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Preliminary communication

Synthesis and structure of bis(pentamethylcyclopentadienyl)selenium

C. Matthew Bates [a], Christopher P. Morley [a,*], Michael B. Hursthouse [b], K.M. Abdul Malik [b]

[a] *Department of Chemistry, University College of Swansea, Singleton Park, Swansea SA2 8PP, UK*
[b] *School of Chemistry and Applied Chemistry, University of Wales College of Cardiff, PO Box 912, Cardiff CF1 3TB, UK*

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Abstract

Reaction of bis(diethyldithiocarbamato)selenium with pentamethylcyclopentadienyllithium gives bis(pentamethylcyclopentadienyl)selenium, the structure of which has been determined by an X-ray diffraction study.

Keywords: Selenium; Cyclopentadienyl; Crystal structure

Cyclopentadienyl derivatives of Main Group elements have attracted considerable attention in recent years, but compounds containing the elements of Group 16 (the chalcogens) are rare. Indeed, permethylation of the cyclopentadienyl ring is required for the isolation of such compounds. Bis(pentamethylcyclopentadienyl)sulphur has been prepared [1] by the reaction of LiC_5Me_5 with SCl_2, and may be used as the precursor to a number of mono(pentamethylcyclopentadienyl)sulphur derivatives [2]. No reports, however, have appeared on analogous reactions of selenium or tellurium; this is doubtless due in part to the non-availability of simple Se(II) or Te(II) halides. We have established, however, that bis(diethyldithiocarbamato)-selenium [3] serves as an excellent starting material for Se(II) chemistry, and report here its conversion into $Se(C_5Me_5)_2$, and present the crystal structure of the product.

Room temperature reaction of $Se(S_2CNEt_2)_2$ with two equivalents of LiC_5Me_5 in toluene leads to formation of a yellow solution and a white precipitate of LiS_2CNEt_2. Passage of the solution through a short silica column and removal of the solvent left the product $Se(C_5Me_5)_2$, which was crystallised from hexane at −20°C as yellow prisms. It is apparently air-stable, but thermally somewhat unstable, and unless it is stored at low temperature in the dark, significant decomposition is evident after a few days. It has been characterised spectroscopically and by a single crystal X-ray diffraction study. At room temperature the compound is static on the NMR timescale, giving rise to three signals in the ^1H NMR spectrum. The thermal sensitivity of the compound precludes the observation of spectra at higher temperatures, but its non-fluxional behaviour at room temperature parallels that of $S(C_5Me_5)_2$, and is in contrast with that of most other η^1-cyclopentadienyl derivatives.

The X-ray diffraction study (see Fig. 1) reveals that $Se(C_5Me_5)_2$ is isostructural with $S(C_5Me_5)_2$ [1]. The quality of the data for the selenium compound is, however, much better, and allows us to discuss the details of the structure with more confidence. Each C_5Me_5 group is bonded to the selenium atom through a single carbon atom, and exhibits two short C–C distances consistent with the presence of isolated double bonds. The Se–C bond lengths (av. 2.000 Å) are much larger than the sum of the covalent radii (1.930 Å), and the C–Se–C angle (109.6°) is the largest known for a simple diorganoselenide [4]. These data imply considerable distortion of the bonding about selenium as a consequence of the size of the pentamethylcyclopentadienyl groups. The almost coplanar alignment of the two C_5Me_5-rings is also notable (inter-plane angle = 173.22°). The distances between the rings (> 3 Å) are, however, too great for operation of a significant electronic interaction and the coplanar arrangement has been identified as the one that minimises unfavourable steric interactions [1]. Steric interactions are presumably also responsible for the slight but distinct bending away of the methyl groups out of the cyclopentadienyl plane.

We are now examining the reactions of $Se(C_5Me_5)_2$

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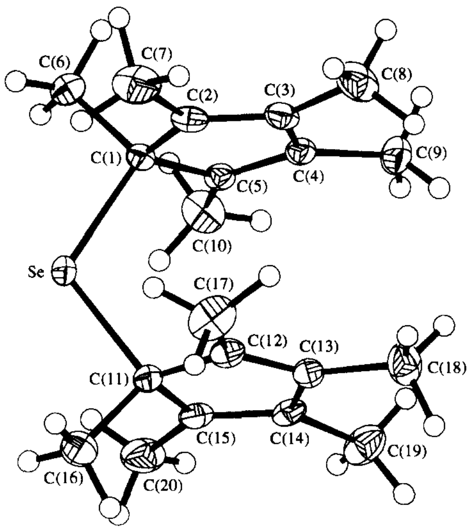

Fig. 1. Molecular structure of $Se(C_5Me_5)_2$. Some relevant bond distances (Å) and angles (^{0}): C(1)–Se 1.995(4), C(11)–Se 2.004(4), C(2)–C(1) 1.509(5), C(6)–C(1) 1.533(5), C(3)–C(2) 1.338(4), C(7)–C(2) 1.497(4), C(4)–C(3) 1.478(4), C(8)–C(3), 1.497(4), C(11)–Se–C(1) 109.6(2), C(5)–C(1)–Se 113.3(2), C(6)–C(1)–Se 102.7(2), C(5)–C(1)–C(2) 103.5(3), C(3)–C(2)–C(1) 108.9(3), C(4)–C(3)–C(2) 109.3(3).

with unsaturated transition metal fragments, since the strained geometry about the selenium atom implies that the compound may exhibit unusual behaviour, in addition to functioning as a Lewis base via the selenium lone pairs.

Crystal data: $C_{20}H_{30}Se$; $M = 349.42$; monoclinic, space group $P2_1/c$, $a = 10.313(2)$, $b = 11.116(1)$, $c = 16.332(2)$ Å, $\beta = 92.08(1)^0$, $V = 1871$ Å^3; $Z = 4$; $D_c = 1.240$ gcm^{-3}; $F(000) = 736$; $\mu(\text{Mo K}_\alpha) = 19.8$ cm^{-1}; crystal size $0.25 \times 0.20 \times 0.20$ mm.

The intensity data were collected at 150K on a FAST TV area detector diffractometer with Mo Kα radiation ($\lambda = 0.71069$ Å) by previously described procedures [5]. 13367 reflections were measured giving 3575 unique data. The structure was solved by direct methods (SHELX-S) [6] and refined by full-matrix least-squares on Fo (SHELXL-80) [7] using 3116 observed data [$Fo > 4\sigma(Fo)$] corrected for absorption (DIFABS) [8]. Final wR and R (on F) were 0.0285 and 0.0244 (3116 data, 310 parameters, unit weight). All non-H atoms were treated anisotropically. The hydrogens were kept isotropic and refined freely.

A full list of bond lengths and angles and tables of atomic coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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