Cyclopentadienone Cyclopentadienediyl Diselenoketals

Georg Thaler, Klaus Wurst, and Fritz Sladky*

Institut für Allgemeine, Anorganische und Theoretische Chemie der Universität Innsbruck,
A-6020 Innsbruck, Innrain 52a, Austria
Fax: (internat.) + 43(0)512/507-2934
E.mail: fritz.sladky@uibk.ac.at

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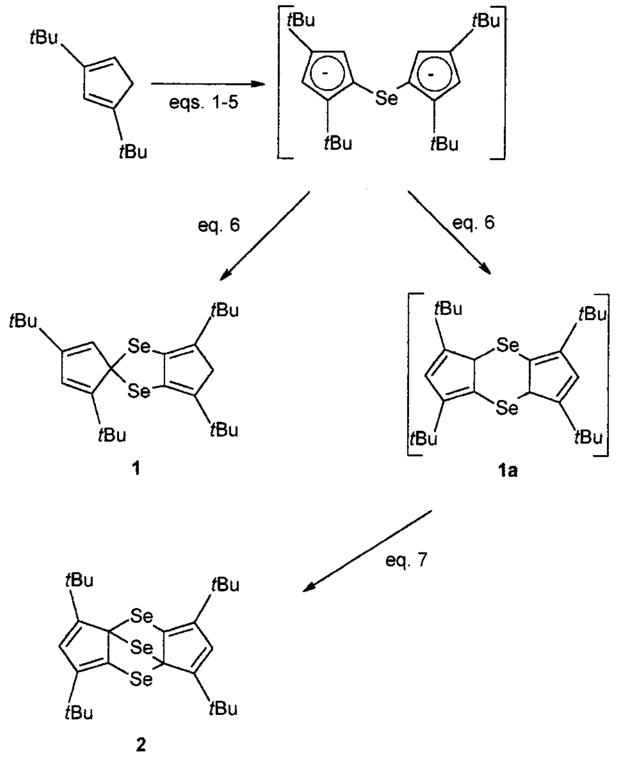
Reaction of di-*tert*-butylcyclopentadiene with excess potassium *tert*-butoxide in the presence of elemental selenium leads to cyclopentadienes bridged by two or three selenium atoms through one or two diselenoketal functionalities. 2,5,4′,6′-Tetra-*tert*-butyl-5′*H*-spirocyclopentane-1,2′-cyclopenta[*b*][1,3]diselena-2,4-diene (**1**) and 1,3,5,7-tetra-*tert*-butyl-3a,7a-dihydro-3a,7a-*epi*-selenodicyclopenta[*b,e*][1,4]diselenine (**2**) have been characterized by single-crystal X-ray diffraction.

Introduction

We have recently reported that lithium cyclopentadienides substituted by *t*Bu or Me_3Si groups, obtained by deprotonation of the corresponding cyclopentadiene with *n*-butyllithium, insert several equivalents of elemental selenium with formation of lithium cyclopentadienylpolyselenolates[1]. Subsequent in situ disproportionation leads to substituted bis(cyclopentadienyl)selanes, cp'_2Se_n ($n = 1-5$). If *n*-butyllithium is replaced by potassium *tert*-butoxide, a base of low nucleophilicity which itself reacts with elemental selenium and is able to cleave C−Se and Se−Se bonds if present in excess, the reaction pathway changes drastically. The hitherto unknown doubly and triply selenium-bridged cyclopentadienes **1** and **2** are obtained in moderate to good yield in a one-pot reaction. Bridging occurs through a previously unknown cyclopentadiene-centered diselenoketal functionality. Other identified products are labile and could not be isolated, e.g. $(tBu_2C_5H_3)_2Se$[2], which is formed primarily in the initial stages of the reaction, while a small amount of tetra-*tert*-butylpentafulvalene[3] was obtained as deep-red crystals (Scheme 1).

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



Results and Discussion

The formation of **1** and **2**, although entirely unexpected, can be understood in terms of a sequence of established reactions (Scheme 2).

