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Tetramethylcyclopentadienylselenium derivatives

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Bis(1,2,3,4-tetramethylcyclopentadienyl)selane (**1**) has been prepared by the reaction of tetramethylcyclopentadienyllithium (Cp^{t}Li) with selenium bis(diethyldithiocarbamate). Treatment of Cp^{t}Li with elemental selenium, followed by air oxidation, led to loss of the allylic hydrogen atom, and formation of the novel tricyclic compound 1,4,5,6,7,10,11,12-octamethyltricyclo[7.3.0.0]-2,8-diselenadodeca-3,5,9,11-tetraene (**2**). The sulfur analogue of **2** has been obtained by a similar procedure. The X-ray crystal structures of compounds **1** and **2** have been determined, and the molecular geometry observed for **1** has been probed using DFT calculations.

Introduction

We have previously described the synthesis and structure of a number of pentamethylcyclopentadienylselenium compounds. Bis(pentamethylcyclopentadienyl)selane, Cp^*_2Se ($Cp^* = C_5Me_5$), shows unusual reactivity towards low-valent transition metal fragments, leading to complexes of the diselenide $Cp^*_2Se_2$.[1] Two routes to monocyclopentadienylselenium derivatives have been developed: methyl(pentamethylcyclopentadienyl)selane,[2] Cp*SeMe, can be prepared by the reaction of methyl iodide with Cp^*Se_xLi; treatment of diferrocenyl diselenide with Cp*Li leads to ferrocenyl(pentamethylcyclopentadienyl)selane,[3] Cp*SeFc (Fc = [Fe(η^5-C_5H_5)(η^5-C_5H_4)]).

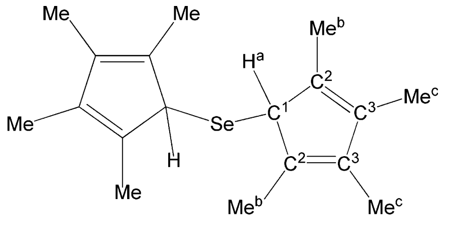
Steric protection is required for the stabilisation of these compounds containing selenium bound in the allylic position. An alternative approach is the incorporation of cyclopentadienyl substituents which allow the chalcogen atom to occupy one of the preferred vinylic positions. Sladky *et al.* have used this strategy to prepare a series of bis- and tris(trimethylsilyl)cyclopentadienylselenium and -tellurium compounds.[4,5] The presence of an allylic hydrogen atom offers the possibility of further functionalisation *via* deprotonation of the cyclopentadienyl ring.[6] With this in mind, we have now examined the chemistry of selenium in combination with the tetramethylcyclopentadienyl group.

Results and discussion

Bis(1,2,3,4-tetramethylcyclopentadienyl)selane (**1**), Cp^t_2Se ($Cp^t = C_5Me_4H$), was synthesised in the same way as Cp^*_2Se, *via* the room temperature reaction of tetramethylcyclopentadienyllithium (Cp^{t}Li) with the convenient Se(II) precursor $Se(S_2CNEt_2)_2$, as summarised in eqn (1). The product was obtained as an orange solid after column chromatography, and was recrystallised from diethyl ether at −10 °C. Compound **1** is air-stable for a few days, but is best stored under an inert atmosphere in the dark at −10 °C.

$$2\ Li(C_5Me_4H) + Se(S_2CNEt_2)_2 \xrightarrow[\text{RT, 18 h}]{\text{Toluene}} \underset{\mathbf{1}}{Se(C_5Me_4H)_2} \qquad (1)$$

NMR spectroscopic data for **1** are summarised in Table 1; Fig. 1 explains the labels used for the assignments. The ^{1}H NMR spectrum of **1** contains three characteristic peaks. There are two singlets in the methyl region of the spectrum, each of which integrates to the equivalent of twelve hydrogens. These peaks are assigned to the two sets of methyl groups Me^b and Me^c, with the lower field resonance believed to correspond to Me^b. The third peak is a singlet in the aliphatic region of the spectrum that integrates to the equivalent of two hydrogens. This peak is assigned to the pair of protons H^a. The ^{13}C NMR spectrum contains five distinct peaks. The first two peaks appear in the expected region for the methyl groups Me^b and Me^c. The third peak at 52.2 ppm is assigned to the more deshielded sp^3 carbon atoms C^1. The final two peaks occur in the expected region for C=C double bonds and are assigned to C^2 and C^3. The NMR spectra of **1** show that both Cp^t ligands are bound in an η^1-fashion with the selenium in the allylic position. The chemical shifts of the methyl groups are slightly downfield compared to the chemical shifts observed for Cp^*_2S,[7] and Cp^*_2Se.[1] The downfield shift for the methyl groups is also apparent in the ^{13}C NMR spectrum. The ^{13}C chemical shifts of the carbon atoms on the cyclopentadienyl ring behave similarly, although the resonance for the allylic carbons in **1** is slightly upfield of the corresponding signal for the pentamethylcyclopentadienyl derivatives. In the ^{1}H-coupled ^{77}Se NMR spectrum, the selenium resonance is observed as a triplet. This is due to coupling to the pair of protons H^a on C^1 in the Cp^t rings. If a methyl group was present in this position, then the coupled ^{77}Se NMR spectrum would give a multiplet as observed for Cp^*_2Se.[1] The ^{77}Se chemical shift of **1** is also at slightly higher field than that observed for Cp^*_2Se.



