Synthesis and Structure of Bis(2,4-di-*tert*-butyl-1,3-cyclopentadien-1-yl)disulfane, $S_2(tBu_2C_5H_3)_2$, and Bis[2,4-di-*tert*-butyl-5-(trimethylsilyl)-1,3-cyclopentadien-1-yl]disulfane, $S_2[tBu_2(Me_3Si)C_5H_2]_2$

Georg Thaler, Klaus Wurst, and Fritz Sladky*

Institut für Allgemeine, Anorganische und Theoretische Chemie der Universität Innsbruck,
A-6020 Innsbruck, Innrain 52a, Austria

Received August 2, 1995

Key Words: Disulfanes / Cyclopentadienyl

Reaction of 1,3-di-*tert*-butylcyclopentadienyllithium and 1,3-di-*tert*-butyl-4-(trimethylsilyl)cyclopentadienyllithium with S_2Cl_2 gives bis(2,4-di-*tert*-butyl-1,3-cyclopentadien-1-yl)disulfane (**1**) and bis[2,4-di-*tert*-butyl-5-(trimethylsilyl)-1,3-cyclopentadien-1-yl)disulfane (**2**), respectively. The structure of **2** was determined by single-crystal X-ray diffraction. Compounds **1** and **2** are the first biscyclopentadienylchalcogens with the chalcogen in vinylic position.

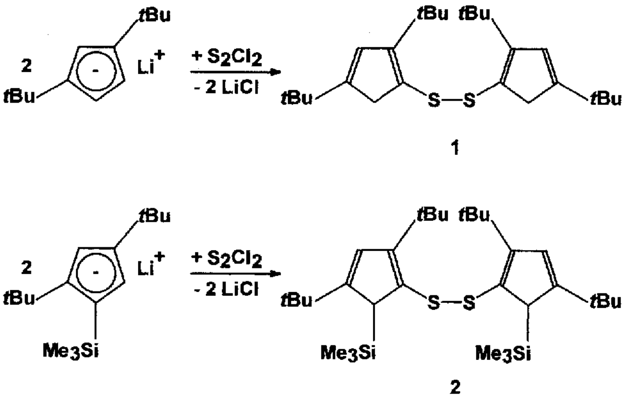
Cyclopentadienyl derivatives of the elements of group 16 (the chalcogens) are rare, despite the considerable interest in cyclopentadienyl-substituted main group elements in recent years. Jutzi et al. prepared and structurally characterized the first biscyclopentadienylchalcogen compound, $S(C_5Me_5)_2$, by the reaction of LiC_5Me_5 with SCl_2[1]. Very recently, $Se(C_5Me_5)_2$ was synthesized[2], and there is spectroscopic evidence for the existence of $S_2(C_5Me_5)_2$[1] and $Li_2[S(C_5H_5)_2]$[3]. Such compounds are of special interest as starting materials for the synthesis of ansa-metallocenes and because of their bifunctional ligand properties. As a consequence of the use of C_5Me_5 as a ligand which was thought to be essential for the existence of the reported compounds, the chalcogens are attached to an allylic position of the ring.

Our intention was to explore other suitable but not fully substituted cyclopentadienes with free vinylic positions. This should lead to even more stable cyclopentadienylchalcogen compounds because of the possibility of overlapping of chalcogen lone pairs with the π system of the ring[4].

Results and Discussion

We found that less than five but more bulky substituents lead to stable biscyclopentadienyldisulfanes. At least two *t*Bu groups are required, and whereas $tBu_3C_5H_2Li$ does not show any reactivity toward sulfur chlorides, $tBu_2(Me_3Si)C_5H_2Li$, a so-called supracyclopentadienyl[5], does, and the addition of a Me_3Si group further enhances the stability of the corresponding disulfane (Scheme 1).

Scheme 1. Synthesis of **1** and **2**



Depending on the reaction temperature, small amounts of the corresponding mono-, tri-, and tetrasulfane could be detected by mass spectroscopy which suggests that the reaction is less straightforward than expected.

