

# Reactions of MSeW(CO)<sub>3</sub>cp (M = Li, Na) with Organodi- and -tetrahalides – X-ray Crystal Structures of C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>W(CO)<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), μ-[*m*-C<sub>6</sub>H<sub>4</sub>{CH<sub>2</sub>SeW(CO)<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>], μ-[*p*-C<sub>6</sub>H<sub>4</sub>{CH<sub>2</sub>SeW(CO)<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>], and C<sub>6</sub>H<sub>5</sub>CH[SeW(CO)<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]

Wolfgang Eikens, Stefan Jäger, Peter G. Jones, Jörg Laube, and Carsten Thöne\*

Institut für Anorganische und Analytische Chemie der Technischen Universität,  
Postfach 3329, D-38023 Braunschweig, Germany

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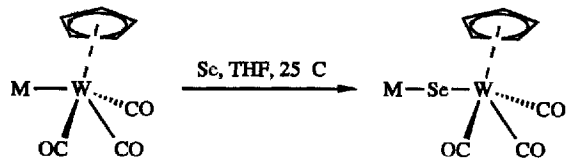
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Organotungsten-selenolato complexes were prepared in moderate yields by insertion of selenium into the alkali metal-tungsten bonds of MSeW(CO)<sub>3</sub>cp (M = Li, Na) and subsequent reactions with the organohalides *o*-, *m*-, and *p*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>Br)<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>CHBr<sub>2</sub>, *m*-C<sub>6</sub>H<sub>4</sub>(CHBr<sub>2</sub>)<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>CCl<sub>3</sub>. The <sup>77</sup>Se-NMR data of the new complexes are discussed and compared with those of related complexes derived from or-

ganomonohalides. Moreover, the X-ray crystal structures of C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>W(CO)<sub>3</sub>cp (**1**), μ-[*m*-C<sub>6</sub>H<sub>4</sub>{CH<sub>2</sub>SeW(CO)<sub>3</sub>cp]<sub>2</sub> (**3**), μ-[*p*-C<sub>6</sub>H<sub>4</sub>{CH<sub>2</sub>SeW(CO)<sub>3</sub>cp]<sub>2</sub> (**4**), and C<sub>6</sub>H<sub>5</sub>CH[SeW(CO)<sub>3</sub>cp]<sub>2</sub> (**5**) were determined. In complex (**1**), the W-CH<sub>2</sub> bond length is 2.374 Å; the W-Se bond lengths in the complexes **3**, **4**, and **5** are all in the range 2.625–2.655 Å, corresponding to W-Se single bonds.

Organometallic selenolato complexes have attracted increasing attention during the last few decades because of their potential use as single-source precursors for solar-cell technology<sup>[2]</sup>. Various synthetic routes to organoselenolato complexes were published, e.g. metatheses of transition-metal complexes with alkali metal organoselenolates or oxidative additions of organic diselenides to metal-carbonyl complexes<sup>[3]</sup>. Recent synthetic studies revealed the applicability of metatheses to organic selenolates with bulky substituents such as -E(SiMe<sub>3</sub>)<sub>3</sub> (E = C, Si, Ge)<sup>[4–8]</sup>. However, this route requires the accessibility of the organic selenolates.

Recently, we developed a synthesis for the preparation of organometallic selenolates via selenium insertion into alkali metal carbonylates. In this paper we report on the reactions of the organotungsten selenolates MSeW(CO)<sub>3</sub>cp (M = Li, Na; cp = η<sup>5</sup>-cyclopentadienyl) with organodi- and -tetrahalides. We previously described reactions of MSeW(Mo)-(CO)<sub>3</sub>cp with C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Cl and (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>Cl<sup>[9]</sup>.