1

Fig. 1 Labelling scheme for assignment of NMR data for **1**.

The mass spectra of **1** and Cp^*_2Se exhibit a similar fragmentation pattern as well as a molecular ion. The IR spectrum contains a number of peaks in the usual regions for C–H, C–C and C=C bonds, although they are not assigned unequivocally. The lack of unexpected features in the spectrum supports the proposed structure. The IR spectrum of **1** is similar to that observed for Cp^*_2Se.[1] The broad band apparent at 1636 cm^{-1}

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Table 1 NMR spectroscopic data for compounds in $CDCl_3$ solution

	Assignment[a]	**1** (δ/ppm)	Assignment[b]	**2** (δ/ppm)	**3** (δ/ppm)
^{1}**H**	H^b	3.29 (s)	Me^d	1.73	1.32
	Me^b	1.87 (s)	Me^c	1.78	1.37
	Me^c	1.68 (s)	Me^b	2.00	1.50
			Me^a	2.18	1.75
^{13}**C**	C^2, C^3	135.7	Me^d	10.6	9.1
		135.5	Me^c	11.2	10.0
	C^1	52.2	Me^b	13.7	11.1
	Me^b	12.6	Me^a	22.3	23.9
	Me^c	11.4	C^5	60.3	60.3
			C^4	132.4	134.5
			C^3	134.8	137.9
			C^2	143.5	140.1
			C^1	144.8	142.9
^{77}**Se**		292 (t, $^{2}J_{Se-H}$ = 19.2 Hz)		377	—

[a] For key to assignments see Fig. 1. [b] For key to assignments see Fig. 3.

Table 2 Mass, infrared and UV/vis spectroscopic data

	1		**2**	**3**
Mass spectra: *m/z* (relative abundance)[a]				
M^+	322 (20%)	M^+	400 (38%)	304 (7%)
$Cp^t{}_2{}^+$	242 (24%)	$M^+ - E$	320 (25%)	272 (56%)
Cp^tSe^+	201 (47%)	$(C_5Me_4)_2{}^+$	240 (100%)	240 (66%)
Cp^{t+}	121 (100%)	$C_5Me_4E^+$	200 (45%)	152 (33%)
		$C_5Me_4{}^+$	120 (86%)	120 (100%)
Infrared spectra:[b] ν/cm^{-1}				
	2964 (s)		2923 (s)	Not recorded
	2929 (s)		2851 (s)	
	1636 (br)		1636 (m)	
	1479 (m)		1437 (m)	
	1416 (m)		1361 (m)	
	1264 (m)		1322 (m)	
	1207 (m)		1271 (m)	
	986 (m)		1064 (m)	
	911 (m)		1010 (m)	
	838 (w)			
UV/vis spectra:[c] λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})				
	270 (900)		290 (3700)	Not recorded
	235 (1200)		205 (15700)	

[a] Recorded using FAB; figures are for isotopomers containing ^{80}Se. [b] Recorded as KBr disks; selected bands only; s = strong, m = medium, w = weak, br = broad. [c] Recorded in hexane solution, concentration 5 × 10^{-4} mol dm^{-3}.

(*cf.* $Cp^*{}_2Se$: 1658 cm^{-1}) is possibly two unresolved peaks corresponding to the carbon–carbon double bond stretching frequencies. For the parent diene (Cp^tH) these frequencies have been estimated at 1613 (symmetric) and 1658 cm^{-1} (asymmetric) by Mironov and co-workers,[8] and more recently values of 1624 and 1656 cm^{-1} have been reported.[9] The UV/vis spectrum of **1** is slightly different from that recorded for $Cp^*{}_2Se$. Both compounds have two main absorption bands in the near-UV, but in $Cp^*{}_2Se$ (λ_{max} = 210 nm, ε = 1800 dm^3 mol^{-1} cm^{-1}; λ_{max} = 300 nm, ε = 300 dm^3 mol^{-1} cm^{-1}) these are more widely separated and the difference in their intensities is greater. The band at 235 nm is at a higher wavelength than the corresponding absorption in both $Cp^*{}_2Se$ and the parent hydrocarbon (Cp^tH λ_{max} = 205 nm), but still lies in the expected region for a diene-containing system, and supports the presence of the distinct double bonds in the structure of **1**.

