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Self-Addition of a Sterically Hindered Alkynylselenolate

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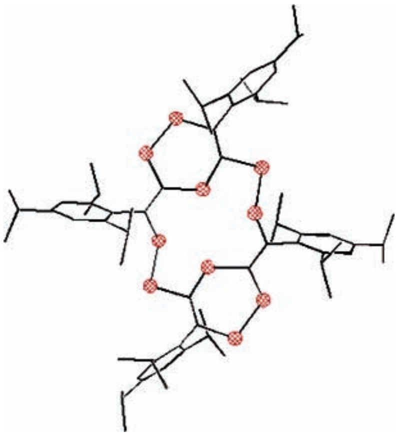
ABSTRACT



The unprecedented formation of a complex macrocyclic selenium–carbon ring system, which is initiated by the action of coordinating reagents upon a sterically hindered alkynylselenolate, has been observed. The crystal structure of the product could be obtained and shows a rigid tricyclic arrangement consisting only of selenium and sp^2-hybridized carbon atoms. This reactivity stands in contrast to the corresponding unsubstituted alkynylselenolates and is an example where a bulky substituent destabilizes an adjacent unsaturated π-system.

Alkynylchalcogenolates have been studied as unusual complex ligands[1,2] and are potential precursors for chalcogenoketenes.[3,4] Usually, they can be prepared by reacting metalated alkynes with the corresponding elemental chalcogen.[5−8] In the case of sulfur, the resulting alkynylthiolates are very prone to being attacked by nucleophiles, which is accompanied by degradation of the C−C triple bond.[9−12] Likewise, nucleophilic additions to alkynyl-selenolates are well-known, and here the favorable NMR properties of the ^{77}Se nucleus have been a valuable tool for monitoring these reactions.[13,14] Recently, we have utilized this reactivity of

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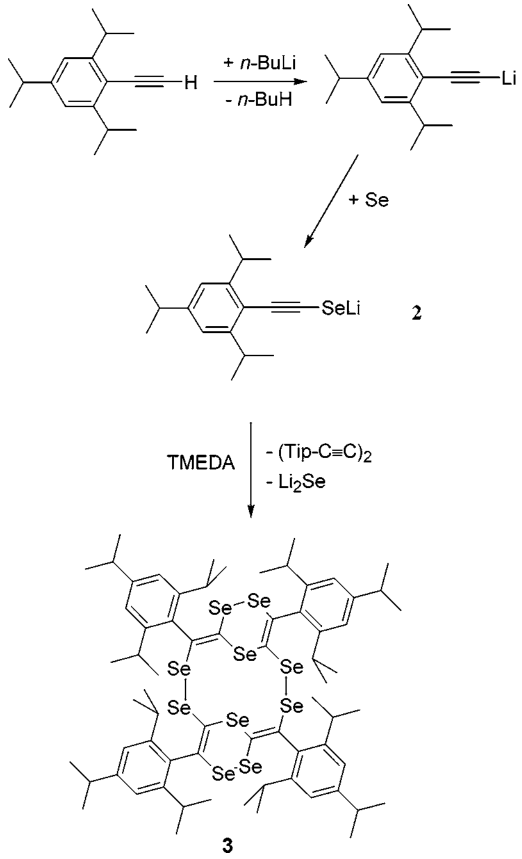
alkynylsulfides to synthesize a novel conducting polymer.[15] Similarly, we are interested in the corresponding selenides and investigated the reactivity of a bulky substituted acetylide toward selenium.

Due to the steric protection, we expected a reduced reactivity and therefore a high degree of kinetic stabilization for this unsaturated system. However, to our surprise, this sterically crowded alkynylselenolate **2** turned out to be rather unstable in solution and undergoes self-addition, which eventually yields uniformly a complex macrocyclic ring system (Scheme 1). This conversion seems to be greatly accelerated by coordinating reagents such as tetramethyl ethylenediamine (TMEDA), which can be exploited for an efficient one-pot synthesis for this unusual selenium-rich macrocycle.