The main driving force is the successive deprotonation of cyclopentadiene and subsequent insertion of elemental selenium into the formed cyclopentadienide anions (Eqs. 1 and 2). These processes are accelerated in a cascade-like manner owing to the increased acidity of the cyclopentadiene protons that results from the increasing selenium substitution of the cyclopentadiene. Disproportionation of the intermediate cyclopentadienylpolyselenolates leads to selenium-bridged cyclopentadiene species (Eq. 3). Bridges containing more than one selenium atom are known to be increasingly unstable and are degraded by lithium cyclopentadienide (Eq. 4). Repetition of these steps finally affords **1** and **2** (Eqs. 5−7). **1** is generated if bridging occurs with formation of a 1,3-diselenolane heterocycle. If, on the other hand, the postulated heterocyclic intermediate 1,4-diselenane **1a** is formed, an additional deprotonation−insertion−disproportionation sequence leads to **2**. The two *t*Bu groups serve to control the above reactions and thus prevent extensive oxidation and/or polymerization of cyclopentadiene.

The molecular structure of **1** consists of a 1,3-diselenolane heterocycle, which spans between an allylic spiro car-

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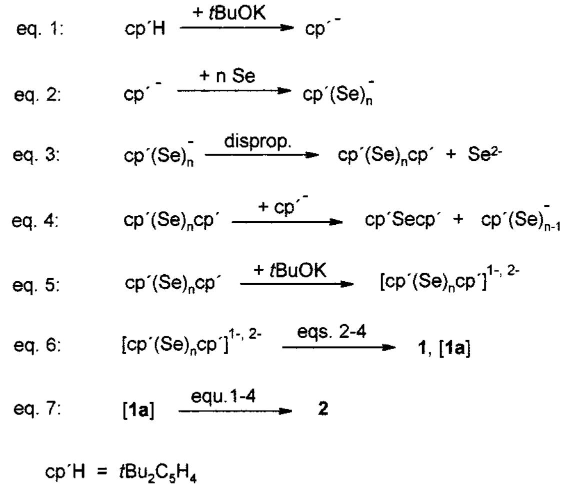
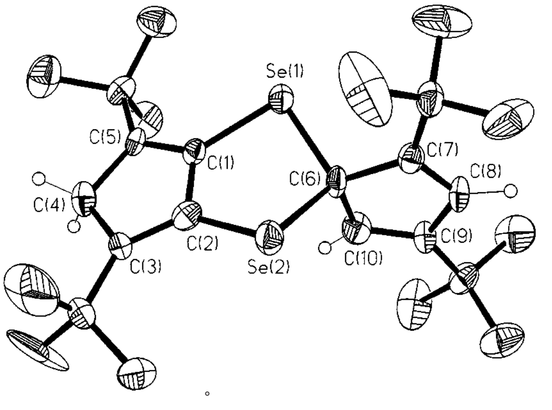
Scheme 2. Proposed reaction steps leading to **1** and **2**



bon atom of the cyclopentadiene bearing the diselenoketal functionality, and the other cyclopentadiene, which is annelated via vicinal vinylic carbon atoms (Figure 1). This results in an almost mutually perpendicular orientation of the two cyclopentadiene rings [interplane angle: 87.7(3)°] and consequently to an optimal staggering of all the *t*Bu groups. The angle at the selenium atoms of 92.5(3)° is comparable to that found in other diorganylselanes such as $[(Me_3Si)_2C_5H_3]_2Se$ (97.9°)[2] and Me_2Se (96.3°)[4] and indicates negligible ring strain. However, the difference between the $C(sp^2)-Se$ and $C(sp^3)-Se$ bond lengths [1.914 A compared to 1.986 A (mean values)] is striking. The extreme shortening of the former represents a further example of a strong electronic interaction between selenium bound in a vinylic position and the π system of cyclopentadiene[1][2][5][6] (Table 1).