## Results and Discussion

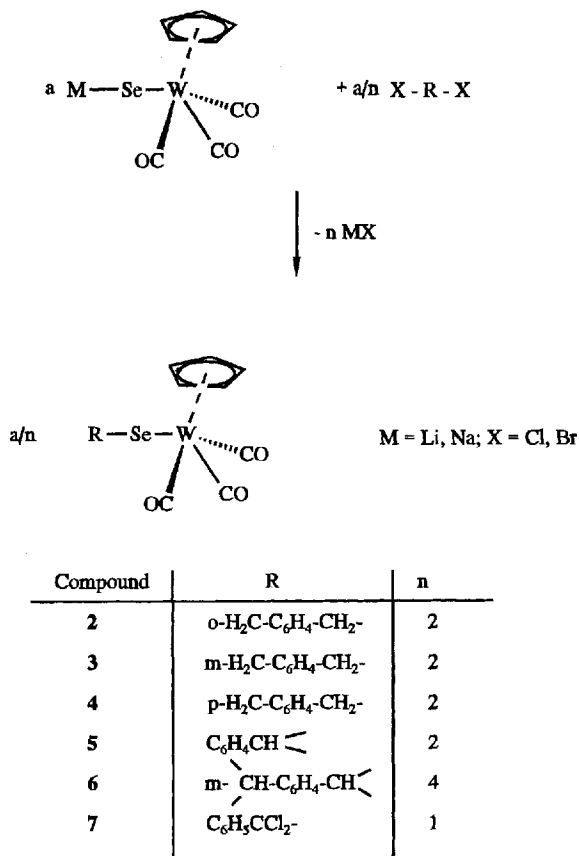
The organotungsten selenolates MSeW(CO)<sub>3</sub>cp (M = Li, Na) react with *o*-, *m*-, and *p*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>Br)<sub>2</sub> in a 2 : 1 ratio

[1] Part III: Ref.<sup>[1]</sup>.

to form the corresponding xylyl-bridged bis-selenolates *o*-, *m*-, and *p*-μ-C<sub>6</sub>H<sub>4</sub>[CH<sub>2</sub>SeW(CO)<sub>3</sub>cp]<sub>2</sub> in moderate yields under mild conditions (Scheme 1). The products can be separated easily by using conventional chromatographic methods. A complete halogen abstraction from the organohalides can be also observed if C<sub>6</sub>H<sub>5</sub>CHBr<sub>2</sub> or *m*-C<sub>6</sub>H<sub>4</sub>(CHBr<sub>2</sub>)<sub>2</sub> are used in the appropriate ratios, whereas the application of *o*-C<sub>6</sub>H<sub>4</sub>(CHBr<sub>2</sub>)<sub>2</sub> led to serious decomposition of the reaction mixture, which is probably due to the steric requirements of the -SeW(CO)<sub>3</sub>cp substituent. Only in the case of C<sub>6</sub>H<sub>5</sub>CCl<sub>3</sub> the monosubstituted product C<sub>6</sub>H<sub>5</sub>CCl<sub>2</sub>SeW(CO)<sub>3</sub>cp is obtained independent of the organohalide/MSeW(CO)<sub>3</sub>cp ratio. All these reactions can be carried out advantageously as one-pot syntheses in THF or toluene.

The moderate yields of the new complexes indicate that several other species must be present in the reaction mixtures. Thus, in the case of C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>SeW(CO)<sub>3</sub>cp, a yellow by-product could be separated first and fully characterised as the selenium-free σ complex C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>W(CO)<sub>3</sub>cp **1** by spectroscopic means and an X-ray crystal structure analysis. From the chromatographic work-up of crude C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>SeW(CO)<sub>3</sub>cp, it can be assumed that in some cases the first (yellow) bands on the columns are the selenium-free organotungsten complexes. If the reactions are stopped after a shorter period, green bands appear and the corresponding products can be isolated under the usual work-up conditions. In the case of C<sub>6</sub>H<sub>5</sub>CCl<sub>3</sub>, this band always appears, indicating that the reaction mechanism must be complicated. The green compound is in all cases the diselenide complex [cpW(CO)<sub>3</sub>]<sub>2</sub>Se<sub>2</sub>, characterised by

Scheme 1



means of literature data<sup>[1]</sup>. When CH<sub>2</sub>Cl<sub>2</sub> or CH<sub>2</sub>Cl<sub>2</sub>/hexane mixtures were used for the chromatographic work-up, brown immobile residues were observed on the column. They can easily be removed by using acetone as eluent, but spectroscopic studies showed that they are complex mixtures of several unknown and inseparable by-products.