The structure of disulfanes, diselanes, and ditellanes, especially with sterically demanding groups, is of current interest[6]. Usually, such compounds exist in two anticlinal (C_2, *gauche*), enantiomeric conformations. The torsion angles of these nonplanar conformations are between about 80 and 100°. Interconversion of the enantiomers by rotation around the chalcogen-chalcogen bond proceeds via an antiperiplanar (C_{2h}, *trans*) or synclinal (C_{2v}, *syn*) transition state. Only the very bulky tris(trimethylsilyl)methyl (Tsi) group was found to enforce the energetically less favored antiperiplanar conformation for the respective disulfane, diselane, and tritellane[6d,e,7]. Other bulky groups frequently used like 2,4,6-tri-*tert*-butylphenyl (mes*), 2,4,6-trimethylphenyl (mes), and triphenylmethyl (trityl) adopt the "normal" anticlinal conformation. The structure of **2** therefore should give some information about steric and/or electronic factors, which are responsible for the stability of **1** and **2**.

The molecular structure of **2** determined by single-crystal X-ray diffraction analysis is the first reported structure of a biscyclopentadienyldichalcogen (Figure 1).

Each sulfur atom is within bonding distance to only one sp^2-hybridized carbon atom which proves η^1 attachment. The conformation is "normal" anticlinal which means that there is no excessive steric strain between the ligands. The dihedral angle of 74.9°, the smallest one reported for diorganyldisulfanes so far, is the consequence of an optimal staggering of the vinylic *t*Bu groups. The carbon-sulfur bonds [175.7(4) pm, mean value] are the shortest bonds found for all structurally characterized diorganyldisulfanes, indicating substantial electronic interaction of the sulfur orbitals with the π system of cyclopentadiene. For comparison, the C−S bond length (mean values) in $S(C_5Me_5)_2$ is 185.6 pm[1], in Tsi_2S_2[6e] 184.6 pm, and in $S_2(C_6F_5)_2$, the shortest one so far reported, 177.0 pm[6b]. The Me_3Si groups appear to enhance the formal electronegativity of cyclopentadiene according to their −I effect, thus strengthening the carbon-sulfur bonds. This could also explain the

0009−2940/96/0101−0069 $ 10.00+.25/0

higher stability of **2** compared to **1**, since the Me_3Si groups point away from the S–S bridge and out of the ring plane as a consequence of their allylic positions, and do not directly contribute to the bulkiness of the ligand. The S–S bond length [207.6(2) pm] is normal and almost excatly the sum of the covalent radii for a single bond.

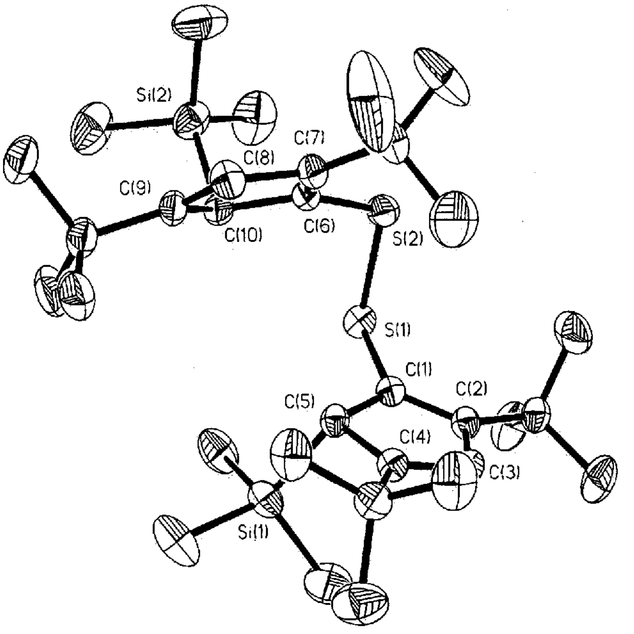


Figure 1. Molecular structure of **2**; selected bond lengths [pm] and angles [°]: S(1)–S(2) 207.6(2), S(1)–C(1) 175.9(4), S(2)–C(6) 175.5(4); C(1)–S(1)–S(2) 103.90(14), C(6)–S(2)–S(1) 103.5(2), C(1)–S(1)–S(2)–C(6) 74.91(0.15)

From the ^{1}H- and ^{13}C-NMR spectroscopic data a similar conformation and bonding can be inferred for **1**. Compounds **1** and **2** are thus the first biscyclopentadienyl-substituted chalcogens with the chalcogen attached to a vinylic position of the ring.

