(Figure 3). Again, excitation of the proton H^{2b} yields a cross relaxation signal at the resonance of the catalyst proton H^3, whereas excitation of the proton H^{2f} does not.

Experimental Section

All NMR experiments were conducted at 298 K using a Bruker DRX200 spectrometer. The chemicals were used as obtained by Aldrich. The enrichment of parahydrogen was performed at 77 K catalyzed by activated charcoal. For the PHIP experiments, the resulting 50:50 mixture of ortho- and parahydrogen was bubbled through the reactive solution inside of the magnetic field for 3 s.

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Hexaaryltetragermabuta-1,3-diene: A Molecule with Conjugated Ge=Ge Double Bonds**

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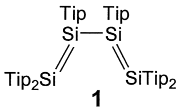
With the recent isolation of the first diplumbenes,[1, 2] molecules containing a short lead–lead double bond, homonuclear double bonds of the type $R_2E{=}ER_2$ (E = C, Si, Ge, Sn, Pb) are now known between all elements of Group 14.[3] The strong decrease in bond dissociation energies of these double bonds from silicon to lead is reflected in the distinctly different behavior in the crystalline state and in solution. Under exclusion of air and moisture all compounds are stable in the solid state. This is also true for solutions of most disilenes, whereas digermenes tend to dissociate partly into germylenes R_2Ge:. Distannenes and diplumbenes, on the other hand, exist almost exclusively as stannylenes R_2Sn: and plumbylenes R_2Pb: in solution.[3]

Recently, we obtained the tetrasilabuta-1,3-diene **1**, the first and to date only molecule containing conjugated Si=Si double bonds. The most remarkable feature of this brownish-red substance **1** is that it adopts the s-*cis* conformation in the solid state,[4] which is also the favored form in solution. We have now examined if the germanium compound **6** analogous to **1** is accessible by following a similar synthetic approach (Scheme 1).



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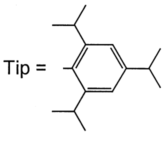
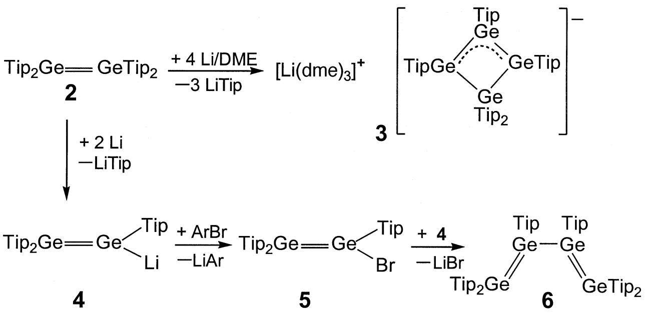


As a starting compound we chose the tetraaryldigermene **2** whose structural integrity, according to previous investiga-



Scheme 1. Ar = 2,4,6-$Me_3C_6H_2$ (Mes), 2,4,6-$iPr_3C_6H_2$ (Tip).

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tions, is also retained in solution,[5, 6] and for which we recently found a synthetic approach that yields acceptable quantities.[7] In contrast to a previous report,[5] treatment of **2** with an excess of lithium did not afford the digermenyllithium compound **4**, but instead we obtained a dark-red solid, which, owing to its insolubility and low volatility, could only be characterized by an X-ray structure analysis (Figure 1).[8]