The new complexes are air-stable crystalline solids, soluble in many organic solvents, e.g. CH<sub>2</sub>Cl<sub>2</sub>, acetone, or toluene. The solutions are somewhat air- and light-sensitive. The spectroscopic data of the complexes are in good accordance with their structures. <sup>1</sup>H-NMR and <sup>13</sup>C{<sup>1</sup>H}-NMR data show all resonances at the expected values. The ipso carbon atoms of the phenyl rings are shifted downfield because of the -I effect of the electron-withdrawing group SeW(CO)<sub>3</sub>cp.

The <sup>77</sup>Se-NMR data are given in Table 1. They reflect the electronic influence of the organic substituents on selenium. In view of the paucity of published <sup>77</sup>Se-NMR data on organotungsten selenolato complexes, we present here a short discussion.

A comparison of the simple selenolato complexes RSeM(CO)<sub>3</sub>cp (R = Me<sub>3</sub>SiCH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>; M = Mo, W) shows a downfield shift of the molybdenum derivatives relative to the corresponding tungsten complexes, which can be explained by a lower electron density on the molybdenum atoms. Similar values for the <sup>77</sup>Se shift can be found in the case of the disubstitution products of *o*-, *m*-, and *p*- $\alpha,\alpha'$ -dibromxylylene **2**, **3**, and **4**. From a comparison with

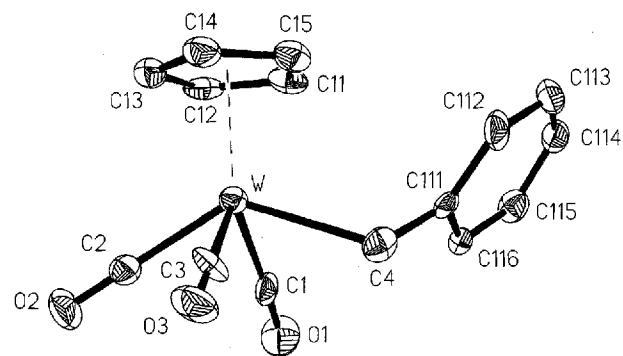
Table 1. <sup>77</sup>Se-NMR data of organotungsten- and -molybdenum-selenolato complexes (solvent CDCl<sub>3</sub>, rel. to Me<sub>2</sub>Se ext.)

Compound	$\delta^{77}\text{Se}$	Compound	$\delta^{77}\text{Se}$
<i>o</i> -C <sub>6</sub> H <sub>5</sub> [CH <sub>2</sub> SeW(CO) <sub>3</sub> cp] <sub>2</sub>	-356.2 <sup>[a]</sup>	C <sub>6</sub> H <sub>5</sub> CCl <sub>2</sub> SeW(CO) <sub>3</sub> cp	+782.0 <sup>[a]</sup>
<i>m</i> -C <sub>6</sub> H <sub>5</sub> [CH <sub>2</sub> SeW(CO) <sub>3</sub> cp] <sub>2</sub>	-328.4 <sup>[a]</sup>	Me <sub>3</sub> SiCH <sub>2</sub> SeW(CO) <sub>3</sub> cp	-530.3 <sup>[b]</sup>
<i>p</i> -C <sub>6</sub> H <sub>5</sub> [CH <sub>2</sub> SeW(CO) <sub>3</sub> cp] <sub>2</sub>	-322.7 <sup>[a]</sup>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SeW(CO) <sub>3</sub> cp	-316.1 <sup>[b]</sup>
C <sub>6</sub> H <sub>5</sub> CH[SeW(CO) <sub>3</sub> cp] <sub>2</sub>	-160.3 <sup>[a]</sup>	Me <sub>3</sub> SiCH <sub>2</sub> SeMo(CO) <sub>3</sub> cp	-479.3 <sup>[b]</sup>
<i>m</i> -C <sub>6</sub> H <sub>5</sub> [CH[SeW(CO) <sub>3</sub> cp] <sub>2</sub> ]	-159.5 <sup>[a]</sup>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SeMo(CO) <sub>3</sub> cp	-271.2 <sup>[b]</sup>