An X-ray diffraction study provided further structural information. Two different views of the symmetry-independent molecule are shown in Fig. 2. Selected bond lengths and angles are listed in Table 3. The crystal structure confirms that the Cp^t

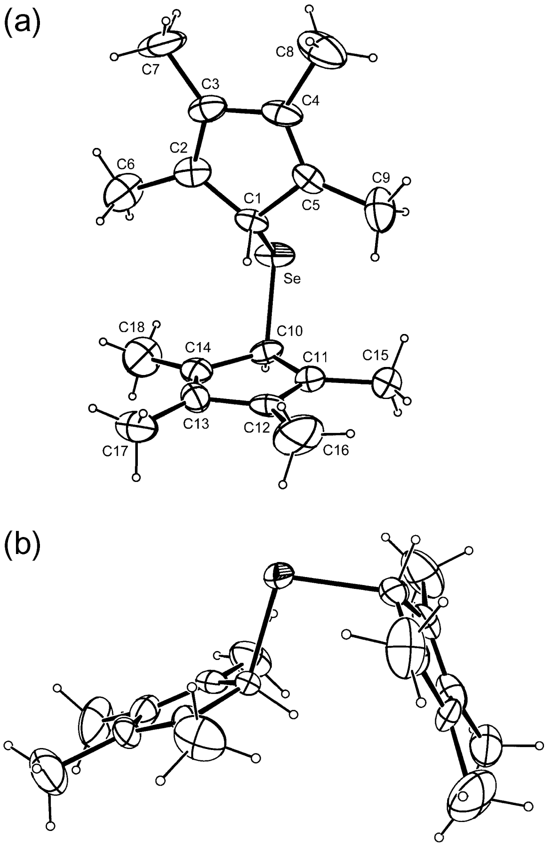


Fig. 2 (a) A view of the structure of a molecule of **1**, with atomic labelling. Here and in the following figures, 30% probability thermal ellipsoids are shown and hydrogen atoms are represented as spheres of arbitrary radii; (b) alternative view of the molecule of **1**.

Table 3 Selected bond lengths (Å) and angles (°) in the structure of **1**

Se–C(1)	1.974(3)	Se–C(10)	1.986(3)
C(1)–C(2)	1.492(5)	C(10)–C(11)	1.492(4)
C(2)–C(3)	1.335(5)	C(11)–C(12)	1.337(5)
C(3)–C(4)	1.473(5)	C(12)–C(13)	1.467(4)
C(4)–C(5)	1.339(5)	C(13)–C(14)	1.335(5)
C(5)–C(1)	1.501(4)	C(14)–C(10)	1.488(5)
C(1)–Se–C(10)	99.7(1)	Se–C(10)–C(11)	112.0(5)
Se–C(1)–C(2)	110.4(4)	Se–C(10)–C(14)	111.1(5)
Se–C(1)–C(5)	114.4(5)	C(11)–C(10)–C(14)	104.3(2)
C(2)–C(1)–C(5)	103.8(2)		

ligands are bound to the selenium atom by a single bond in the allylic position. The average carbon–selenium bond length of 1.98 Å is greater than the sum of the covalent radii (1.93 Å), and slightly shorter than that seen in Cp*$_2$Se (2.00 Å).[10] The value of the C(10)–Se–C(11) angle (99.7(1)°) is considerably smaller than its equivalent in Cp*$_2$Se (109.6(2)°),[10] and resembles that in $(C_5Bu^t_2H_3)$SePh (100.3(3)°)[4] and Cp*SeFc (101.8(4)°),[3] where the two allylic methyl groups are also absent.

