

Pentamethylcyclopentadienylselenium derivatives IV. Synthesis and characterisation of methyl(pentamethylcyclopentadienyl)selenium and its pentacarbonyltungsten complex $[W(CO)_5\{Se(C_5Me_5)Me\}]$

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Abstract

The novel alkyl(pentamethylcyclopentadienyl)selenium derivative $Se(C_5Me_5)Me$ has been prepared by treatment of LiC_5Me_5 sequentially with Se and MeI. It reacts with $[W(CO)_5THF]$ to form $[W(CO)_5\{Se(C_5Me_5)Me\}]$. Spectroscopic characterisation of the new compounds includes the measurement of the first reported value for the coupling constant $^1J(^{77}Se-^{183}W)$.

Keywords: Selenium; Cyclopentadienyl; Tungsten; Carbonyl

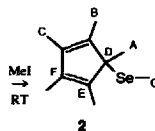
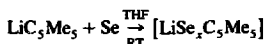
1. Introduction

We have previously described the synthesis and structure of bis(pentamethylcyclopentadienyl)selenium $Se(C_5Me_5)_2$ [1]. This compound shows unusual reactivity towards low valent transition metal fragments [2], as a result of the steric crowding at the selenium atom. We were therefore interested in preparing alkyl(pentamethylcyclopentadienyl)selenium derivatives containing less bulky alkyl groups in order to compare their behaviour with that of 1.

2. Results and discussion

Solutions of LiC_5Me_5 in THF readily dissolve up to three equivalents of selenium to generate $LiSe_3C_5Me_5$ [3]. We have now examined the reactions of this potential source of pentamethylcyclopentadienyl-selenium compounds with simple alkyl halides. Dropwise addition of an equimolar quantity of methyl iodide to a THF

solution of $LiSe_2C_5Me_5$ produced a yellow solution and a white suspension of LiI:



(1)

Filtration and subsequent passage of the solution through a short silica column under an inert atmosphere using petroleum ether (b.p. 30–40 °C) as the eluting solvent afforded firstly a sample of $(C_5Me_5)_2$ [4] and then the new product $Se(C_5Me_5)Me$ (2). NMR spectroscopic data for 2 are summarised in Table 1.

The 1H and ^{13}C NMR spectra of 2 confirm that the C_5Me_5 ring is σ -bonded to the selenium atom as it is in 1. The ^{77}Se NMR chemical shift is close to that predicted by halving the sum of the chemical shifts of the symmetrical derivatives (1: $\delta = 324$; $SeMe_2$: $\delta = 0$).

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Table 1
NMR spectroscopic data for 2 and 4^a

		2 (CDCl ₃)	4 (C ₆ D ₆)
¹ H (400 MHz)	H _A	1.10	1.03
	H _B	1.72	1.60
	H _C	1.74	1.64
	H _G	1.76	1.88
¹³ C (100 MHz)	C _A	9.9	11.1
	C _B	10.9	11.7
	C _C	18.9	17.2
	C _D	58.4	60.8
	C _E	134.3	126.9
	C _F	137.8	136.9
	C _G	10.3	9.3
	C _H	—	196.3 ^b
	C _I	—	198.4 ^c
	⁷⁷ Se (47.7 MHz)	193	228 ^d

^a For labelling schemes, see Eqs. (1) and (2).

^b ¹J(¹³C–¹⁸³W) = 128 Hz.

^c ¹J(¹³C–¹⁸³W) = 162 Hz.

^d ¹J(⁷⁷Se–¹⁸³W) = 49 Hz.

This has often been found to be the case for unsymmetrical dialkyl selenides [5].

In the proton-coupled ⁷⁷Se NMR spectrum a multiplet with 10 identifiable peaks was observed (see Fig. 1). The spacing between the peaks was 10 Hz. This can be understood if ¹J(⁷⁷Se–¹H) = 20 Hz, as it is in 1, and ²J(⁷⁷Se–¹H) = 10 Hz, as is observed in other com-

pounds containing Se–Me bonds, e.g. SeMe₂: ²J(⁷⁷Se–¹H) = 10.5 Hz [6]. 10 peaks would then be expected, arising from an overlapping quartet of quartets, with the following intensity ratio: 1:3:6:10:12:12:10:6:3:1.

The chemical ionisation mass spectrum of 2 has an intense cluster of ions around *m/e* = 230, corresponding to the molecular ion, with an isotope pattern that matches that expected for a compound containing one selenium atom. We have, however, been unable to obtain 2 in an analytically pure form. ⁷⁷Se NMR spectroscopy reveals that this is due to the presence of a small amount of the diselenide C₅Me₅SeSeMe (3). In addition, a small cluster of peaks is present in the mass spectrum, which corresponds to the parent ion for 3. These observations are consistent with the presence in the LiSe₂C₅Me₅ solution of species containing more than one selenium atom, as has previously been established [3].