[<sup>a</sup>] This work. - [<sup>b</sup>] For synthesis see ref. [9]).

C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>SeW(CO)<sub>3</sub>cp, it can be assumed that values of  $\delta = -300$  to  $-400$  are typical of this class of complexes. The downfield shift of the sterically more crowded complexes **5** and **7** ( $\delta = -160$ ) can be explained by an easier excitation of the selenium lone pairs. The extreme downfield shift of the C<sub>6</sub>H<sub>5</sub>CCl<sub>2</sub> complex **6** ( $\delta = +782$ ) reflects the strong electron-withdrawing character of the chlorinated organic substituent. Unfortunately, decomposition of the solutions under NMR conditions was too rapid to permit observation of the <sup>183</sup>W-<sup>77</sup>Se coupling (the selenium signals themselves require less time); at low temperature the solubility of the complexes is not adequate.

The molecular structure of the selenium-free by-product C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>W(CO)<sub>3</sub>cp **1** is shown in Figure 1. It is isostructural to the corresponding molybdenum complex<sup>[10]</sup>. The benzyl ligand is bound to tungsten in a simple  $\sigma$ -mode with a corresponding bond length of 2.374(7) Å [cf. 2.387(3) Å in C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Mo(CO)<sub>3</sub>cp]. Similar arrangements were found in various  $\sigma$ -bonded complexes RW(CO)<sub>3</sub>cp, e.g. R = ethoxycarbonylmethyl, 1-methylcyclopropylmethyl, or pentamethyldisilylmethyl-C<sup>[11-13]</sup>. The tungsten- $\sigma$ -carbon bond lengths in these complexes are similar to those in **1**. As in many other M(CO)<sub>x</sub>cp fragments, the W(CO)<sub>3</sub>cp moiety displays a "piano-stool" arrangement.

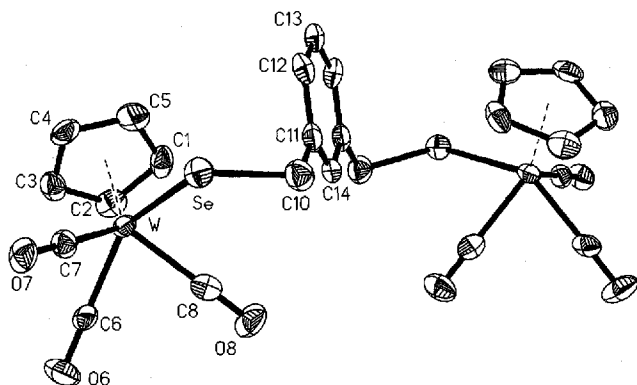
Figure 1. Molecular structure of C<sub>15</sub>H<sub>12</sub>O<sub>3</sub>W (**1**) (ORTEP, 50% probability ellipsoids, H atoms omitted for clarity)<sup>[a]</sup>

[<sup>a</sup>] Selected bond lengths [Å] and angles [°]: W-cp (ring center) 2.017(3), W-C1 1.980(8), W-C2 1.996(8), W-C3 1.988(7), W-C4 2.374(7), C4-C111 1.501(10); C1-W-C4 76.2(3), C2-W-C4 131.0(3), C3-W-C4 75.2(3), W-C4-C111 112.6(5).