Perhaps the most interesting difference between the crystal structures of **1** and Cp*$_2$Se is the arrangement of the cyclopentadienyl ligands in space. In **1** the Cp^t ligands are in an almost perpendicular arrangement with the single hydrogen atom of one ring over the other ring. In Cp*$_2$Se the Cp* ligands are in a coplanar arrangement; the sulfur derivative Cp*$_2$S also has coplanar Cp* ligands.[7] However, to describe Cp*$_2$S and Cp*$_2$Se as 'slipped metallocenes' is inappropriate as it implies a much greater ring–chalcogen interaction than the observed carbon–chalcogen σ-bond. The different arrangements found for **1** and Cp*$_2$Se may be due to a subtle balance of factors like intramolecular attractive and repulsive interactions, local geometry modifications caused by substitution of a methyl group for a hydrogen and effects of packing forces in the solid. In order to gain some insight on these aspects, DFT geometry optimisations were performed on three model geometries, both for the Cp$^t{}_2$Se and the Cp*$_2$Se systems. These were the 'perpendicular' and 'coplanar' arrangements mentioned above and, in addition, a third 'open' arrangement in which the two rings lay as far apart as possible from each other. For Cp$^t{}_2$Se, the lowest energy geometry was found to be that of the perpendicular arrangement, in agreement with the results of the solid-state study, with a 101.9° C–Se–C angle (*cf.* the 99.7(1)° experimental value). The angle between the ring planes was 79.6° (experimental 84.2°). The coplanar arrangement for Cp$^t{}_2$Se lay 4.16 kcal mol^{-1} in energy above the former, whereas the 'open' arrangement was calculated to be only 0.18 kcal mol^{-1} less stable than the perpendicular one. The choice between open and perpendicular arrangements might be determined by packing forces. For the Cp*$_2$Se system, the coplanar arrangement was found to be the most stable one, again in agreement with experiment, with a 112.1° C–Se–C angle, *cf.* the experimental 109.6(2)°; the computed dihedral angle between the ring planes was 10.5° (experimental 6.8°). The perpendicular and the open arrangements for Cp*$_2$Se were respectively 0.48 and 3.58 kcal mol^{-1} in energy above the coplanar arrangement. These results suggest that the intramolecular interactions, effective for the gas phase models, are also determinant for the geometries in solid-state conditions. As for the different conformational preferences of the two systems, it should not be ignored that the presence of the fifth methyl group on the rings in Cp*$_2$Se introduces local changes, *e.g.* causing a *ca.* 3° decrease in the values of the Se–C–C angles and a corresponding decrease in the dihedral angle between the ring planes, with respect to Cp$^t{}_2$Se in the coplanar setting. The possibility to achieve a better coplanarity for Cp*$_2$Se might enhance the effect of attractive interactions between the rings.

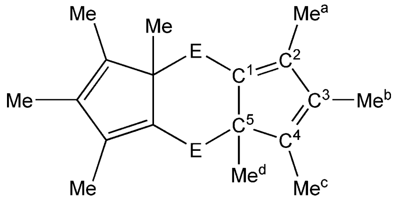
Previous work in our laboratory[11] has shown that treatment of the pentamethylcyclopentadienylselenolate anion with water, followed by an aerobic work-up, gives a mixture of the polyselenides Cp*Se$_n$Cp* where $n = 2, 3, 4$. The oxidation of the tetramethylcyclopentadienyl analogue, Cp^{t}Se$_x$Li, was examined to determine if a polyselenide mixture is also formed in this case. The Cp^{t}Se$_x$Li intermediate was generated *in situ* by the addition of three molar equivalents of elemental selenium to Cp^{t}Li to give a darkly coloured solution in THF. The mixture was then exposed to air and stirred at room temperature for 18 hours. The overall synthesis is outlined in eqn (2). The orange crystalline product after chromatography was found not to be a mixture of polyselenides, but the novel compound 1,4,5,6,7,10,11,12-octamethyltricyclo[7.3.0.0]-2,8-diselenadodeca-3,5,9,11-tetraene (**2**). This is thermally stable and can be stored at ambient temperature in air.

$$\mathrm{Li(C_5Me_4H)} + \mathrm{E\ (3\ equiv.)} \xrightarrow[\mathrm{RT,\ 3\ h}]{\mathrm{THF}}$$

$$\mathrm{LiE}_x\mathrm{(C_5Me_4H)} \xrightarrow[\mathrm{RT,\ 18\ h}]{\mathrm{Air,\ THF}} \mathrm{E_2(C_5Me_4)_2} \qquad (2)$$