Attempts to form Se(C₅Me₅)Et, Se(C₅Me₅)Pr or Se(C₅Me₅)Bu by the addition of ethyl, propyl or butyl iodide to LiSe₂C₅Me₅ also resulted in the formation of a yellow solution with a white suspension. When these products were investigated by means of ⁷⁷Se NMR spectroscopy, however, it was found that they were composed of many components which were inseparable by means of column chromatography.

The reactivity of 2 towards the complexes [M(CO)₅THF] (M = W, Mo, Cr) was investigated. Each of the metal carbonyl derivatives was stirred overnight at room temperature with an equimolar quantity of 2:

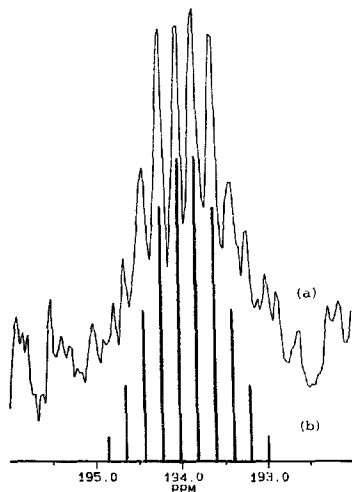
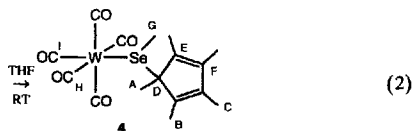
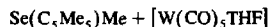


Fig. 1. ¹H-coupled ⁷⁷Se NMR spectrum of 2: (a) observed, (b) calculated.

In the reactions with the chromium and tungsten complexes a gradual colour change was observed from the characteristic yellow of the THF adduct to a deeper orange. The solutions were concentrated and the products passed through a short silica column using petroleum ether (b.p. 30–40 °C) as the eluting solvent. The single orange band was collected and reduced in volume to yield the products [M(CO)₅{Se(C₅Me₅)Me}] (4: M = W; 5: M = Cr). The experiment conducted using the molybdenum-containing starting material did not afford any tractable products.

Compounds 4 and 5 were isolated as mobile orange oils in approximately 30% yield. They were found to be stable in air for a short time, but were best stored under

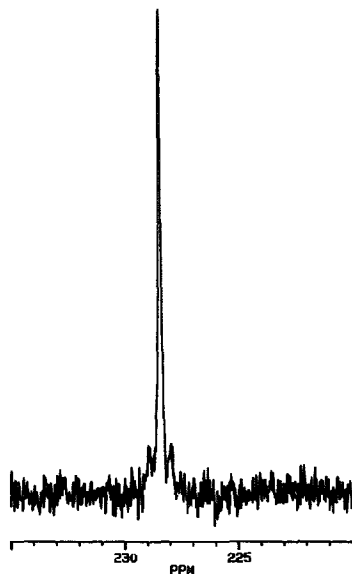


Fig. 2. $^{77}\text{Se}(^1\text{H})$ NMR spectrum of **4** showing ^{183}W satellites.

inert gas, in the dark at low temperature, to prevent decomposition. As was observed for the complexes $[\text{M}(\text{CO})_5\{\text{Se}_2(\text{C}_5\text{Me}_5)_2\}]$ ($\text{M} = \text{W}, \text{Cr}$) [2], the stability in solution of the tungsten complex was far greater than that of the chromium analogue. Only **4** has therefore been fully characterised. NMR spectroscopic data are summarised in Table 1.

The ^1H and ^{13}C NMR spectra of **4** are in general only slightly shifted from those of **2**, the chemical shifts for the selenium-bound methyl group being comparable with those obtained previously [7]. It is apparent that the C_5Me_5 ring is still σ -bonded to the selenium atom. The ^{13}C resonances for the carbonyl groups show carbon–tungsten coupling: the value of $^1J(^{13}\text{C}–^{183}\text{W})$ is significantly greater for the carbon atom *trans* to selenium, reflecting the σ -donating properties of the selenide ligand. Similar observations have been made in relation to other metal–ligand coupling constants, most notably $^1J(^{31}\text{P}–^{195}\text{Pt})$ [8].

The ^{77}Se NMR spectrum of **4** shows one resonance, shifted to lower field (as is usual on coordination) by 35 ppm compared with that of **2**. This signal exhibits ^{183}W satellites (see Fig. 2). The one-bond coupling constant data for complexes of monodentate selenium and tellurium ligands are mostly limited to couplings to

^{195}Pt . As far as can be ascertained, the value for **4** is the first example of $^1J(^{77}\text{Se}–^{183}\text{W})$ to be recorded.

The molecular ion of **4** is readily observed in the FAB mass spectrum. Comparison of the theoretical isotopic distribution with the distribution obtained experimentally produces a perfect match. Three infrared-active stretching frequencies are observed in the region $1935–2070\text{ cm}^{-1}$ which are associated with the carbonyl ligands. This observation is consistent with the formulation of **4** as a species of the type $[\text{M}(\text{CO})_5\text{L}]$ where L is a point ligand.