Scheme 1. Synthesis of **2** and **3**



The reaction of 2,4,6-triisopropylphenylethynyllithium **1** with gray selenium cleanly affords lithium 2,4,6-triisopropylphenylalkynylselenolate **2**.[16] The ^{1}H, ^{13}C, ^{7}Li, and ^{77}Se NMR data of **2** are in the expected range, and the ^{13}C chemical shift values for the alkynyl unit are, with values of 83.01 and 84.55 ppm, quite close together. This suggests a rather nonpolar π-system and a localization of the negative charge at the selenium atom.

While compound **2** is stable in the solid state, in ether or THF solution, a slow disproportionation takes place by which the selenium is transferred from one molecule of **2** to another. This reaction can be accelerated with TMEDA. In both cases, macro heterocycle **3**[17] is formed along with selenium-free byproducts.

We have been able to grow crystals of **3** that were suitable for X-ray diffraction studies.[18] The structure shows that macrocycle **3** consists of a tricyclic ring system (Figure 1).

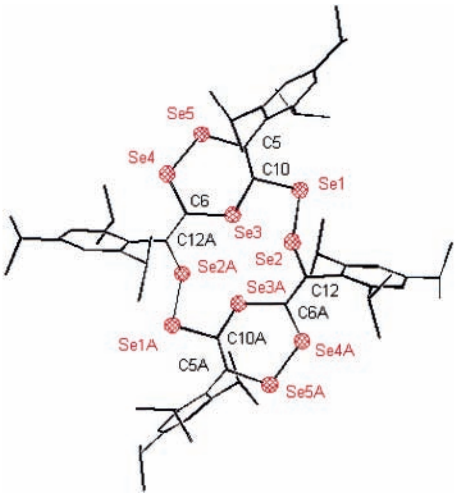


Figure 1. Crystal structure of **3** (top view).

This ring system can be described as a single 16-membered ring built from alternating diselenylen- and vinylidene-units with two additional transannular selenium bridges. In sum-

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[16] **Synthesis of 2.** 2,6-Triisopropylphenylacetylene[19] (1.15 g, 5 mmol) was dissolved in 100 mL diethyl ether at −78 °C, and a solution of *n*-butyllithium (5 mmol) in hexanes was slowly added while stirring. The mixture was slowly warmed to room temperature. After 1 h, gray selenium powder (0.4 g, 5 mmol) was added and stirring was continued for an additional 10 h. Then, the solvent was removed in a vacuum and the remaining residue was washed with hexanes; the hexanes fraction was discarded. After recrystallization from hexanes/benzene, **2** was obtained as a yellow-orange solid (1.1 g, 67%). ^{1}H NMR (250 MHz, THF-d_8): 1.35 (d, $J = 6.9$ Hz, 6H), 1.50 (d, $J = 6.9$ Hz, 12H), 2.88 (spt, $J = 6.9$ Hz, 1H), 4.02 (spt, $J = 6.9$ Hz, 2H), 7.13 (2H). ^{13}C NMR (62.9 MHz, THF-d_8): 24.39, 24.63, 32.38, 35.05, 83.01, 84.55, 120.58, 121.84, 147.56, 151.17. ^{77}Se NMR (47.7 MHz, THF-d_8): −64.6. ^{7}Li NMR (97.1 MHz, THF-d_8): −0.8.[21]

[17] **Synthesis of 3.** To a solution of lithium-2,6-triisopropylphenyl ethynyl selenolate 2 (0.6 g, 2 mmol) in benzene (5 mL) was added TMEDA (0.1 mL), which led to precipitation of an orange solid. The latter was separated and recrystallized from toluene, which yields red-orange crystals (0,2 g, 55%). Anal. Calcd (%) for $C_{68}H_{92}Se_{10}$: C, 48.07; H, 5.46. Found: C, 47.74; H, 5.62. ^{1}H NMR (250 MHz, THF-d_8): 1.25−1.40 (m, 36H), 2.89 (2H), 3.19 (1H), 3.46 (2H), 3.94 (1H), 6.94 (2H), 7.60 (2H). ^{77}Se NMR (47.7 MHz, THF-d_8): 548.4, 485.5, 466.9, 367.5, 358.8. Crystal data for $C_{68}H_{92}Se_{10}$, $M = 1699.02$, triclinic, space group P-1, $a = 10.459(3)$ Å, $b = 12.983(3)$ Å, $c = 13.711(4)$ Å, $a = 101.621(5)$, $b = 96.648(5)$, $g = 94.940(5)$°, $Z = 1$, $D_c = 1.567$ Mg/m^3, m(Mo Kα) = 5.108 mm^{-1}, 9388 reflections collected, 6265 independent reflections ($R_{int} = 0.0520$). The final wR(F2) was 0.1195 (all data).