Figure 1. Molecular structure of **1**; anisotropic displacement parameters depicting 50% probability; hydrogen atoms of methyl groups have been omitted for clarity[a]



[a] Selected bond lengths [A] and angles [°]: Se(1)−C(1) 1.915(7), Se(1)−C(6) 1.992(7), Se(2)−C(2) 1.913(7), Se(2)−C(6) 1.980(7); C(1)−Se(1)−C(6) 92.5(3), C(2)−Se(2)−C(6) 92.5(3); interplane angle 87.7(3).

The molecular structure of **2** can be described as a kind of hexagonal pyramid, based on a 1,4-diselenane heterocycle in boat conformation (Figure 2). The unique Se(1) atom is at the top of the pyramid and is common to two 1,3-diselenolane heterocycles, which each bridge the two cyclopentadiene moieties in a similar manner as in **1**. The molecule possesses a twofold symmetry axis which passes through Se(1) and bisects the Se(2)−Se(2a) vector. The key difference between **1** and **2** is that in **2** the allylic positions of both cyclopentadienes are substituted by a diselenoketal functionality. Also in contrast to **1**, there appears to be considerable strain within the heterocyclic framework, as indicated by the extremely acute C−Se(1)−C angle of 82.6(2)°. Nevertheless, the striking difference in the $C(sp^2)-Se$ and $C(sp^3)-Se$ bond lengths seen in **1** is also seen in **2** [1.888 A compared to 1.985 A (mean values)]. In fact, these are amongst the shortest and longest C−Se bonds ever reported [e.g. 1.879(5) A in TMTSF[7] and 2.018(5) A in 3,3,5,5-tetrakis(trimethylsilyl)-1,2,4-triselenolane[8]] (Table 1). Whereas other cyclopentadienylselenium compounds form $W(CO)_5$ complexes[2][5][9], the multisubstitution of cyclopentadiene with selenium reduces the donor capacity of each selenium and no interaction of **2** with $[(CO)_5W(THF)]$ occurs.

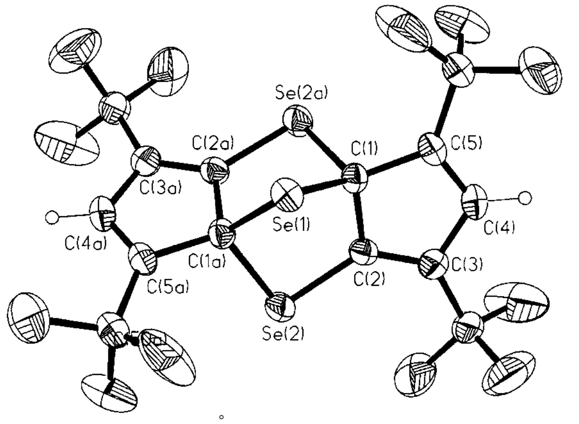
Table 1. Crystal structure data of compounds **1** and **2**

	1	**2**
formula	$C_{26}H_{40}Se_2$	$C_{26}H_{38}Se_3$
M_r	510.50	587.44
cryst. size [mm]	0.60 × 0.50 × 0.20	0.51 × 0.18 × 0.13
T [K]	213(2)	293(2)
crystal system	monoclinic	monoclinic
space group	$P2_1/c$ (no. 14)	$P2/c$ (no. 13)
a [A]	9.681(2)	11.969(1)
b [A]	11.267(2)	6.177(1)
c [A]	24.366(4)	18.573(1)
β [°]	99.66(1)	106.12(1)
V [A^3]	2620.1(8)	1319.2(3)
Z	4	2
$\rho_{calcd.}$ [g cm^{-3}]	1.294	1.479
μ [mm^{-1}]	2.831	4.192
F(000)	1056	592
2 θ_{max} [°]	45.00	55.00
reflections collected	4570	6227
independent reflections	3380	2954
reflections [$I > 2\ \sigma(I)$]	2429	2110
absorption correction	ψ scan	ψ scan
T_{min}, T_{max}	0.524, 1.000	0.565, 1.000
parameters	294	132
$R1$ [$I > 2\ \sigma(I)$][a]	0.0534	0.0374
$wR2$ [$I > 2\sigma(I)$][b]	01325	0.0748
largest diff. peak/hole [eA^{-3}]	1.884, −0.352	0.677, −0.337