2: E = Se
3: E = S

NMR spectroscopic data for **2** are summarised in Table 1; Fig. 3 explains the labels used for the assignments. The ^{1}H NMR spectrum of **2** contains four singlets in the methyl region, each of which integrates to the equivalent of six protons. These were assigned to the four non-equivalent pairs of methyl groups Me$^{a–d}$. Based on published data for related compounds,[12] the higher field resonance is believed to correspond to Me^d. The lack of a peak in the 2.5–4.0 ppm region confirmed the loss of the single proton from the starting Cp^t ligand. The ^{13}C NMR spectrum also contained four peaks in the methyl region, which were assigned to the methyl groups Me$^{a–d}$. The single peak at 60.3 ppm is in the expected region for a deshielded sp^3 carbon atom and is assigned to C^5. The final four peaks are in the expected region for C=C double bonds and are assigned to the carbon atoms C$^{1–4}$. The ^{1}H and ^{13}C NMR spectra show that the four methyl groups on each cyclopentadienyl ring are non-equivalent, and that the molecule has two-fold symmetry. These data imply that only the *meso*-stereoisomer is present in solution. The assignments are based on data from related compounds, but alternatives are possible. The ^{77}Se NMR spectrum shows a single peak at 377 ppm, which indicates that the two selenium atoms are equivalent. The NMR data for **2** correlate well with those for the all-carbon analogue $(C_5Me_4)_2C_2$ synthesised by Jutzi and co-workers.[12] The ^{1}H and ^{13}C chemical shifts for the vinylic methyl groups are slightly more downfield for the selenium derivative, although the chemical shifts for the sp^2 carbon atoms are similar in both compounds. The most obvious difference between them relates to the ^{1}H resonance of the allylic methyl group Me^d, which is shifted 1 ppm downfield by the presence of the adjacent selenium atom.



2: E = Se; **3**: E = S

Fig. 3 Labelling scheme for assignment of NMR data for **2** and **3**.

As for **1**, the IR spectrum contains a number of peaks in the usual regions for C–H, C–C and C=C bonds, and the UV/vis spectrum has two major absorption bands below 300 nm.

The X-ray structure of the centrosymmetric molecule in **2** is shown in Fig. 4. It confirms the stereochemistry inferred from the NMR data and shows some similarities to the all-carbon

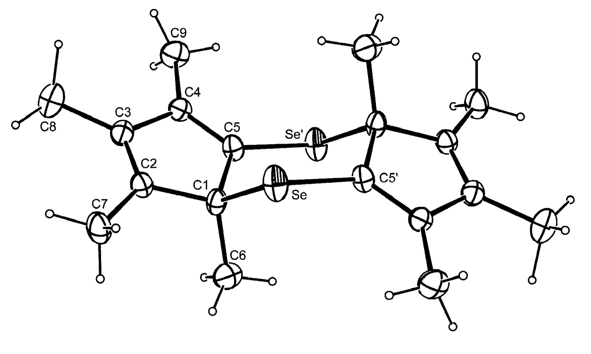


Fig. 4 A view of the molecular structure of **2**. Primed atoms are related to the corresponding unprimed ones by an inversion centre (*i.e.* at equivalent position $-x, -y, -z$).

Table 4 Selected bond lengths (Å) and angles (°) in the structure of **2**

Se–C(1)	2.010(5)	C(3)–C(4)	1.482(7)
Se–C(5)[a]	1.894(5)	C(4)–C(5)	1.335(7)
C(1)–C(2)	1.510(6)	C(5)–C(1)	1.496(6)
C(2)–C(3)	1.324(7)		
C(1)–Se–C(5)[a]	97.0(2)	C(3)–C(4)–C(5)	107.9(4)
Se–C(1)–C(5)	108.0(3)	C(4)–C(5)–C(1)	110.3(4)
C(1)–C(5)–Se[a]	122.3(3)	C(2)–C(1)–C(6)	114.5(5)
C(5)–C(1)–C(2)	102.6(4)	C(5)–C(1)–C(6)	115.0(5)
C(1)–C(2)–C(3)	109.0(4)	Se–C(1)–C(6)	109.9(4)
C(2)–C(3)–C(4)	110.0(4)		

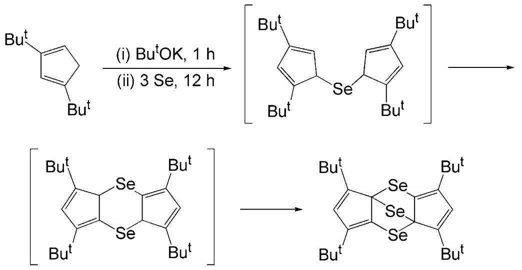
[a] Symmetry operation: $-x$, $-y$, $-z$..

analogue. The central six-membered ring has a 'chair' conformation. The planes of the two cyclopentadienyl rings are parallel, and form an angle of 59.9° with the plane formed by the centrosymmetric pairs of Se and C(1) atoms. The lengths of the carbon–selenium bonds show the effect of the selenium being bound to different types of carbon atoms (see Table 4). The longer distance of 2.010(5) Å is for the selenium bound to an sp^3 carbon, and is in the expected region for this type of bond (*cf.* 1.98 Å in **1**). The shorter distance of 1.894(5) Å is for the selenium bound to an sp^2 carbon atom. The bond lengths for **2** also show the presence of two distinct double bonds in the cyclopentadienyl rings. The methyl groups bound to the sp^2 carbons ($Me^{a,b,c}$) are only slightly out of the planes of the cyclopentadienyl rings, as is also observed in the crystal structure of **1**. The methyl groups on the sp^3 carbons (Me^d) are pointing out of the planes at an angle of 39.8° with the normal to the respective plane.

