Pentamethylcyclopentadienylselenium derivatives III. Synthesis and ^{77}Se NMR spectroscopy of bis(pentamethylcyclopentadienyl) polyselenides, $Se_n(C_5Me_5)_2$ $(n = 2, 3, 4)$

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Abstract

Treatment of LiC_5Me_5 with either Se_2Cl_2 or elemental Se followed by oxidation leads to the formation of a mixture of the polyselenides $Se_n(C_5Me_5)_2$ ($n = 2, 3$ and 4). The ^{77}Se–^{77}Se coupling constants measured by NMR spectroscopy for these compounds are the largest yet reported for acyclic systems.

Keywords: Selenium; Cyclopentadienyl; Nuclear magnetic resonance

1. Introduction

We have previously reported [1] the preparation of the first cyclopentadienylselenium derivative $Se(C_5Me_5)_2$ (1). The reaction of 1 with chromium and tungsten carbonyl complexes [2] unexpectedly yields products containing the diselenide ligand $Se_2(C_5Me_5)_2$ (2). We have now attempted to synthesize 2 free of the transition metal fragment.

2. Results and discussion

Bis(pentamethylcyclopentadienyl)disulphur, $S_2(C_5Me_5)_2$, has been isolated [3] as a yellow oil from the reaction of S_2Cl_2 with LiC_5Me_5. The analogous reaction using Se_2Cl_2 proceeds in a different and unusual fashion:

$$Se_2Cl_2 + LiC_5Me_5$$

$$\xrightarrow[-78\,^{\circ}C \text{ to RT}]{\text{toluene}} Se_n(C_5Me_5)_2 + (C_5Me_5)_2 \qquad (1)$$
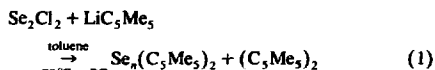
2: $n = 2$; 3: $n = 3$; 4: $n = 4$

A solution of LiC_5Me_5 in toluene was treated with 0.5 molar equivalents of Se_2Cl_2 at low temperature. The mixture was allowed to warm to room temperature overnight, after which time a white suspension of LiCl had formed in a yellow solution. Thin layer chromatography using hexane as eluting solvent revealed the presence of four products: $Se_2(C_5Me_5)_2$ (2) as expected, but also the polyselenides $Se_3(C_5Me_5)_2$ (3) and $Se_4(C_5Me_5)_2$ (4), and the hydrocarbon $C_{10}Me_{10}$ [4]. Passage of the products through a silica column using petroleum ether (b.p. 40–60 °C) as eluent was successful in separating the C_5Me_5 dimer from the polyselenide mixture, but further separation of the polyselenides using preparative chromatography or chemical reaction could not be accomplished.
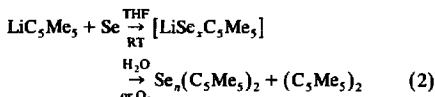
The formation of 3 and 4 in this reaction cannot be ascribed to impurities in the Se_2Cl_2, which was distilled immediately prior to use. The presence of the C_5Me_5 dimer in the product mixture implies that they are formed as a result of the reductant action of LiC_5Me_5. Analogous results have been obtained using Se_2Br_2 [5].

Another potential means of preparing 2 is the generation of the pentamethylcyclopentadienylselenide anion $C_5Me_5Se^-$ or its equivalent and its subsequent oxidation. It has previously been established that, like sulphur, selenium is sufficiently electrophilic to react with

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Scheme 1.

methyllithium in THF to give the methylselenide anion [6]. We have found that pentamethylcyclopentadienyl-lithium dissolved in THF at room temperature has a large appetite for elemental selenium, consuming up to 3 equiv. of the chalcogen to produce a clear, deep red, almost black solution of $LiSe_xC_5Me_5$. Addition of de-

Fig. 1. $^{77}Se\{^1H\}$ NMR spectrum of a mixture of the polyselenides **2**, **3** and **4**. Insets shows details of the satellite structure.

