treated with a solution of (tBuNGe)<sub>x</sub> [10], (tBuNSn)<sub>x</sub> [10] (0.58 mmol) in toluene (30 mL) in the strict absence of moisture. On heating the mixture to boiling the reaction was allowed to stand. After a few hours, rhombus-shaped crystals separated out. Yields: 1, 0.36 g (75.6%); 2, 0.38 g (65%). The crystals gave correct elemental analyses.

CAS Registry numbers:

1, 95156-17-5; 2, 95156-18-6; (t-BuNGe)<sub>x</sub>, 84805-53-8; (1-BuNSn)<sub>x</sub>, 95156-19-7; Al, 7429-90-5; Sn, 7440-31-5.

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**Mechanism of Purpurogallin Formation:**

**An Adduct from 3-Hydroxy-o-benzoinoquine and 4,5-Dimethyl-o-benzoquinone**

By Walter Dürckheimer* and Erich F. Paulus

Dedicated to Professor Rolf Sammet on the occasion of his 65th birthday

Purpurogallin 1, found in nature as a glycoside, is formed upon oxidation of pyrogallol in water. The mechanism of this reaction is still largely speculative. *Salfield* and *Horner* et al. [10] postulated an intermediate 3 formed

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[10] Dr. W. Dürckheimer, Dr. E. F. Paulus

Hochschul-Aktiengesellschaft, Pharma-Synthese

Postfach 800320, D-6320 Frankfurt am Main 80 (FRG)