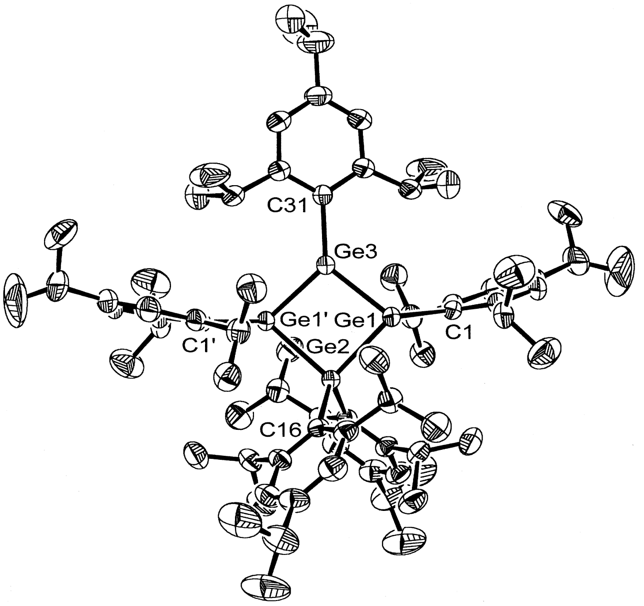

Figure 1. Structure of the anion of **3** in the crystal (hydrogen atoms omitted, ellipsoids at the 50% probability level). Selected bond lengths [pm] and angles [°]: Ge1–Ge2 251.16(6), Ge1–Ge3 236.79(6), Ge1–C1 202.2(5), Ge2–C16 203.2(4), Ge3–C31 200.3(6); Ge1–Ge3–Ge1′ 97.71(3), Ge3–Ge1–Ge2 85.93(2), Ge1–Ge2–Ge1′ 90.44(3)

In accordance with the observed properties we found an ionic compound (**3**) containing an allyl-like Ge_3 ion as part of a four-membered ring. Within this planar ring (sum of angles 360°) the Ge–Ge multiple bonds differ substantially in length from the Ge–Ge single bonds. This bond type in the anion of **3**, unusual to germanium chemistry, can best be compared to the acyclic, allyl-like Ge_3 anion, obtained by Power et al. from the cleavage of a cyclotrigermyl radical with KC_8.[10]

Precisely how **3** is formed remains unclear, since it not only involves the cleavage of Ge–C bonds in **2**, but also the formation of Ge–Ge bonds. In order to eliminate all subsequent reactions of the primarily expected compound **4**, we shortened the reaction time of **2** with lithium to such an extent, that most of the digermene **2** had reacted before the formation of **3** could become the main reaction. This approach did indeed lead to compound **4**, which by subsequent reaction with an aryl bromide presumably resulted in the bromine derivative **5**, from which compound **6** was formed by intermolecular coupling under elimination of LiBr.

The X-ray structure analysis[8] of the resulting greenish-black crystals did not only confirm the constitution of the tetragermabutadiene **6**, it also revealed some remarkable details (Figure 2). Similar to **1**, compound **6** does adopt the s-*cis* form. The dihedral angle of the Ge_4 framework (22.5°) is notably smaller than in the corresponding Si_4 unit (51°). With an average value of 235 pm the Ge–Ge double bonds are considerably elongated in comparison to those in the digermene **2** (221.3(1) pm), although they are still in the range of typical digermenes.[3, 11] The length of the formal Ge–Ge single bond (245.81(5) pm) in **6** is in good agreement with the normal bond length. Compared to the analogous bonds in **3**, a considerable shortening is observed. In analogy to the angles in **1** the Ge-Ge-Ge bond angles in **6** are also widened significantly with a mean value of 135.5°.