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. – [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

The packing of **2** shows a highly oriented stacking along the *y* axis (Figure 3). This is accomplished by Se−Se interactions between the unique Se(1) of one molecule and Se(2) and Se(2a) of the neighbouring molecule. The former fits into a cavity formed by the latter (Figure 4). The intrastack Se(1)−Se(2, 2a) distances of 3.978 A are almost identical to the Se−Se intrastack distances in selenium-based organic metal superconductors $(TMTSF)_2X$[10]. In contrast to these materials, however, there are no Se−Se interstack interactions in **2**. Attempts at chemical doping have to date been unsuccessful. TCNQ does not interact, while nitrosyl salts react too vigorously with extrusion of elemental selenium.

Figure 2. Molecular structure of **2**; anisotropic displacement parameters depicting 50% probability; hydrogen atoms of methyl groups have been omitted for clarity[a]



[a]Selected bond lengths [Å] and angles [°]: Se(1)−C(1) 1.979(3), Se(2)−C(2) 1.888(3), Se(2)−Se(1a) 1.990(3); C(1)−Se(1)−C(1a) 82.6(2), C(2)−Se(2)−C(1a) 89.56(13); interplane angle 57.6(1).

Figure 3. Packing plot of **2** along the *y* axis

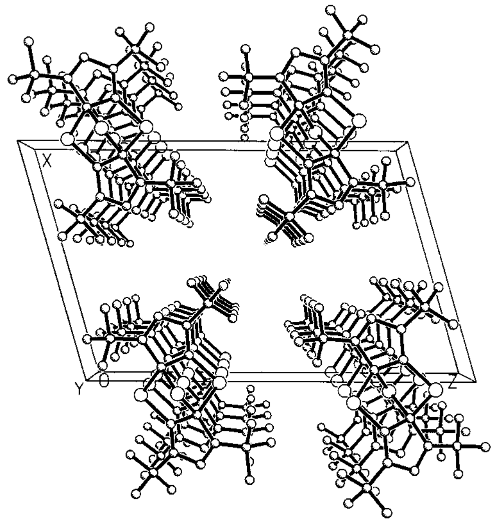
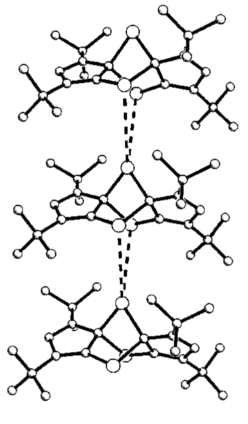


Figure 4. Intrastack Se−Se interactions in **2**



We thank Dr. *L. Call,* Institut für Organische Chemie der Universität Innsbruck, for his assistance in naming **1** and **2** according to the latest IUPAC proposals for the nomenclature of fused and bridged fused ring systems and of spiro compounds.

Experimental Section

General: All reactions were performed under argon by using standard Schlenk techniques. THF was purified and dried according to standard methods. KO*t*Bu and elemental grey selenium were obtained from Aldrich and Fluka, respectively. $t\mathrm{Bu}_2\mathrm{C}_5\mathrm{H}_4$[11] was prepared as described previously. Flash chromatography was performed on Merck silica gel (Type 60, 230−400 mesh ASTM) with petroleum ether as eluent. − ^{1}H- and ^{13}C-NMR spectra were recorded with a Bruker AC 200 spectrometer. ^{1}H and ^{13}C chemical shifts are referred to solvent signals [$\mathrm{CDCl_3}$: (residual $\mathrm{CHCl_3}$): δ_H = 7.26; δ_C = 77.7]. − Mass spectra were recorded with a Varian CH-7 instrument.

