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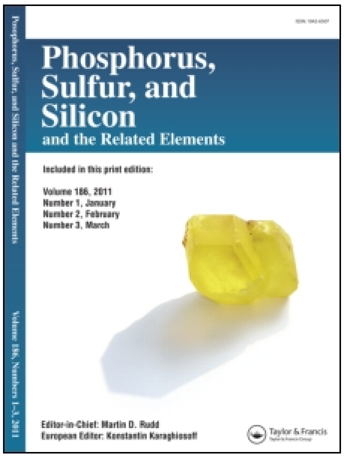

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ORGANOSELENIDO COMPLEXES OF TUNGSTEN

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Organometallic tungsten selenido complexes of the type $[cpW(CO)_3]_2Se_m$; m = 2 (**1**), 3 (**2**), 4 (**3**), can be easily synthesized via insertion of selenium into the alkali-metal tungsten bond of $LiWcp(CO)_3$ in appropriate ratios and subsequent oxidation of the produced W-selenolates with O_2/SiO_2. In contrast, reactions of K_2Se_6 with $[cpW(CO)_3Cl]$ and 18-crown-6 in DMF lead to a mixture of $[cpW(CO)_3]_2Se_4$ (**3**), the η^1 Se-bonded selenocarbamato complex $[cpW(CO)_3SeC(O)NMe_2]$ (**4**) and the ionic complex $[(18\text{-crown-}6)K]^+[cpW(Se_4)_2]^-$ (**5**). The crystal structures of **3** and **4** together with their ^{77}Se NMR data are presented.

Keywords: Selenido complexes; ^{77}Se NMR; Crystal structure

INTRODUCTION

Metatheses of transition-metal halide complexes with alkali-metal polyselenides are widely applicable and the resulting oligoselenido complexes are of interest because of the versatile binding modes of Se_n^{2-} [1]. However, the composition of the alkali-metal polyselenides is difficult to predict, since complicated equilibria can be observed in solution [2]. In the case of W, these difficulties can be avoided by using an alternative method, namely the insertion of Se into the alkali-metal transition-metal bond of appropriate W carbonylates and subsequent oxidation of the resulting organometallic selenolates with O_2 in the presence of commercial silica gel [3]. Additionally, we report on the oxidation of W-selenolates and on the reaction of $[cpW(CO)_3Cl]$ with K_2Se_6 and 18-crown-6.

SYNTHESES

$LiW(CO)_3cp$ readily inserts grey selenium in 1:1, 1:2 and 1:3 ratio in THF solution. Addition of commercial silica gel and stirring overnight afforded the oligoselenido complexes $[cpW(CO)_3]_2Se_m$; m = 2, 3, 4 as the oxidation products:

$$\mathrm{LiW(CO)_3cp} \xrightarrow{\mathrm{Se}_n} \mathrm{LiSe_nW(CO)_3cp}$$

$$\xrightarrow{\mathrm{SiO_2}\,/\,\mathrm{O_2}} \mathrm{[cpW(CO)_3]_2Se_m}$$

[n = 1; m = 2, 55%] **1**
[n = 2; m = 3, 51%] **2**
[n = 3; m = 4, 74%] **3**

However, the reaction of $[cpW(CO)_3Cl]$ with K_2Se_6 and 18-crown-6 in DMF leads to the products $[cpW(CO)_3]_2Se_4$ **3**, $[cpW(CO)_3SeC(O)NMe_2]$ **4** and $[(18\text{-crown-6})K]^+[cpW(Se_4)_2]^-$ **5** (Fig. 1). Selected NMR data of the new complexes are presented in Table 1. From the ^1H and ^{77}Se NMR data, it can be seen that **2** is in equilibrium with **3** and **4** in solution. The assignment of the Se signals was made by comparison with related complexes (**2**, **3**) or from a ^{77}Se-^{183}W coupling constant of 80 Hz (**5**). Comparable ^{77}Se-^{183}W coupling constants lie in the range 35 Hz in $[cpW(CO)_3SeC(O)Ph]$ to 112 Hz in $[W_3Se_9]^{2-}$ [4, 5].