It can be seen therefore that, in contrast to the behaviour of **1**, the expected Lewis base type reactivity of **2** has been observed in these reactions. Although no structural information is available for **2**, it would seem likely that the lesser steric demands of the methyl group, when compared with those of the C_5Me_5 group in **1**, allow for a shorter and hence stronger Se–C bond. This would account for the ligand being able to coordinate intact and not having been subject to reduction within the transition metal coordination sphere.

3. Experimental

All reactions were performed using standard Schlenk techniques and pre-dried solvents under an atmosphere of dinitrogen. ^1H and ^{13}C NMR spectra: Bruker AC400, tetramethylsilane as internal standard. ^{77}Se NMR spectra: Bruker WM250, dimethyl selenide as external standard. IR spectra: Perkin–Elmer 1725X. Mass spectra were recorded by the EPSRC Mass Spectrometry Centre, using chemical ionisation (CI) or fast atom bombardment (FAB). LiC_5Me_5 was prepared from equimolar amounts of pentamethylcyclopentadiene [9] and butyllithium (1.7 M in hexanes) in petroleum ether (b.p. $40–60^\circ\text{C}$). $[\text{M}(\text{CO})_5\text{THF}]$ ($\text{M} = \text{W}, \text{Cr}$) was prepared as described in the literature [10].

3.1. Preparation of methyl(pentamethylcyclopentadienyl)selenium, **2**

LiC_5Me_5 (1.85 g, 13 mmol) was dissolved in THF (50 cm^3). Powdered vitreous selenium (3.00 g, 38 mmol) was added slowly in portions to generate a clear, deeply coloured solution. On dropwise addition of iodomethane (0.80 cm^3 , 1.85 g, 13 mmol), the colour lightened to yellow and a white precipitate of lithium iodide was produced. The solution was filtered, reduced in volume and passed through a short silica column using petroleum ether (b.p. $40–60^\circ\text{C}$) as eluent. The first band to be collected contained $(\text{C}_5\text{Me}_5)_2$; the second band was reduced in volume to give **2** as an obnoxious smelling yellow oil. Yield 1.64 g (55%). NMR: see Table 1. MS (CI, ^{80}Se): $m/e = 230$ (M^+ , 100%).

Methyl(pentamethylcyclopentadienyl)diselenium, **3** is present as a minor impurity (around 5%). ^{77}Se NMR (CDCl_3 , 47.7 MHz): $\delta = 267$ (q, $J(^{77}\text{Se}-^1\text{H}) = 11$ Hz), 372 (q, $J(^{77}\text{Se}-^1\text{H}) = 13$ Hz). MS (CI, $^{80}\text{Se}_2$): $m/e = 310$ (M^+ , 5%).

3.2. Preparation of $[\text{W}(\text{CO})_5\{\text{Se}(\text{C}_5\text{Me}_5)\text{Me}\}]_4$

Stirring a mixture of **2** (0.50 g, 2.2 mmol) and $[\text{W}(\text{CO})_5\text{THF}]$ (1.00 g, 2.8 mmol) in THF solution (50 cm^3) at room temperature led overnight to a gradual deepening of the colour from yellow to orange. The solution was reduced to dryness by evaporation of the solvent in vacuo, and the residue then dissolved in the minimum volume of petroleum ether (b.p. 30–40°C). The products were passed through a short silica column using this solvent as eluent under an inert atmosphere. An orange band afforded **4** as a foul smelling oil. Yield 0.36 g (30%). NMR: see Table 1. MS (FAB, ^{80}Se , ^{184}W): $m/e = 554$ (M^+ , 9%), 470 ($[\text{W}(\text{CO})_2\{\text{Se}(\text{C}_5\text{Me}_5)\text{Me}\}]^+$, 7%), 455 ($[\text{W}(\text{CO})_2\text{SeC}_5\text{Me}_5]^+$, 20%), 270 ($\text{C}_{10}\text{Me}_{10}^+$, 100%). IR (KBr disk, cm^{-1}): 2962 (s), 2920 (s), 2854 (s), 2070 (m), 1977 (m), 1936 (vs), 1443 (m).

$[\text{Cr}(\text{CO})_5\{\text{Se}(\text{C}_5\text{Me}_5)\text{Me}\}]$, **5** was prepared by an analogous procedure using $[\text{Cr}(\text{CO})_5\text{THF}]$. ^1H NMR (C_6D_6 , 400 MHz): $\delta = 1.15$ (s, 3H, H_A), 1.61 (s, 6H, H_B), 1.66 (s, 3H, H_C), 1.84 (s, 3H, H_D). MS (FAB, ^{80}Se , ^{52}Cr): 422 (M^+ , 20%), 282 ($[\text{Cr}\{\text{Se}(\text{C}_5\text{Me}_5)\text{Me}\}]^+$, 76%), 270 ($\text{C}_{10}\text{Me}_{10}^+$, 100%). IR (KBr disk, cm^{-1}):

2960 (s), 2922 (s), 2854 (m), 2063 (s), 1985 (m), 1942 (vs), 1444 (m).

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