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Organometallic Selenolates. 3.[1] Oxidation of (Cyclopentadienyl)tungsten Selenolates and Crystal Structure of $[(cp)W(CO)_3]_2Se_3$

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Introduction

Transition-metal polyselenide complexes have attracted extensive interest because of the versatile binding modes of Se_n^{2-} ($n = 2-6$) and the potential use as solid state precursors.[2,3] In recent studies attention has been focused on the reactivity of $Fe_2(CO)_6(Se_2)$, unusual binding modes of polyselenide anions, and synthetic and structural investigations of metal polychalcogenides.[4−6] There are only a few reported general synthetic procedures for selenido complexes; the most common methods are the addition of selenium to unsaturated metal complexes and the reaction of alkali chalcogenides with halogenido metal complexes.[3]

Here we report on the synthesis of (oligoselenido)organotungsten(II) complexes via oxidation of the corresponding selenolates with commercial silica gel.

Experimental Section

General Procedures. All manipulations were carried out under dinitrogen using standard Schlenk techniques. Solvents were dried and distilled under dinitrogen prior to use. $(cp)W(CO)_3Cl$ was prepared according to the literature method.[7] ^1H, ^{13}C, and ^{77}Se NMR spectra were recorded in C_6D_6 solutions using TMS as internal reference (^1H, ^{13}C) or Me_2Se as external reference (^{77}Se).

Preparation of $[(cp)W(CO)_3]_2Se_2$ (1). $LiSeW(cp)(CO)_3$ was prepared from $(cp)W(CO)_3Cl$ (1 g, 2.71 mmmol), a 1 *m* $LiBEt_3H$ solution in THF (6 mL, 6 mmol) and gray Se (0.21 g, 2.71 mmol) in 50 mL of THF by the literature method. The reaction mixture was treated with 2 mL of TMEDA and 2 g of SiO_2. Stirring overnight afforded a green reaction mixture, which was filtered. The residue was washed with the acetone until the filtrate was almost colorless. The combined organic extracts were evaporated to dryness and the remaining crude product was dissolved in 30 mL of toluene. Filtration over Celite, concentration of the solution, and addition of hexanes afforded a dark-green microcrystalline product (0.65 g) with satisfactory purity in 55% yield. An analytically pure sample can be obtained by chromatography workup on silica gel using toluene as eluent. Anal. Calcd for $C_{16}H_{10}O_6Se_2W_2$: C, 23.32; H, 1.22. Found: C, 23.05; H, 1.29. ^1H NMR: 4.89 s (cp), 4.80 s (cp). ^{13}C NMR: 224.5, 213.0, 212.1 s (CO), 93.9, 93.2 s (cp). ^{77}Se NMR: −173.7 s. IR [NaCl, toluene solution, ν(CO), cm^{-1}]: 2021 s, 2012 s, 1997 vs, 1922 vs.

Table 1. Crystallographic data for $C_{16}H_{10}O_6Se_3W_2$ (**2**)

chem formula: $C_{16}H_{10}O_6Se_3W_2$
$a = 8.998$ (2) Å
$b = 10.007$ (2) Å
$c = 11.588$ (2) Å
$\alpha = 101.38$ (2)°
$\beta = 93.71$ (2)°
$\gamma = 90.97$ (2)°
$V = 1020.3$ (4) Å^3
$Z = 2$

fw = 902.82
space group: $P\bar{1}$ (No. 2)
$T = -100$ °C
$\lambda = 0.710\,73$ Å
$\rho_{calcd} = 2.939$ g cm^{-3}
$\mu = 166$ cm^{-1}
$R(F) = 0.038^a$
$R_w(F^2) = 0.090^b$

[a] $R(F) = \sum||F_o| - F_c||/\sum|F_o|$ for $F > 4\sigma(F)$. [b] $R_w(F^2) = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{0.5}$ for all reflections.

Preparation of $[(cp)W(CO)_3]_2Se_3$ (2). **2** was prepared as above, employing 0.43 g of gray Se (5.43 mmol). The workup procedure afforded 0.62 g of a red-brown microcrystalline product in 51% yield. Anal. Calcd for $C_{16}H_{10}O_6Se_3W_2$: C, 21.29; H, 1.12. Found: C, 21.09; H, 1.11. ^1H NMR: 4.95 s (cp), 4.88 s (cp). ^{13}C NMR: 224.1, 223.1, 213.9, 213.0, 184.4 s (CO), 93.9, 93.1 s (cp). ^{77}Se NMR: 711.6 s, 670.8 s, 54.3 s, 19.8 s. IR [NaCl, toluene solution, ν(CO), cm^{-1}]: 2020 vs, 1951 m, 1925 vs.