TABLE 1 Selected NMR data of the new complexes

Complex	^{1}H-NMR	^{77}Se-NMR[a]	conditions
2	4.8 s, 4.88 s, 4.95 s (cp)	-173.7 s, 19.8, 54.3 (W-Se-**Se**), 670.8, 711.6 (W-**Se**) s	C_6D_6, 25° C
3	4.95 s, (cp)	19.4 s (W-Se-**Se**), 670.7 s (W-**Se**)	C_6D_6, 25° C
4	2.65, 2.87 s (CH_3), 4.9 s (cp)	- 136.1 s	C_6D_6, 25° C
5	3.47 s (CH_2), 5.02 s (cp)	486.1 s (W-Se-**Se**), 866.4 s (W-**Se**)[b]	$CDCl_3$, 25° C

[a] rel. to $Me_2Se_{ext.}$ [b] in d_6-acetone

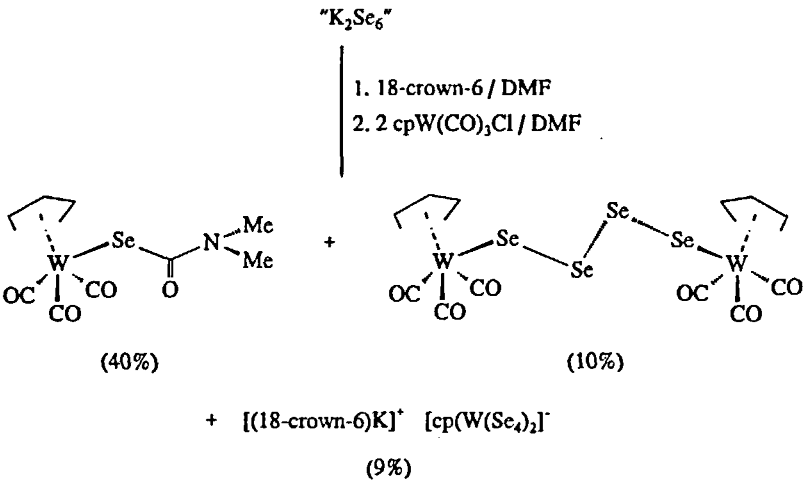

FIGURE 1 The reaction of [cpW(CO)$_3$Cl]with K_2Se_6 and 18-crown-6

CRYSTAL STRUCTURES

The crystal structures of **3** and **4** are presented in Fig. 2. **3** consists of two cpW(CO)$_3$ moieties, linked by a helical Se_4 chain in a μ^2-η^1 fashion with W-Se bond lengths of 2.6399(11) and 2.6429(10) Å. The Se-Se bond lengths lie in the range 2.321(2) to 2.367(2) Å with almost tetrahedral angles at selenium.

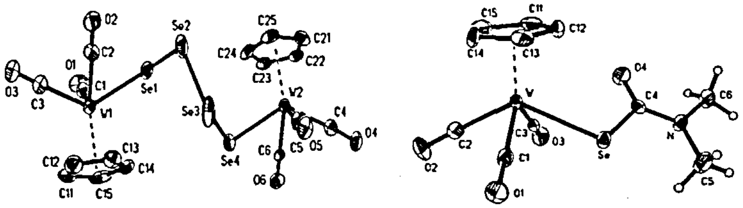

FIGURE 2 Molecular structures of $[cpW(CO)_3]_2Se_4$ **3** and $[cpW(CO)_3SeC(O)NMe_2]$ **4**

4 represents the first crystal structure with an η^1 Se-bonded selenocarbamato ligand. The atoms W, C4, O4, N, C5 and C6 are approximately coplanar (mean deviation 0.013 Å); the selenium atom lies 0.2 Å out of this plane. The W-Se bond length of 2.6308(8) Å is consistent with observed values in W-selenolato complexes with terminal organoselenolato ligands [6-8].

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