Pentamethylcyclopentadienylselenium Derivatives: Synthesis and X-Ray Crystal Structures of $[M(CO)_5\{Se_2(\sigma\text{-}C_5Me_5)_2\}]$ (M = Cr, W)

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Bis(pentamethylcyclopentadienyl)selenium reacts with sources of $M(CO)_5$ (M = Cr, W) fragments, to yield complexes of the diselenide $Se_2(\sigma\text{-}C_5H_5)_2$, which are characterised spectroscopically and by X-ray crystallography: these are the first examples of selenide to diselenide reduction within the coordination sphere of a transition metal, and the first structures of complexes containing a terminal diselenide ligand to be reported.

Cyclopentadienyl derivatives of many main group elements have been prepared and studied in recent years, but the elements of Group 16 (the chalcogens) have received comparatively little attention. Permethylation of the cyclopentadienyl ring generally facilitates the isolation of such compounds, and the synthesis and structure of bis(pentamethylcyclopentadienyl)sulfur were reported in 1985.[1] A number of monocyclopentadienylsulfur derivatives were subsequently prepared from this compound.[2] We have recently used an analogous synthetic procedure to prepare bis(pentamethylcyclopentadienyl)selenium [$Se(\sigma\text{-}C_5Me_5)_2$, **1**],[3] and now report the unexpected results of reactions between **1** and sources of $M(CO)_5$ (M = Cr, W) fragments.

Stirring an equimolar mixture of **1** and $[W(CO)_5(THF)]$[4] or $[W(CO)_3(MeCN)_3]$[5] in THF solution at room temp. led overnight to a gradual darkening of the solution. After subsequent column chromatography and low-temperature recrystallisation from hexane, the product isolated in each case was $[W(CO)_5\{Se_2(\sigma\text{-}C_5Me_5)_2\}]$ **2**. Analogous behaviour was observed in reactions involving the $Cr(CO)_5$ precursors $[Cr(CO)_5(THF)]$, $[Cr(CO)_4(nbd)]$ (nbd = norbornadiene)[6] and $[Cr(CO)_3(MeCN)_3]$, leading to the formation of $[Cr(CO)_5\{Se_2(\sigma\text{-}C_5Me_5)_2\}]$ **3**.

The carbonyl redistribution implied by these results, for reactions starting from a metal tetra- or tri-carbonyl derivative, is not unprecedented. The reduction of a selenide to a diselenide, within the coordination sphere of a transition metal, is however completely new. The selenide complexes $[M(CO)_5(SeR_2)]$ (M = Cr, W; R = Et,[7] Ph[8]) have, for example, previously been prepared in straightforward fashion by similar methods. The mechanism of the transformation is unclear, in part because, whilst **2** and **3** are the major products, their yields are comparatively low (*ca.* 15%). The thermal decomposition of **1**, or its reaction with elemental selenium, to yield $Se_2(\sigma\text{-}C_5Me_5)_2$, can however be ruled out as intermediate steps, as neither of these processes takes place in the absence of the transition metal under the conditions employed.

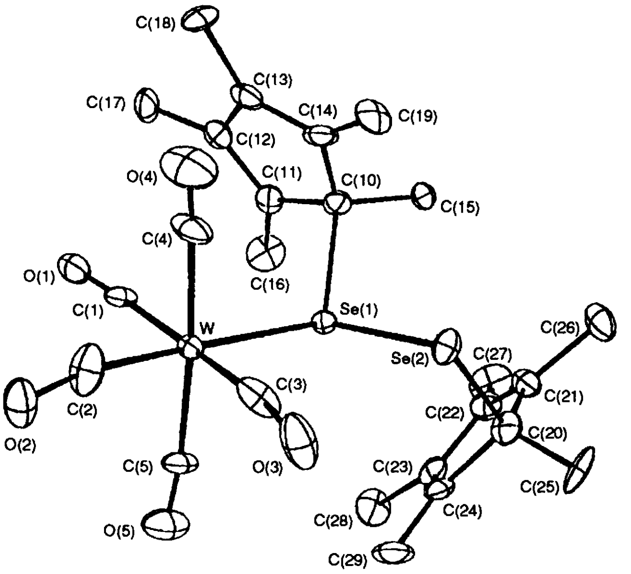

Fig. 1 Structure of **2** (shown) and **3** (with hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (°). **2**: W–Se(1) 2.671(1), W–C(1) 2.022(10), W–C(2) 1.968(11), W–C(3) 2.032(12), W–C(4) 2.019(13), W–C(5) 2.013(12), Se(1)–Se(2) 2.330(1), Se(1)–C(10) 2.038(9), Se(2)–C(20) 2.034(10), W–Se(1)–Se(2) 107.1(1), W–Se(1)–C(10) 114.2(3), Se(2)–Se(1)–C(10) 103.7(3), Se(1)–Se(2)–C(20) 100.3(3). **3**: Cr–Se(1) 2.545(1), Cr–C(1) 1.874(9), Cr–C(2) 1.828(9), Cr–C(3) 1.880(9), Cr–C(4) 1.896(8), Cr–C(5) 1.875(9), Se(1)–Se(2) 2.327(1), Se(1)–C(10) 2.033(7), Se(2)–C(20) 2.023(8), Cr–Se(1)–Se(2) 109.7(1), Cr–Se(1)–C(10) 114.9(2), Se(2)–Se(1)–C(10) 103.9(2), Se(1)–Se(2)–C(20) 99.1(2).