gassed water (to generate the unstable selenol) or exposure of the solution to the atmosphere did not yield a single product, but again resulted in the formation of a mixture of $C_{10}Me_{10}$, 2, 3 and 4:

$$LiC_5Me_5 + Se \xrightarrow[RT]{THF} [LiSe_xC_5Me_5]$$

$$\xrightarrow[or\ O_2]{H_2O} Se_n(C_5Me_5)_2 + (C_5Me_5)_2 \qquad (2)$$

2: $n = 2$; 3: $n = 3$; 4: $n = 4$

The same result was obtained in experiments in which half, one or three equivalents of selenium were added. A series of species in equilibrium must therefore be present in the $LiSe_xC_5Me_5$ solution, with $x = 1, 2, 3$ or greater. The C_5Me_5 dimer, together with Li_2Se_y, may be formed from two molecules of $LiSe_xC_5Me_5$. On oxidation, coupling of all possible $Se_xC_5Me_5$ radicals can occur, but the products $Se_n(C_5Me_5)_2$ with $n > 4$ are presumably too unstable with respect to selenium extrusion to be isolated.

We have also investigated a third possible route to 2 via the reaction of Na_2Se_2 with BrC_5Me_5 [7]. This did not, however, yield any tractable products, possibly because of the inherent instability of BrC_5Me_5. The results of all three reactions are summarised in Scheme 1.

The analysis of the polyselenide mixtures was performed by observation of selenium satellites in the proton-decoupled ^{77}Se NMR spectra (Fig. 1). These selenium satellites arise from molecules containing more than one ^{77}Se atom. Since the relative abundance of such species is only 0.6%, concentrated solutions must be used. If the two ^{77}Se nuclei are found in non-equivalent positions they will couple and give rise to an AB satellite spectrum placed around the chemical shifts of the mother peaks. It therefore follows that AB satellite patterns will not be observed for a dialkyl diselenide, due to the equivalence of the two selenium nuclei. Dialkyl triselenides are expected to show one AB satellite pattern around the two ^{77}Se chemical shifts corresponding to a one bond ^{77}Se homonuclear coupling. In a dialkyl tetraselenide, the two non-equivalent ^{77}Se nuclei can either be connected to each other or separated by a selenium atom. Thus, in the spectra of these compounds two mother peaks surrounded by two satellite AB spec-

tra corresponding to one and two bond ^{77}Se–^{77}Se couplings are expected.

Also, observation of proton–selenium coupling in the proton-coupled ^{77}Se NMR spectrum enables the assignment of the terminal or α-selenium resonances. Only ^{77}Se nuclei next to an alkyl group, i.e. α-Se, show sizeable spin coupling to both the α- and β-protons of the alkyl group; β-Se and γ-Se, within a resolution of 0.5 Hz, give singlets in the proton-coupled spectra.

The results obtained are summarised in Table 1. It can be seen that the α-selenium atom in 3 has a chemical shift higher than that of the β-selenium atom; in 4, however, the ordering is reversed. A similar observation was made by Eggert et al. [8]: in half of the dialkyl triselenides investigated, the α-selenium atom had the higher chemical shift, whereas in all of the dialkyl tetraselenides the chemical shift of the β-selenium was higher.

The magnitude of $J(Se-Se)$ in polyselenides is determined by the extent of the lone pair–p orbital overlap, and is thus dependent on the torsion angles at the selenium atoms. These in turn depend on the nature of the substituents. The largest values of $^1J(Se-Se)$ have been observed in cyclic five- and six-membered diselenides [9], but those for 3 and 4 are larger than all those previously recorded for acyclic systems. It has been suggested [8,10] that decreasing the chain length of the substituents results in an increase in $^1J(Se-Se)$. Re-examination of the data shows, however, that the trend is more properly expressed in terms of an increase in the degree of branching, or steric bulk. The large coupling constants observed for 3 and 4 may therefore be ascribed to the bulkiness of the C_5Me_5 group.

The constitution of the polyselenide mixture was confirmed by mass spectrometry. The FAB mass spectrum contained clusters of peaks around $m/e = 430$ and 508, corresponding to the molecular ions of 2 and 3 respectively. Experimental and calculated isotopic distributions were in close agreement. Only very weak signals for the parent ion of 4 were observed. This is not unexpected as a common feature of the mass spectra of dialkyl polychalcogenides is that they are prone to chalcogen extrusion [11].