Preparation of $[(cp)W(CO)_3]_2Se_4$ (3). **3** was prepared as above, employing 0.64 g of gray Se (8.14 mmol). A dark-brown microcrystalline product (0.98 g) was obtained in 74% yield. Anal. Calcd for $C_{16}H_{10}O_6Se_4W_2$: C, 19.60; H, 1.03. Found: C, 19.77; H, 1.27. ^1H NMR: 4.95 s (cp), 4.88 s (cp), 4.87 s (cp). ^{13}C NMR: 224.0, 223.3, 213.9, 209.5, 184.2, s (CO), 93.1, 92.9 s (cp). ^{77}Se NMR: 670.7 s, 19.4 s. IR [solid, KBr, ν(CO), cm^{-1}]: 2008 vs, 1910 vs, br.

X-ray Structure Determination of $[(cp)W(CO)_3]_2Se_3$ (2). Red-brown crystals of $[(cp)W(CO)_3]_2Se_3$ suitable for X-ray analysis were obtained from diffusion of hexanes into a dichloromethane solution. A crystal of 0.4 × 0.10 × 0.05 mm^3 was mounted on a glass fibre in inert oil and transferred to the cold gas stream (−100 °C) of a Siemens P4 diffractometer, equipped with an LT-2 low-temperature attachment. Mo Kα radiation ($\lambda = 0.710\,73$ Å, graphite monochromator) was used to collect the intensity data with the ω-scan technique in the 2θ range 6−50°. Cell constants were refined from setting angles of 62 reflections in the 2θ range 8−23°. An absorption correction based on Ψ-scans was applied.

The crystallographic program system used was SHELXL-93.[8] The structure was solved by direct methods and refined by a full-matrix least-squares procedure on F^2. All non H atoms were refined anisotropically; hydrogens were included using a riding model. The weighting scheme was of the form $w^{-1} = [\sigma^2(F_o)^2 + (aP)^2 + bP]$ with $P = (F_o^2 + 2F_c^2)/3$. The final difference Fourier map was featureless with the highest peak of 2.86 e Å^{-3} near W2. Additional crystallographic data are presented in Table 1. Selected bond lengths and angles are listed in the caption to Figure 1.

Results and Discussion

Lithium (cyclopentadienyl)(carbonyl)tungsten(0) readily inserts elemental gray selenium in 1:1, 1:2, and 1:3 ratios in THF solution, forming lithium (mono-, di- and triselenolato)(cyclopentadienyl)(carbonyl)tungsten(II) compounds with unknown structures (Scheme 1). These complexes can be easily oxidized with silica gel. Common oxidizing agents for organic selenolates, RSe^-, such as I_2, Br_2, $K_3[Fe(CN)_6]$, or even air, lead to serious side reactions and some decomposition. It can be assumed that at first $LiSe_nWcp(CO)_3$ ($n = 1-3$) is transformed

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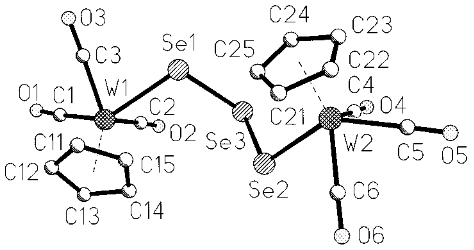
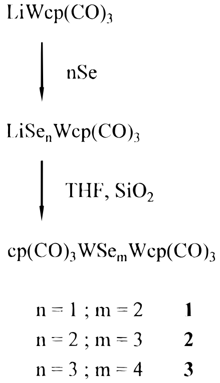


Figure 1. Structure of $[(cp)W(CO)_3]_2Se_3$. Selected bond distances (Å): W1–ring center (C_5H_5 C11–C15), 2.007(11); W2-ring center (C_5H_5 C21–C25), 2.012(6); W1–Se1, 2.632(1); W2–Se2, 2.651(2); Se1–Se3, 2.342(2); Se2–Se3, 2.348(2). Selected bond angles (deg): C1–W1–Se1, 132.9(4); W1–Se1–Se3, 108.2(1); Se1–Se3–Se2, 105.2(1); W2–Se2–Se3, 107.6(1); C5–W2–Se2, 133.7(3).