The orange crystalline complexes **2** and **3** have been characterised spectroscopically and by single-crystal X-ray diffraction. They are moderately air stable at room temperature in the crystalline state, but decompose rapidly in aerated solution or at elevated temperatures. In the ^1H NMR spectrum of both compounds there are six signals, indicating that the diselenide ligand is static on the NMR timescale, and bound to the transition metal through only one selenium atom. Two previous examples of a terminal diselenide ligand have been reported:[9] variable-temperature NMR studies of the compounds $[M(CO)_5\{Se_2(CH_2SiMe_3)_2\}]$ and $[M(CO)_5(\overline{SeSeCH_2CMe_2CH_2})]$ (M = Cr, Mo, W) showed that they undergo a number of fluxional processes. A similar study was not possible here due to the thermal instability of **2** and **3**.

The presence of the $Se_2(\sigma\text{-}C_5Me_5)_2$ fragment is confirmed by the X-ray crystallographic results.† Complexes **2** and **3** have essentially the same molecular structure (see Fig. 1), although the packing is different. The bond lengths in the $M(CO)_5$ fragments are normal and show typical shortening of the M–C bond *trans* to the non-carbonyl ligand. There appear to be no comparable data available for chromium selenide complexes, but the W–Se distance in **2** (2.671 Å) is similar to that in $[W(CO)_5(\overline{SeCPh_2CH_2CMe{=}CMeCH_2})]$ (2.674 Å),[10] and only slightly shorter than that in $[W(CO)_5\{Se(SnMe_3)_2\}]$ (2.736 Å).[11] Each selenium atom is bonded to a single carbon of one C_5Me_5-ring, the Se–C distances (**2**: av. 2.036 Å; **3**: av. 2.028 Å) being the longest thus far reported, and much greater than the sum of the covalent radii (1.930 Å).[12] This feature has already been noted in the structure of **1**, and may provide an insight into its novel reactivity.[3] The bonding within the C_5Me_5 groups is as expected for σ-coordination, with two short C–C distances indicating the presence of isolated double bonds.

The results presented here indicate that **1** has properties unique amongst organoselenides. We are now proceeding to examine its reactivity towards other unsaturated transition metal fragments.

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Footnote

† *Crystal data* for **2**: $C_{25}H_{30}O_5Se_2W$, M = 752;28, orange block (0.4 × 0.4 × 0.6 mm^3); triclinic, space group $P\bar{1}$, a = 9.049(4), b = 11.322(6), c = 14.930(9) Å, α = 99.28(5), β = 95.89(5), γ = 109.91(4)°, V = 1399(1) $Å^3$, Z = 2, D_c = 1.786 g cm^{-3}; μ(Mo-Kα) = 68.2 cm^{-1}. Measurements were carried out with an Enraf-Nonius CAD4 diffractometer (Mo-Kα radiation, λ = 0.71069 Å), ω–2θ scans, 2θ = 5–54°, 6071 independent reflections, 4680 observed with $I \geqslant 3\sigma(I)$. Empirical absorption correction; solution by Patterson and Fourier methods and refinement using SHELX76[13] (anisotropic W, Se, O, C; H atoms in calculated positions with C–H = 0.96 Å and rigid CH_3 groups). With 328 parameters convergence attained at R = 0.053 (R_w = 0.059).

Crystal data for **3**: $C_{25}H_{30}CrO_5Se_2$, M = 620.43, orange block (0.2 × 0.5 × 0.5 mm^3) protected by coating (no decomposition); monoclinic, space group $P2_1/c$, a = 8.916(4), b = 15.647(9), c = 20.119(10) Å, β = 96.34(4), V = 2790(2) $Å^3$, Z = 4, D_c = 1.477 g cm^{-3}, μ(Cu-Kα) = 67.5 cm^{-1}. Data collected as for **2**, with Cu-Kα radiation (λ = 1.5418 Å), 2θ = 6–110°, 6969 independent reflections, 3029 observed with $I \geqslant 3\sigma(I)$. Data treatment, structure solution, and refinement as for **2**; 328 parameters, convergence at R = 0.067 (R_w = 0.082).

For both structures, atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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