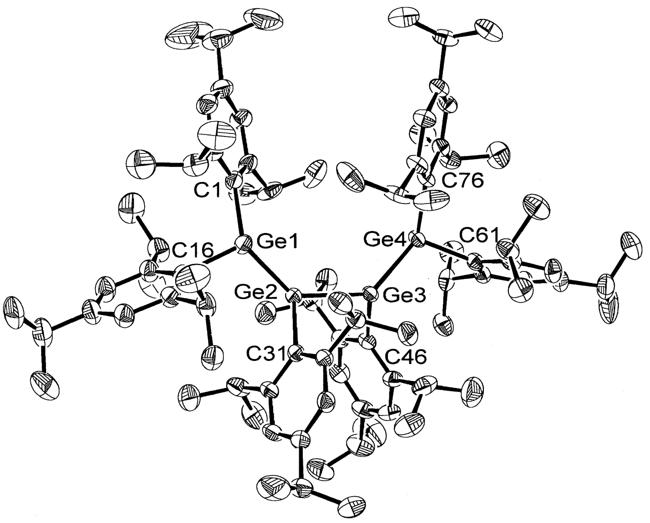

Figure 2. Structure of **6** in the crystal (hydrogen atoms omitted, ellipsoids at the 50% probability level). Selected bond lengths [pm] and angles [°]: Ge1–Ge2 235.68(6), Ge2–Ge3 245.81(5), Ge3–Ge4 234.39(5), Ge1–C1 198.5(4), Ge1–C16 199.6(4), Ge2–C31 200.3(3), Ge3–C46 199.7(4), Ge4–C61 193.3(4), Ge4–C76 198.6(3); Ge1–Ge2–Ge3 136.18(2), Ge2–Ge3–Ge4 134.99(2), Ge2–Ge1–C1 126.0(1), Ge2–Ge1–C16 109.8(1), Ge1–Ge2–C13 108.9(1), Ge4–Ge3–C46 101.25(10), Ge3–Ge4–C61 112.56(10), Ge3–Ge4–C76 126.2(1)

Both Ge–Ge double bonds display a considerable *trans* bending of the substituents away from the respective Ge=Ge vector. The values of 35.4 and 31.1° for the Ge1–Ge2 bond and 33.3 and 31.1° for the Ge3–Ge4 bond are among the largest *trans* pyramidalization so far observed in digermenes.[3, 11] In addition, both double bonds show a small but noticeable torsion, with values of 22.4° (Ge1–Ge2) and 21.3° (Ge3–Ge4).

Even though the crystal structure of **6** reveals the existence of two Ge–Ge double bonds, it does not give any information about a possible conjugation between these bonds. The electronic spectrum is more revealing: The dark blue solution of **6** in *n*-hexane shows a longest wavelenth absorption at 560 nm, which compared to the yellow or orange digermenes,[11] corresponds to a bathochromic shift of about 140 nm and even exceeds the absorptions of tetrasilyldigermenes[12] by almost 100 nm.

With compound **6**, we have succeeded for the first time in the isolation, albeit in a low yield, of a thermally stable, yet extremely air-sensitive molecule with conjugated Ge–Ge double bonds. Owing to the nearly complete dissociation of distannenes and diplumbenes in solution into stannylenes and plumbylenes, it seems doubtful whether this result may be applied to the heavier homologues tin and lead.

Experimental Section

Lithium powder (0.100 g, 14.4 mmol) was added to a solution of **2** (1.23 g, 1.28 mmol) in DME (70 mL). The initially black mixture turned red and was stirred for five hours at room temperature. Insoluble compounds were filtered off and the solution was treated with 1-bromo-2,4,6-triisopropylbenzene (0.220 g, 0.78 mmol) at −18 °C. Over a period of ten hours the solution was slowly warmed to room temperature. DME was removed and the precipitate was dissolved in *n*-hexane (10 mL). Renewed filtration, concentration to a volume of 3 mL, and cooling to −30 °C afforded greenish-black crystals of **6** (0.103 g; 11 % yield). M.p. 175 – 182 °C. ^{1}H NMR (500 MHz, [D$_8$]THF, 25 °C): $\delta = 0.02-0.10$ (m, 6H), 0.19 (d, 6H, $J = 6.6$ Hz), 0.29 (d, 6H, $J = 6.6$ Hz), 0.35 (d, 6H, $J = 6.6$ Hz), 1.05 – 1.17 (m, 48H), 1.21 (d, 12H, $J = 6.6$ Hz), 1.42 (d, 6H, $J = 6.6$ Hz), 1.51 (d, 6H, $J = 6.6$ Hz), 1.56 (d, 6H, $J = 6.6$ Hz), 1.60 (d, 6H, $J = 6.6$ Hz), 2.70 (sept, 4H), 2.75 (sept, 2H), 2.84 (sept, 2H), 3.09 (sept, 2H), 3.24 (sept, 2H), 3.35 (sept, 2H), 4.11 (sept, 2H), 4.27 (sept, 2H), 6.55 (s, 2H), 6.76 (s, 2H), 6.78 (s, 2H), 6.80 (s, 2H), 6.94 (s, 2H), 7.11 (s, 2H); ^{13}C NMR (125 MHz, [D$_8$]THF, 25 °C): $\delta = 14.39$, 23.49, 23.93, 24.11, 24.20, 24.28, 24.36, 24.51, 27.07, 32.51, 32.51, 34.99, 35.04, 35.27, 35.39, 37.99, 39.93, 122.14, 122.33, 122.64, 122.76, 123.52, 123.69, 142.00, 144.52, 148.05, 149.41, 150.47, 151.21, 152,45, 153.58, 154.12, 154.59; UV/Vis (*n*-hexane): $\lambda_{max}(\varepsilon) = 405$ (10450), 560 (12750) nm; C,H analysis: calcd: C 71.56, H 9.21; found: C 71.30, H 9.03.