Scheme 1. Synthesis of the Oligoselenido(cyclopentadienyl)tungsten Complexes



into the corresponding selenols under the acidic reaction conditions, since the silica gel was neither dried nor stored under inert gas atmosphere. In a second step the selenols are oxidized by dissolved oxygen. For $[(cp)W(CO)_3]_2Se_2$ this process can be directly monitored by a color change from red-brown to dark green within a few minutes. It is remarkable that the oxidation of $LiSe_2W(cp)(CO)_3$ and $LiSe_3W(cp)(CO)_3$ is accompanied by precipitation of elemental selenium whereas $LiSeW(cp)(CO)_3$ reacts directly to the diselenido complex. Further studies on the precise mechanism are in progress.

The main advantage of the described oxidation procedure is the easy removal of side products and precipitated selenium by simple filtration. The new tungsten(II) complexes are formed in good yield. They are air-stable microcrystalline solids, soluble in many organic solvents such as acetone, THF, toluene, and CH_2Cl_2. Solutions of $[(cp)W(CO)_3]_2Se_3$ and $[(cp)W(CO)_3]_2Se_4$ are somewhat air-sensitive and decompose within hours accompanied by precipitation of selenium.

The ^1H-NMR spectra of $[(cp)W(CO)_3]_2Se_n$ ($n = 2, 3, 4$) indicate the inequivalence of the cyclopentadienyl rings in solution. This is accompanied by the observation of inequivalent carbonyls in the ^{13}C-NMR spectra. Unfortunately, a possible coalescence of the inequivalent cyclopentadienyl resonances at higher temperature could not be detected because of decomposition of the solutions upon heating. In the case of $[(cp)W(CO)_3]_2Se_3$ two different conformers can also be detected in the ^{77}Se-NMR spectrum. Because of insufficient stability of the solutions under NMR conditions, an exact assignment of the different selenium atoms in the ^{77}Se NMR spectra was not possible (^{183}W satellites were not detected). From comparison with tungsten–selenide anions, it can be assumed that the tungsten-bonded selenium of the tri- and tetraselenide is shifted downfield.[6b]

The molecular structure of $[cpW(CO)_3]_2Se_3$ consists of two $cpW(CO)_3$ moieties, linked by an angled Se_3 chain in a $\mu^2{-}\eta^1$ fashion. The Se atoms display a slightly distorted pseudotetrahedral geometry with bond angles ranging from 105.2(1) to 108.2(1)°. The Se–Se bond lengths are 2.342(2) and 2.348(2) Å and therefore considerably shorter than those observed in the symmetric $W_2Se_{10}^{2-}$ and the asymmetric $W_2Se_9^{2-}$ anion, in which the Se_3-units are bound in 1,3-η^2 fashion (Se–Se 2.372(9)–2.64(1) Å).[6b] Other complexes containing a Se_3 unit are $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^1{:}\eta^3\text{-}Se_3)(THF)$ (Se–Se: 2.326(1), 2.377(1) Å)[5a] and $[Ni_4Se_4(Se_3)_5(Se_4)]^{4-}$ (Se–Se: 2.231(9)–2.343(6) Å).[9]

Comparison with the corresponding Se–Se bond lengths in elemental selenium ((a) amorphous Se, 2.33 Å;[10] (b) α-Se, 2.34(2) Å;[11] and (c) trigonal Se, 2.373(5) Å[12]) indicates Se–Se single bond character in **2**. The W–Se bond lengths in **2** are 2.632(1) and 2.651(2) Å. Similar values can be observed in mononuclear organoselenolato tungsten complexes [2.623(1) Å in $(cp)W(CO)_3(SeCH_2Ph)$;[1] 2.588(2) Å in $(\eta^7\text{-}C_7H_7)W(CO)_2(SePh)$[13]] and in the cation $[W_2(CO)_{10}(Se_4)]^{2+}$ [2.626(1), 2.631(1) Å][14]. A wider range of W–Se bond lengths was found in tungsten selenide anions [e.g. 2.253(2)–2.561(4) Å in $W_2Se_{10}^{2-}$,[6b] 2.357(1) Å in $[Ni(Se_2)(WSe_4)]^{2-}$,[15] and 2.435(1)–2.488(1) Å in $WS(Se_4)_2^{2-}$.[16]

In conclusion, the oxidation of organotungsten selenolates with commercial silica gel represents a convenient method for the preparation of oligoselenidotungsten complexes. Extension of this method to other metals is conceivable, and appropriate studies are in progress.

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Supporting Information Available: Tables of crystallographic details, positional parameters, bond distances and angles, and anisotropic thermal parameters of non-hydrogen atoms (5 pages). Ordering information is given on any current masthead page.

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