Although proton NMR spectroscopy was of little use as a diagnostic tool in the identification of the polyselenides, it was observed that all resonances fell in the region $\delta = 1.20$–1.80. This is in accord with the σ-bonded structures shown in Scheme 1, which are analogous to those proposed for $S_2(C_5Me_5)_2$.

3. Experimental

All reactions were performed using standard Schlenk techniques and pre-dried solvents under an atmosphere of dinitrogen. NMR spectra: Bruker WM250, tetrameth-

Table 1
^{77}Se NMR spectroscopic data for 2, 3 and 4 (47.7 MHz, $CDCl_3$)

	Chemical shift (δ)		Coupling constants (Hz)		
	α-Se	β-Se	$^1J(Se-Se)$	$^2J(Se-Se)$	$^3J(Se-H)$
2	526	—	—	—	10.7
3	627	550	70	—	13.9
4	640	700	89	109	14.1

ylsilane (internal, ^{1}H), dimethyl selenide (external, ^{77}Se) as standards. Mass spectra were recorded by the EPSRC Mass Spectrometry Centre, using fast atom bombardment (FAB). LiC$_5$Me$_5$ was prepared from equimolar amounts of pentamethylcyclopentadiene [12] and butyllithium (1.7 M in hexanes) in petroleum ether (b.p. 40–60°C). Se$_2$Cl$_2$ was prepared by the method of Stammreich and Forneris [13].

3.1. Preparation of Se$_n$(C$_5$Me$_5$)$_2$, n = 2 (2), 3 (3), 4 (4)

3.1.1. From Se$_2$Cl$_2$

LiC$_5$Me$_5$ (2.51 g, 18 mmol) was dissolved in toluene (30 cm^3) and cooled to −78°C. Freshly prepared Se$_2$Cl$_2$ (2.13 g, 9 mmol) was added slowly dropwise to generate a brick red solution. The mixture was allowed to warm slowly to room temperature, becoming paler in colour, and stirred for a further 24 h to generate a yellow solution and a white precipitate. The solution was filtered through a bed of neutral alumina and reduced in volume by evaporation of the solvent under reduced pressure. Thin layer chromatography of the product mixture revealed the presence of four products: (C$_5$Me$_5$)$_2$, which was separated by column chromatography using silica and petroleum ether (b.p. 40–60°C), and the polyselenides 2, 3 and 4. Combined yield of 2, 3 and 4: 2.67 g.

Composition (by ^{77}Se NMR): 2 (15%), 3 (56%), 4 (29%).

MS (FAB, ^{80}Se): m/e = 590 (4$^+$, < 1%), 510 (3$^+$, 3%), 430 (2$^+$, 19%), 134 (C$_{10}$H$_{14}^+$, 100%).

3.1.2. From elemental selenium

LiC$_5$Me$_5$ (1.00 g, 7 mmol) was dissolved in THF (50 cm^3). Powdered vitreous selenium (1.67 g, 21 mmol) was added slowly in portions to generate a clear, deeply coloured solution. Degassed water (30 cm^3) was added to give a yellow organic layer and a red aqueous layer. The organic layer was separated and dried over magnesium sulphate. The solvent was removed by evaporation under reduced pressure to leave the product as a dark yellow oil. Thin layer chromatography revealed that the same four products were present as in Section 3.1.1 above. After separation of the (C$_5$Me$_5$)$_2$, the combined yield of 2, 3 and 4 was 1.12 g.

Composition (by ^{77}Se NMR): 2 (44%), 3 (49%), 4 (6%).

3.2. Attempted separation of 2, 3 and 4

Attempted separation of the polyselenides using preparative thin layer chromatography or a chromata-

tron with hexane as the eluting solvent in both cases was unsuccessful. The failure to separate the products using these techniques, although a good separation of the products was evident during analytical thin layer chromatography, was attributed to the fact that the composition of the silica surface is different in each case: preparative thin layer chromatography and the chromatatron require the use of more binding agent in order to adhere the active surface to the glass base.

Attempts to separate the polyselenide mixture by chemical means, either by reduction with NaBH$_4$ to yield NaSeC$_5$Me$_5$ and subsequent oxidation to 2, or by reaction of the product mixture with halogen to yield Se(C$_5$Me$_5$)X (X = Br, I) were also unsuccessful, yielding only (C$_5$Me$_5$)$_2$ and deposited red selenium.

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