The molecular structures of *m*-, and *p*-C<sub>6</sub>H<sub>4</sub>-[CH<sub>2</sub>SeW(CO)<sub>3</sub>]<sub>2</sub> **3** and **4** are shown in Figures 2 and 3. Both possess crystallographic symmetry. In the *m*-complex two ring carbon atoms of the bridging xylylidene group lie on a twofold axis, whereas the *o*-complex exhibits inversion

symmetry. The W–Se bond lengths are similar in both complexes [2.625(1) Å in **3**; 2.637(1) Å in **4**] and also comparable to those observed in  $C_6H_5CH_2SeW(CO)_3cp$  [2.621(1) Å, av. of two molecules]<sup>[9]</sup>,  $\eta^7-C_7H_7W(CO)_2-SeC_6H_5$  [2.588(2) Å]<sup>[14]</sup> and the thioselenocarboxylic ester derivative  $PhCHC(tBu)C(SMe)=SeW(CO)_5$  [2.639(1) Å]<sup>[15]</sup>. W–Se bond lengths in unbridged binuclear complexes with terminal organoselenolato groups are significantly shorter, because of the different electronic effects in different oxidation states of tungsten [e.g. 2.432(2) Å in  $W_2(SeC_6H_2Me_3)_6$  ( $W\equiv W$ )]<sup>[16]</sup>. Additionally, the W–Se bond lengths are sensitive to steric effects. If the organoselenolato group bridges two tungsten atoms, the corresponding W–Se bonds become shorter than those observed in **3** and **4** [e.g. 2.513(5) Å in  $W_2Cl_4(\mu-SePh)(\mu-Cl)(dppm)_2$  and 2.549(1) Å in  $[PPh_4]_2[Cl_3W\{\mu-Se(Cl)\}(\mu-SePh)_2WCl_3] \cdot 2 CH_2Cl_2$ ]<sup>[17,18]</sup>. The geometry at selenium is essentially tetrahedral in both complexes [C–Se–W 109.2(3)°].

Figure 2. Molecular structure of the *m*-complex  $C_{24}H_{18}O_6Se_2W_2$  (**3**) (ORTEP, 50% probability ellipsoids, H atoms omitted for clarity)<sup>[a]</sup>

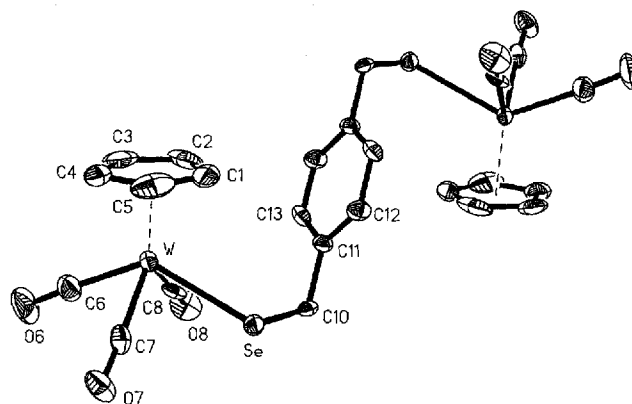


<sup>[a]</sup> Selected bond lengths [Å] and angles [°]: W–cp (ring center) 2.011(3), W–Se 2.625(1), W–C6 1.975(8), W–C7 1.991(7), W–C8 2.012(8), Se–C10 1.973(8), C10–C11 1.495(10); C6–W–Se 130.7(2), C7–W–Se 74.5(2), C8–W–Se 77.2(2), C10–Se–W 109.5(2), C11–C10–Se 115.3(5).