[18] Intensity data have been collected using a Bruker-AXS−SMART diffractometer (Mo Kα radiation, ω-scan, $T = 203$ K). The structure has been solved with direct methods (SHELXS 97) and refined by full-matrix least-squares methods on F2 (SHELXS 97). Hydrogen atom positions were initially determined by geometry and refined by a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters.

mary, this gives a central 12-membered ring fused together with two outer six-membered rings.

Due to the position of the alkenylidene units, the flexibility of this selenium-rich macrocycle is very limited and a crownlike arrangement of the selenium atoms is not possible. The rigid tricyclic backbone of the rings consists only of selenium and quarternary alkenylidene units, in which the bridgehead atoms are formally sp^2-hybridized carbon atoms.

Looking at the macrocycle from the side shows the boat conformation of the six-membered rings in which selenium atoms adopt the top positions and the bottoms of the two boats point at each other (Figure 2). In contrast, the central ring shows a chair conformation. The two selenium atoms Se(3) and Se(3a) act as transannular bridges and are oriented toward the center of the central ring. They are attached to bridgehead atoms, which are formally sp^2-type carbon atoms. Since both of these carbon atoms are parts of C═C double bonds, a rigid and strained tricyclic ring system is formed.

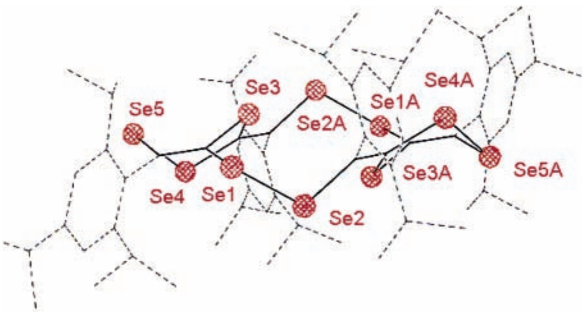

Figure 2. Crystal structure of **3** (side view).

The short transannular selenium distances between the selenium atoms Se(5)−Se(3) (3.436 Å) and Se(3)−Se(2A) (3.256 Å) as well as their symmetry equivalents, which are substantially shorter than twice the van der Waals radius (3.80 Å), are remarkable. For comparison, these distances are similar or shorter than the distances found between the chains of selenium atoms in α-selenium (3.44 Å), which are also reduced compared with the respective van der Waals radii.

The detailed mechanism for the formation of macrocycle **3** from alkynylselenolate **2** remains unclear at present. However, one reason for the spontaneous selenium transfer from **2** is probably the nucleophilicity of the negatively charged selenium atom, which is even increased by complexation of its counterion. Heterolytic bond cleavage in **2** as well as homolytic bond cleavage leading to selenyl radical anions both seem plausible. From the latter species, macrocycle **3** could then be formed stepwise via oxidative selenium transfer to **2**. An alternative mechanism could involve ate complexes in the course of the selenium transfer.[20] During this reaction, selenium-free byproducts are also formed, of which bis-2,4,6-triisopropylphenylbutadiyne could be identified.

In summary, we described the synthesis of a sterically hindered alkynylselenolate and studied its self-addition to form a complex tricyclic macrocycle. The special appeal of this macrocycle is its inorganic ring system consisting only of hydrogen-free carbon and selenium atoms that provides potential donor centers for complexation. It will be interesting to elucidate how modifying the bulky substituents will affect the reactivity of the resulting alkynylselenolate.

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Supporting Information Available: Crystallographic data for structure **3** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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