Whereas the *t*Bu groups in both ligands are not fluxional, the migration of the Me_3Si group give rise to only one signal for the *t*Bu groups in $tBu_2(Me_3Si)C_5H_3$ at ambient temperature[8]. In the NMR spectra of **2** two signals for the *t*Bu groups are observed at ambient temperature, thus indicating that sulfur increases the activation energy for 1,2-sigmatropic shifts of the Me_3Si group[4].

Experimental

All reactions were performed under argon by using standard Schlenk techniques. Diethyl ether was freshly distilled from sodium/benzophenone prior to use. $tBu_2C_5H_4$[9] and $tBu_2(Me_3Si)C_5H_3$[8] were prepared as previously described. Commercially available sulfur chloride (Fluka) was purified according literature methods[10]. – Flash chromatography was performed with Merck silica gel (Type 60, 230–400 mesh ASTM) and petroleum ether (fraction 40–60 °C) as the eluent. – ^{1}H and ^{13}C NMR: Bruker AC 200; all spectra were recorded in $CDCl_3$ and signals referred to 7.26 and 77.7 ppm, respectively. – EI-MS: Varian CH-7 (30 eV); the most intensive peak of the isotope pattern is listed.

Preparation of **1**: 7.02 ml of methyllithium in hexane (1.6 M, 11.2 mmol) was added to an ethereal solution (50 ml) of 2.00 g of $tBu_2C_5H_4$[9] (11.2 mmol) at −30 °C. After stirring for 3 h at ambient temp. the suspension formed was cooled to 0 °C, and 0.450 ml of S_2Cl_2 (5.60 mmol) was slowly added. The reaction started immediately, and after 15 min the precipitate of LiCl was filtered off and the solvent removed in vacuo. The remaining orange oil was purified by column chromatography. Yield: 1.04 g (44%); m.p. 45 °C (ethanol). Since **1** decomposes to a number of unindentified products at ambient temp. especially in solution as judged by NMR spectroscopy and TLC, for NMR spectroscopic determination **1** was crystallized from EtOH at −20 °C as a yellow microcrystalline powder. – ^{1}H NMR: δ = 6.10 (t, ^4J = 0.92 Hz, 1H, 3-H), 3.81 (d, ^4J = 0.92 Hz, 2H, 5-H), 1.21 (s, 9H, *t*Bu), 1.14 (s, 9H, *t*Bu). – ^{13}C NMR: δ = 161.1 (C-4), 158.8 (C-2), 128.1 (C-1), 126.5 (C-3), 46.9 (C-5), 31.5 [4-C(CH_3)$_3$], 31.2 [2-C(CH_3)$_3$], 34.6 [4-*C*(CH_3)$_3$], 34.2 [4-*C*(CH_3)$_3$]. – EI-MS (30 eV), *m/z* (%): 418 (77) [M^+], 386 (41) [M^+ − S], 241 (24) [M^+ − $tBu_2C_5H_3$], 210 (85) [$M^+/2$], 177 (31) [$tBu_2C_5H_3$], 135 (100). – $C_{26}H_{42}S_2$ (418.8): calcd. C 74.57, H 10.11, S 15.31; found C 74.14, H 10.78, S 15.08.

Disulfide **2** was prepared as described for **1** from 1.00 g of $tBu_2(Me_3Si)C_5H_3$[8] (4.00 mmol), 2.00 ml of *n*-butyllithium in hexane (2.0 M, 2.00 mmol), and 0.160 ml of S_2Cl_2 (2.00 mmol). Chromatography and recrystallization from Et_2O/MeOH (2:1) afforded yellow crystals. Yield: 0.330 g (29%); m.p. 110–111 °C (Et_2O/MeOH). In contrast to **1**, **2** is stable in solution and in substance at ambient temp. – ^{1}H NMR ($CDCl_3$): δ = 6.34 (s, 1H, 3-H), 3.93 (s, br, 1H, 5-H), 1.23 (s, 9H, *t*Bu), 1.16 (s, 9H, *t*Bu), 0.07 (s, 9H, Me_3Si). – ^{13}C NMR ($CDCl_3$): δ = 0.60 (Me_3Si), 31.24 (sh, *t*Bu), 127.6 (C-3), quaternary carbon atoms not observed. – EI-MS (30 eV), *m/z* (%): 562 (26) [M^+], 281 (42) [$M^+/2$], 225 (100) [$M^+/2$ − *t*Bu], 73 (56) [Me_3Si], 57 (13) [*t*Bu]. – $C_{32}H_{58}S_2Si_2$ (563.1): calcd. C 68.25, H 10.38, S 11.39; found C 68.64, H 10.01, S 11.56.