The mechanism of the formation of **2** is unclear, but it is reasonable to assume that the last step involves the dimerisation of tetramethylcyclopentadieneselenoketone. The dimerisation of a selenoketone to give a heterocyclic compound under similar circumstances is known in the literature.[13] Back and co-workers have reported that the addition of methyl iodide to a solution of the camphorselenolate anion gives the 1,3-diselenatane: they propose that the formation of the diselenatane occurs *via* the dimerisation of the selenoketone intermediate. In the preparation of **2**, the route from the selenolate to the selenoketone is not fully understood, but may involve the oxidatively induced elimination of LiSeH. The proposed mechanism is outlined in Scheme 1.

The formation of **2** does not occur if the selenolate anion is stirred in THF for 14 days under a dinitrogen atmosphere. The ^1H NMR spectrum of the mixture after this time clearly shows a resonance for the proton on the sp^3 ring carbon and some proton–selenium coupling is visible. The $^2J_{H\text{–}Se}$ value is approximately 19 Hz, which is similar to that observed for **1**. The resonance of the proton on the sp^3 ring carbon is at much higher field than in **1**, and its chemical shift is closer to that observed for tetramethylcyclopentadiene. This also confirms that **1** is not present in the mixture.

The amount of selenium added when the selenolate is generated alters the overall yield of **2**. When a 3 : 1 ratio of selenium to Cp'Li was used, **2** was isolated in about 20% yield. If a 1 : 1 ratio was used, then **2** was isolated in less than 1% yield. This observation supports the proposed mechanism which requires the presence of at least two equivalents of selenium.

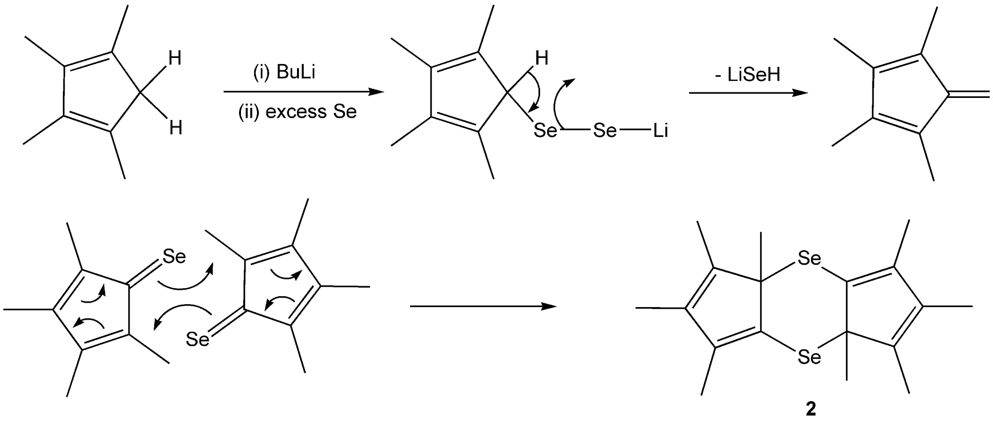


(3)

Thaler and co-workers have recently reported a similar compound to **2**.[14] The reaction of di-*tert*-butylcyclopentadiene with excess potassium *tert*-butoxide in the presence of elemental selenium gives a cyclopentadienyl system with three bridging selenium atoms (a 1,4-diselenine). The overall synthesis is outlined in eqn (3). In this reaction, the compound analogous to **2** (which these authors call a 1,4-diselenane) is only proposed as an intermediate and is not isolated from the final mixture. Thaler and co-workers suggest that deprotonation of the 1,4-diselenane followed by selenium insertion occurs to give the observed product. Of course, this process is not possible in the case of **2** due to complete alkylation of the ring. The C(sp^2)–Se bond lengths are very similar for the 1,4-diselenine and **2** in their crystal structures. The 1,4-diselenine has an average bond length of 1.888 Å, compared to 1.894 Å observed for **2**. The C(sp^3)–Se bond length in **2** is, however, much longer at 2.010 Å, compared to 1.985 Å in the 1,4-diselenine. Another interesting feature of the 1,4-diselenine is the fact that the central ring has a much smaller C–Se–C bond angle of 89.6° than that observed for **2** (97.0°).