Preparation of Compounds **1** *and* **2**: KO*t*Bu (3.72 g, 33.1 mmol) was added to a solution of $t\mathrm{Bu}_2\mathrm{C}_5\mathrm{H}_4$ (1.97 g, 11.1 mmol) in THF (50 ml) at −30°C. After stirring the resulting suspension for 1 h at ambient temp., 2.63 g of grey selenium (33.3 mmol) was added and stirring was continued for a further 12 h. The solvent was then removed in vacuo, 100 ml of petroleum ether was added, and the resulting suspension was filtered through silica gel. Chromatography afforded 0.13 g of tetra-*tert*-butylpentafulvalene (7%) as deep-red crystals, 0.13 g of **1** (5%) as yellow crystals, and 1.28 g of **2** (39%) as yellow crystals. Single crystals of the air-stable compounds **1** and **2** were obtained from $\mathrm{Et_2O/MeOH}$.

1: M.p. 190−191°C. − ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$): δ = 1.11 (s, 9 H, 9-*t*Bu), 1.22 (s, 18 H, 3,5-*t*Bu), 1.37 (s, 9 H, 7-*t*Bu), 3.27 (s, 2 H, 4,4-H), 5.94 [d, $^4J_\mathrm{HH}$ = 1.82 Hz, 1 H, 8-H], 6.28 [d, $^4J_\mathrm{HH}$ = 1.82 Hz, 2 H, 10-H]. − ^{13}C NMR (50 MHz, $\mathrm{CDCl_3}$): δ = 29.9 [9-C(CH$_3$)$_3$], 30.7 [3,5-C(CH$_3$)$_3$], 31.5 [3,5-C(CH$_3$)$_3$], 32.4 [7-C(CH$_3$)$_3$], 33.7 [9-C(CH$_3$)$_3$], 47.5 (4-C), 86.5 (6-C), 127 (8-C), 135 (10-C), 140 (3,5-C), 146 (1,2-C), 148 (9-C), 158 (7-C); 7-C(CH$_3$)$_3$ not observed. − EI MS (70 eV): *m*/*z* (%): 510 (100) [M$^+$], 495 (10) [M$^+$ − Me]. − $\mathrm{C_{26}H_{40}Se_2}$ (510.50): calcd. C 61.17, H 7.90; found C 61.06, H 7.99.

2: M.p. 211−213°C. − ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$): δ = 1.19 (s, $^1J_\mathrm{CH}$ = 18 Hz, 9 H, *t*Bu), 1.40 (s, $^1J_\mathrm{CH}$ = 18 Hz, 9 H, *t*Bu), 6.56 (s, $^1J_\mathrm{CH}$ = 18 Hz, 1 H, 4-H). − ^{13}C NMR (50 MHz, $\mathrm{CDCl_3}$): δ = 29.9 [C(CH$_3$)$_3$], 32.6 [C(CH$_3$)$_3$], 35.1 [C(CH$_3$)$_3$], 92.1 (1-C), 131 (4-C), 138 (5-C), 147 (2-C), 154 (3-C). − EI MS (70 eV): *m*/*z* (%): 588 (100) [M$^+$], 573 (26) [M$^+$ − Me], 512 (21) [M$^+$ − Se]. − $\mathrm{C_{26}H_{38}Se_3}$ (587.44): calcd. C 53.16, H 6.52; found C 53.31, H 6.59.

Solution and Refinement of Structures **1** *and* **2**: Crystal data for structures **1** and **2** are given in Table 1. Data were collected with a Siemens P4 diffractometer with Mo-K_α (λ = 0.71073 A) radiation (graphite monochromator) using ω scans and were corrected for Lorentz and polarization effects. An empirical absorption correction based on a series of ψ scans was applied. The structures were solved by direct methods using SHELXS-86[12], and refined by a full-matrix least-squares procedure on F^2 using SHELXL-93[13]. The positions of the hydrogen atoms were calculated and were included in the refinement with isotropic temperature parameters 1.2 or 1.5 times higher than U_eq of the carbon atom to which they were attached. The methyl groups of *t*Bu at C(3) and C(7) of **1** are disordered by a rotation of 60° about the C−C(CH$_3$)$_3$ bond. The ratios of the two possible orientations are almost 5:3 at C(3) and 4:1 at C(7). Figure 2 shows the methyl groups in the major position. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101066. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44(0)1223-336033; E-mail: deposit@-ccdc.cam.ac.uk].

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