Crystal Structure Determination of **2** (Table 1): Yellow crystals of **2** were obtained by crystallization from Et_2O/MeOH (2:1) at 0 °C. Crystal size 0.5 × 0.45 × 0.4 mm, $C_{32}H_{58}S_2Si_2$, formula weight 563.115 g/mol, orthorhombic, *Pbca* (No. 61), a = 1274.3(2), b = 1728.2(2), c = 3319.5(4) pm, V = 7.310(2) nm^3, Z = 8, $d_{calc.}$ = 1.023 mg/cm^3, T = 293(2) K. Diffractometer Siemens P4, Mo-K_α radiation (graphite monochromator, λ = 71.073 pm), ω scans, Θ range for data collection 2.66 to 20.00°, absorption coefficient μ = 0.229 mm^{-1}, F(000) = 2480. Index ranges $-1 \leqslant h \leqslant 14$, $-1 \leqslant k \leqslant 19$, $-1 \leqslant l \leqslant 36$. Intensities were measured for 3409 (R_{int} = 0.0301) independent reflections of which 2338 were considered as observed [$I \geqslant 2\sigma(I)$]. Lorentz and polarization corrections were made. The structure was solved by direct methods, SHELXS-86[11a], and refined by a full-matrix least-squares procedure on F^2 using SHELXL-93[11b]. The positions of the hydrogen atoms were calculated and included in the refinement with isotropic temperature parameters U_{eq} = 1.5 U_{eq} of parent carbon atoms. Convergence was obtained for 326 parameters with the agreement factor R_1 = 0.0482 and wR_2 = 0.0979 for 2338 reflections. – Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-404235, the names of the authors, and the journal citation.

---

[1] A. J. Bard, A. H. Cowley, J. K. Leland, G. J. N. Thomas, N. C. Norman, P. Jutzi, C. P. Morley, E. Schlüter, *J. Chem. Soc., Dalton Trans.* **1985**, 1303.

[2] C. M. Bates, C. P. Morley, M. B. Hursthouse, K. M. A. Malik, *J. Organomet. Chem.* **1995**, *489*, C60–C61.

[3] K. A. Rufanov, A. V. Churakov, N. B. Kazennova, D. A. Lemenovskii, *J. Organomet. Chem.* **1994**, *481*, C1–C3.

[4] P. Jutzi, *Chem. Rev.* **1986**, *86*, 983–996.

[5] C. Janiak, H. Schumann, *Adv. Organomet. Chem.* **1991**, *33*, 291.

[6] [6a] H. Kessler, W. Rundel, *Chem. Ber.* **1968**, *101*, 3350–3357. – [6b] C. M. Woodard, D. S. Brown, J. D. Lee, A. G. Massey, *J. Organomet. Chem.* **1976**, *121*, 333–344. – [6c] W.-W. du Mont, L. Lange, H. H. Karsch, K. Peters, E. M. Peters, H. G.

von Schnering, *Chem. Ber.* **1988**, *121*, 11–14. – [6d] I. Wagner, W.-W. du Mont, S. Pohl, W. Saak, *Chem. Ber.* **1990**, *123*, 2325–2327. – [6e] M. Ostrowski, J. Jeske, P. G. Jones, W.-W. du Mont, *Chem. Ber.* **1993**, *126*, 1355–1359.

[7] F. Sladky, B. Bildstein, C. Rieker, A. Gieren, H. Betz, T. Hübner, *J. Chem. Soc., Chem. Commun.* **1985**, 1800.

[8] S. T. Abu-Orabi, P. Jutzi, *J. Organomet. Chem.* **1987**, *329*, 169–177.

[9] C. G. Venier, E. W. Casserly, *J. Am. Chem. Soc.* **1990**, *112*, 2809–2809.

[10] G. Brauer (Ed.), *Handbuch der Präparativen Anorganischen Chemie*, vol. 1, Ferdinand Enke Verlag, Stuttgart, **1960**, p. 380.

[11] [11a] G. M. Sheldrick, *SHELXS-86, Program for Crystal Structure Solutions*, University of Göttingen, Germany, **1986**. – [11b] G. M. Sheldrick, *SHELXL-93, Program for the Refinement of Structures*, University of Göttingen, Germany, **1993**.

[95117]