We have also prepared the sulfur analogue of **2** by a similar method. This compound is 1,4,5,6,7,10,11,12-octamethyltricyclo[7.3.0.0]-2,8-dithiadodeca-3,5,9,11-tetraene (**3**, see Fig. 3). The thiolate intermediate was generated *in situ*; the solution was then exposed to air and stirred at room temperature for 18 hours (see eqn (2)). After purification by column chromatography, **3** was isolated as a yellow oil.

The reaction was also attempted at −78 °C. The lithiation and addition of the sulfur powder were carried out at low temperature, before the oxidation at room temperature. However, the product in this case could not be identified. It is thought that under these conditions the formation of the $Cp'S_xLi$ intermediate occurs only very slowly.



Scheme 1

The ^{1}H NMR spectrum of **3** has a similar pattern to that seen for **2** (see Table 1). The spectrum contains four singlets for the methyl groups and they are at slightly higher field than for **2**. An analogous structure to that of **2** is expected, as there is no peak for the single proton on the Cp^t ring. The ^{13}C NMR spectrum also resembles that observed for **2**. The four methyl peaks are mostly at higher field than for **2**, although Me^a has a greater chemical shift in **3**. The peak for the sp^3 carbon C^5 is in the expected region, and there are four peaks in the normal region for C=C double bonds. The chemical shifts of the ring carbon atoms are similar in **2** and **3**. The mass spectrum of **3** also shows a similar pattern to that observed for **2**, with the molecular ion observed together with fragment ions corresponding to sequential loss of chalcogen atoms.

Recently, Thaler and co-workers have reported the sulfur analogue of the 1,4-diselenine in eqn (3).[15] As with the 1,4-diselenine, a compound similar to **3** is proposed as an intermediate. The suggested mechanism involves successive deprotonation of the cyclopentadienyl ring and insertion of a sulfur atom.

It is clear that these tetramethylcyclopentadienylselenium derivatives display significant differences in behaviour from their pentamethylcyclopentadienyl analogues, which we are now beginning to explore in more detail. We will also be reporting the results of a thermogravimetric study of these and related compounds in due course.[16]

Experimental

All reactions were performed using standard Schlenk techniques and pre-dried solvents under an atmosphere of dinitrogen. ^{1}H (400.13 MHz) and ^{13}C NMR (100.61 MHz) spectra: Bruker AC400; tetramethylsilane as internal standard. ^{77}Se NMR spectra (47.69 MHz): Bruker WM250; dimethyl selenide as external standard. IR spectra: Perkin–Elmer 1725X. UV/vis spectra: Philips PU8720 using quartz cuvettes. Mass spectra were recorded by the EPSRC Mass Spectrometry Centre, using Fast Atom Bombardment (FAB). Melting points were recorded on an electrothermal apparatus and are uncorrected. Cp^{t}Li was prepared from equimolar amounts of tetramethylcyclopentadiene (Cp^{t}H)[9] and butyllithium (1.7 M in hexanes) in hexane. $Se(S_2CNEt_2)_2$ was prepared as described in the literature.[17]

Synthesis of bis(2,3,4,5-tetramethylcyclopentadienyl)selenium, 1

Cp^{t}Li (3.4 g, 26.6 mmol) was dissolved in toluene (100 ml). $Se(S_2CNEt_2)_2$ (5.0 g, 13.3 mmol) in toluene (60 ml) was added dropwise and the mixture stirred for 18 h. The resulting solution was filtered to remove the lithium diethyldithiocarbamate and the solvent removed by evaporation under reduced pressure. The crude product was purified by passing it through a short silica column with hexane as eluent. One yellow band was collected which gave an orange solid. The solid was dissolved in Et_2O and cooled to −10 °C to give orange crystals (1.9 g, 44%), mp 122 °C. Spectroscopic details are summarised in Tables 1 and 2.

Synthesis of 1,4,5,6,7,10,11,12-octamethyltricyclo[7.3.0.0]-2,8-diselenadodeca-3,5,9,11-tetraene, 2

Cp^{t}Li (2.1 g, 16.4 mmol) was dissolved in THF (80 ml). Powdered vitreous selenium (3.9 g, *ca.* 50 mmol) was added in portions and the mixture stirred for 3 h to produce a dark red solution. The flask was opened to the air and its contents stirred for approximately 18 h. The solvent was removed by evaporation under reduced pressure to give a brown oil. The crude product was extracted with hexane and purified by passage through a silica column with hexane as eluent. The solution was concentrated and cooled to −10 °C to give orange crystals (0.7 g, 22%), mp 135 °C. Spectroscopic details are summarised in Tables 1 and 2.