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Functionalized Tellurium(II) Thiolates: Tellurium Bis(2-hydroxyethanethiolate) Hydrate, the First H_2O-Te^{II} Complex[**]

Holger Fleischer[*] and Dieter Schollmeyer

Tellurium(II) thiolates, $Te(SR)_2$ (R = alkyl, aryl) are of both chemical[1–5] and biochemical[6] interest. Thiolates $Te(SR)_2$, in which R contains a functional group, have not yet been described, despite their potential interest for synthetic and structural chemistry, for example the synthesis of precursors for the production of HgTe or CdTe semiconductors by chemical vapor deposition (CVD). We report here the synthesis of the first representative of this class of compounds and the crystal structure of its monohydrate.

Reaction of TeO_2 with $HOCH_2CH_2SH$ yields $Te(SCH_2CH_2OH)_2$ by a reductive elimination according to Equation (1).[7] With exclusion of light, solutions of $Te(SCH_2CH_2OH)_2$ in $CDCl_3$ are stable at room temperature for several days. On the other hand, ^{1}H NMR spectroscopy reveals rapid decomposition and the formation of Te and $(SCH_2CH_2OH)_2$, when such a solution is irradtiated with UV light ($\lambda = 254$ nm). The decomposition obeys first-order kinetics, suggesting a monomolecular mechanism for the photolysis. Preliminary results show that the OH groups of $Te(SCH_2CH_2OH)_2$ can be acetylated, and a more comprehensive account of its chemistry will be published in due course.

$$TeO_2 + 4\,HSCH_2CH_2OH \rightarrow Te(SCH_2CH_2OH)_2 + (SCH_2CH_2OH)_2 + 2\,H_2O \quad (1)$$

The complex $Te(SCH_2CH_2OH)_2 \cdot H_2O$ was obtained at −45 °C from an ethanolic solution of $Te(SCH_2CH_2OH)_2$ containing traces of water.[8] The Te ··· O distance (249.5(10) pm) is in the range of known intramolecular dative O →Te interactions, for example 223.7(8) pm in 2-benzamidyl(bromo)tellurium,[11] and 324.4(2) pm in 4-methoxyphenyl(*O*-methylxanthogenato)tellurium.[12] The sum of the bond angles at the tellurium center is approximately 310°; thus, the configuration of the three-coordinate Te atom can be described as distorted trigonal pyramidal. In the solid state, $Te(SCH_2CH_2OH)_2$ molecules form chains through O3–H3 ··· O6′ hydrogen bonds (Figure 1); the structural parameters of the hydrogen bond are similar to those in ice.[13] Adjacent chains are linked through short O–H ··· S hydrogen bonds (cf reference [13]).

The strong intermolecular interactions lead to significant differences between the molecular structure of $Te(SCH_2CH_2OH)_2 \cdot H_2O$ optimized by ab initio methods and its structure in the crystal. In particular, the Te–O bond

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