The molecular structure of the disubstituted complex  $C_6H_5CH[SeW(CO)_3cp]_2$  **5** is shown in Figure 4. The complex crystallises as an ethanol solvate, in which the solvent H atoms could not be located because of high displacement parameters. All atoms of the bridging benzylidene group lie in a mirror plane. This arrangement causes a short non-bonding Se–Se distance of 3.099(1) Å, but the geometry at selenium is not affected, being almost tetrahedral with an angle of 106.4(1)°. The W–Se bond length of 2.655(1) Å is similar to those in the *m*- and *p*-complex **3** and **4**.

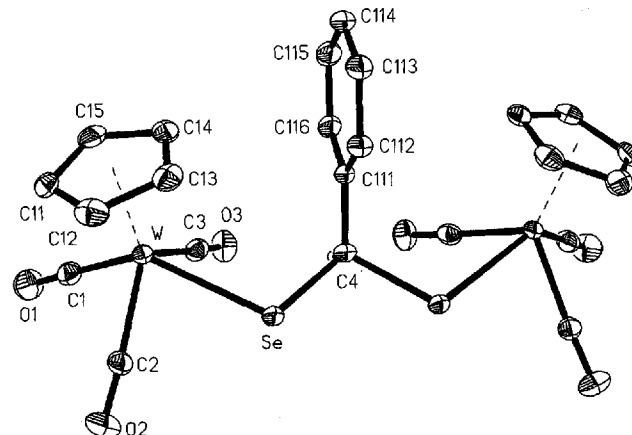
In conclusion, we believe that selenium insertion into alkali metal–transition metal bonds of carbonylates and the subsequent reaction with organic electrophiles is a convenient and simple synthesis of organoselenolato complexes. Moderate yields can be tolerated, since all the preparations can be performed advantageously as one-pot reactions and the starting materials are easily accessible and cheap. Especially for polyhalogenated hydrocarbons, the alternative synthetic route (metalation and selenium inser-

Figure 3. Molecular structure of the *p*-complex  $C_{24}H_{18}O_6Se_2W_2$  (**4**) (ORTEP, 50% probability ellipsoids, H atoms omitted for clarity)<sup>[a]</sup>



<sup>[a]</sup> Selected bond lengths [Å] and angles [°]: W–cp (ring center) 2.007(4), W–Se 2.637(1), W–C6 1.985(9), W–C7 1.992(8), W–C8 2.003(8), Se–C10 1.987(7), C10–C11 1.501(9); C6–W–Se 131.0(3), C7–W–Se 74.3(2), C8–W–Se 76.3(2), C10–Se–W 109.2(2), C11–C10–Se 114.6(5).

Figure 4. Molecular structure of  $C_{23}H_{16}O_6Se_2W_2 \cdot C_2H_5OH$  (**5**) (ORTEP, 50% probability ellipsoids, H atoms and solvent molecule omitted for clarity)<sup>[a]</sup>



<sup>[a]</sup> Selected bond lengths [Å] and angles [°]: W–cp (ring centre) 2.011(2), W–Se 2.655(1), W–C1 1.991(4), W–C2 1.993(4), W–C3 1.993(4), Se–C4 2.003(3), C4–C11 1.480(8); C1–W–Se 134.4(1), C2–W–Se 74.9(1), C3–W–Se 75.9(1), C4–Se–W 106.4(1), C11–C4–Se 114.5(2).

tion in metal–carbon bonds) can be difficult, since complete metalation is not always possible by simple means.

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## Experimental

All manipulations were carried out under purified dried dinitrogen by using standard Schlenk techniques. Solvents were dried and distilled under dinitrogen prior to use. – NMR: AC 200 Bruker, TMS as internal standard for <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} and Me<sub>2</sub>Se as external standard for <sup>77</sup>Se, frequencies <sup>1</sup>H 200.1, <sup>13</sup>C 50.3, and <sup>77</sup>Se 38.2 MHz. – MS: Finnigan MAT 8430. cpW(CO)<sub>3</sub>Cl was prepared according to the literature method<sup>[19]</sup>. *o*-, *m*-, *p*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>Br)<sub>2</sub>,

$C_6H_5CHBr_2$ , *o*-, *m*- $C_6H_4(CHBr_2)_2$ ,  $C_6H_5CCl_3$  and  $C_6H_5CH_2Cl$  were purchased from Aldrich.