Synthesis of 1,4,5,6,7,10,11,12-octamethyltricyclo[7.3.0.0]-2,8-dithiadodeca-3,5,9,11-tetraene, 3

Cp^{t}Li (1.05 g, 8.2 mmol) was dissolved in THF (60 ml). Sulfur powder (1.0 g, *ca.* 25 mmol) was added in portions and the mixture stirred for 3 h to produce a dark red solution. The flask was opened to the air and stirring continued for a further 18 h. The solvent was removed by evaporation under reduced pressure and the crude product extracted with toluene. After filtration, the solution was concentrated and passed through a silica column with toluene as eluent. One band was collected which gave the product as a yellow oil (0.7 g, 56%). Spectroscopic details are summarised in Tables 1 and 2.

X-Ray crystallography

X-Ray diffraction data for **1** were collected on a Siemens–Bruker rotating anode diffractometer equipped with Goebel mirrors, using Cu–Kα radiation ($\lambda = 1.5418$ Å). For **2**, a Nonius CAD4 diffractometer and graphite-monochromated Mo–Kα radiation ($\lambda = 0.71069$ Å) were used. Lattice constants were determined from the angular settings of *ca.* 4000 reflections for **1** and 25 accurately centred reflections for **2**. Crystal data and the main data collection and structure refinement parameters are given in Table 5. Data were corrected for absorption by ψ-scans for **2** (range of transmission coefficients: 0.739–0.995), whereas no correction was applied for **1**, since attempted corrections failed to yield improvements. In the final full-matrix least-squares refinement cycles, all non-hydrogen atoms were refined anisotropically for both structures. Methyl hydrogen atoms of **1** were in calculated positions, with U_H values linked to the U_{eq} of the respective C atom, whereas the allylic hydrogens, located from difference Fourier, were refined with individual isotropic temperature factors. A set of restraints was imposed on groups of C–C distances of **1**, to improve uniformity of values within groups. The absolute structure was determined according to Flack's test.[18] As pointed out by a careful reviewer, refinement in the centric *Pnam* space group would seem appropriate in view of the geometry of the molecule of **1**, closely approaching C_s symmetry. This, however, yields slightly higher *R* values and, more importantly, hides a small distortion also consistently present in the results of the DFT calculations, which may be attributed to hindrance between the hydrogen of the inward pointing C–H bond and the other allylic carbon of the molecule. For **2**, hydrogen atom positions were refined, with restraints

Table 5 Crystal data for **1** and **2**

Compound	1	2
Formula	$C_{18}H_{26}Se$	$C_{18}H_{24}Se_2$
M	321.35	398.31
T/K	293	293
Crystal system	Orthorhombic	Triclinic
Space group	$Pna2_1$	$P\bar{1}$
a/Å	8.418(3)	7.325(2)
b/Å	13.169(9)	8.283(3)
c/Å	15.523(13)	8.758(3)
α/°	90	62.64(3)
β/°	90	84.18(3)
γ/°	90	67.59(3)
U/Å^3	1721(2)	434.5(2)
Z	4	1
D_c/g cm^{-3}	1.240	1.522
$F(000)$	672	200
Crystal size/mm	0.5 × 0.6 × 0.8	0.3 × 0.5 × 0.6
Reflections collected	7697	2339
Indep. data [R_{int}]	1735 [0.040]	2074 [0.030]
Observed data [$I > 2\sigma(I)$]	1689	1564
Data/parameters	1735/192	2074/133
Goodness of fit	1.064	1.153
R_1 [$I > 2\sigma(I)$]	0.0295	0.0489
wR_2 (all data)	0.0748	0.1201

on the C–H values of one methyl group, applying separate overall temperature factors for the H atoms of different methyl groups. Small corrections for extinction were applied for both **1** and **2**. Crystallographic computing programs used included SIR-97,[19] SHELXL-97[20] and PARST.[21] For graphics, ORTEP-3 was employed.[22] Crystallographic data (excluding structure factors) for the structures of **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre (CCDC reference numbers 279726 and 279727). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b510981g.

Computational procedures

In the quantum mechanical calculations the hybrid HF-DFT B3LYP approach[23] and the 6–31G(d,p) basis set were employed, using the GAUSSIAN 98 suite of programs.[24] Frequency calculations were performed to check the nature of stationary states, and zero-point energy corrections were applied. The initial model for the 'perpendicular' geometry of **1** was provided by the X-ray structure; that of the 'coplanar' arrangement was approximately based on the structure of $Cp^*{}_2Se$ and the 'open' one was generated on the basis of reasonable assumptions.

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