**Isolation of Benzyl( $\eta^5$ -cyclopentadienyl)(tricarbonyl)tungsten(II) cp(CO)<sub>3</sub>WCH<sub>2</sub>Ph (1):** cp(CO)<sub>3</sub>WCH<sub>2</sub>Ph was isolated by chromatographic work-up on silica gel of the crude reaction mixture obtained from the synthesis of cp(CO)<sub>3</sub>WSeCH<sub>2</sub>Ph<sup>[9]</sup>. A mixture of CH<sub>2</sub>Cl<sub>2</sub> and hexanes (1:2) afforded first a yellow band, which corresponded to a small amount of **1**. The second (red) band was the selenolato-complex cp(CO)<sub>3</sub>WSeCH<sub>2</sub>Ph as the main product. The <sup>1</sup>H-NMR spectrum of **1** was identical with the published one<sup>[20]</sup>. – <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 27.8 [s, CH<sub>2</sub>], 92.7 [s, C<sub>5</sub>H<sub>5</sub>], 123.7, 127.3, 127.9 [s, C<sub>6</sub>H<sub>5</sub>], 151.8 [s, *ipso*-carbon of C<sub>6</sub>H<sub>5</sub>R], 218.3, 228.7 [s, CO].

**General Synthetic Route for the Synthesis of *o*-, *m*-, and *p*-( $\mu$ -Xylylselenolato)bis[ $\eta^5$ -cyclopentadienyltricarbonyltungsten(II)] (2, 3, 4):** LiSeWcp(CO)<sub>3</sub> was prepared from cpW(CO)<sub>3</sub>Cl (0.5 g, 1.357 mmol), a 1 M LiBEt<sub>3</sub>H solution in THF (4 ml, 4 mmol), grey selenium (0.109 g, 1.357 mmol), and *t*BuOH (0.5 ml, 5.2 mmol) in 50 ml THF according to a method described in the literature<sup>[13]</sup>. The reaction mixtures were treated with *o*-, *m*-, and *p*-C<sub>6</sub>H<sub>5</sub>(CH<sub>2</sub>Br)<sub>2</sub> (0.180 g, 0.679 mmol), respectively. The deep brown mixtures turned deep red immediately. After stirring for 2 h at ambient temperature, the solutions were evaporated to dryness. The crude product mixtures were dissolved in 20 ml of CH<sub>2</sub>Cl<sub>2</sub> and the remaining LiBr was removed via filtration through Celite. Chromatographic work-up on silica gel using a mixture of CH<sub>2</sub>Cl<sub>2</sub> and hexanes (b.p. 40–60°C) in a ratio of 2:1 as eluent afforded traces of yellow by-products. After increasing the ratio up to 3:1, second (red) bands were separated and characterised as [cpW(CO)<sub>3</sub>]<sub>2</sub> in all cases. The third bands, which are likewise red, contained the complexes **2**, **3**, and **4**.

**$\mu$ -(*o*-Xylylselenolato)bis[ $\eta^5$ -cyclopentadienyl)(tricarbonyl)tungsten(II)] (2):** Yield 0.180 g (29%), m.p. 178°C. – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 3.82 [s, CH<sub>2</sub>], 5.43 [s, C<sub>5</sub>H<sub>5</sub>], 7.21 [m, C<sub>6</sub>H<sub>4</sub>]. – <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 20.9 [s, CH<sub>2</sub>], 92.7 [s, C<sub>5</sub>H<sub>5</sub>], 126.9 [s, unsubstituted carbon atoms of C<sub>6</sub>H<sub>4</sub>R<sub>2</sub>], 140.3 [s, *ipso* carbon atoms of C<sub>6</sub>H<sub>4</sub>R<sub>2</sub>], 212.0 [s, CO]. – <sup>77</sup>Se NMR (CDCl<sub>3</sub>):  $\delta$  = –356.2 s. – IR (CH<sub>2</sub>Cl<sub>2</sub>, NaCl) [v(CO)]: 2018 s, 1925 vs. – MS (EI), *m/z*: 824 [cpW(CO)<sub>3</sub>]<sub>2</sub>Se<sup>+</sup>, 768 [cpW(CO)<sub>2</sub>]<sub>2</sub>Se<sup>+</sup>, 740 [cpW(CO)<sub>2</sub>SeSeW(CO)cp]<sup>+</sup> (100%). – C<sub>24</sub>H<sub>18</sub>O<sub>6</sub>Se<sub>2</sub>W<sub>2</sub> (928.00): calcd. C 31.08, H 1.96; found C 30.85, H 1.80.

**$\mu$ -(*m*-Xylylselenolato)bis[ $\eta^5$ -cyclopentadienyl)(tricarbonyl)tungsten(II)] (3):** Yield 0.240 g (38%), m.p. 122°C. – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 3.60 [s, CH<sub>2</sub>], 5.37 [s, C<sub>5</sub>H<sub>5</sub>], 7.21 [m, C<sub>6</sub>H<sub>4</sub>]. – <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 22.8 [s, CH<sub>2</sub>], 92.5 [s, C<sub>5</sub>H<sub>5</sub>], 127.2, 128.5, 129.7 [s, unsubstituted carbon atoms of C<sub>6</sub>H<sub>4</sub>R<sub>2</sub>], 142.4 [s, *ipso* carbon atoms of C<sub>6</sub>H<sub>4</sub>R<sub>2</sub>], 211.9, 222.9 [s, CO]. – <sup>77</sup>Se NMR (CDCl<sub>3</sub>):  $\delta$  = –328.4 s. – IR (CH<sub>2</sub>Cl<sub>2</sub>, NaCl) [v(CO)]: 2019 s, 1921 vs. – MS (EI), *m/z*: 930 [C<sub>6</sub>H<sub>4</sub>[SeWcp(CO)<sub>3</sub>]<sub>2</sub>]<sup>+</sup>, 666 [cpW(CO)<sub>3</sub>]<sub>2</sub><sup>+</sup> = A, 610 [A – 2 CO]<sup>+</sup>, 582 [A – 3 CO]<sup>+</sup>, 554 [A – 4 CO]<sup>+</sup>, 526 [A – 5 CO]<sup>+</sup> (100%), 498 [A – 6 CO]<sup>+</sup>. – C<sub>24</sub>H<sub>18</sub>O<sub>6</sub>Se<sub>2</sub>W<sub>2</sub> (928.00): calcd. C 31.08, H 1.96; found C 31.11, H 2.02.

**$\mu$ -(*p*-Xylylselenolato)bis[ $\eta^5$ -cyclopentadienyl)(tricarbonyl)tungsten(II)] (4):** Yield 0.240 g (38%), m.p. 133°C. – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 3.61 [s, CH<sub>2</sub>], 5.35 [s, C<sub>5</sub>H<sub>5</sub>], 7.20 [s, C<sub>6</sub>H<sub>4</sub>]. – <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 22.6 [s, CH<sub>2</sub>], 92.6 [s, C<sub>5</sub>H<sub>5</sub>], 129.1 [s, unsubstituted carbon atoms of C<sub>6</sub>H<sub>4</sub>R<sub>2</sub>], 140.6 [s, *ipso* carbon atoms of C<sub>6</sub>H<sub>4</sub>R<sub>2</sub>], 211.8, 222.8 [s, CO]. – <sup>77</sup>Se NMR (CDCl<sub>3</sub>):  $\delta$  = –322.7 s. – IR (CH<sub>2</sub>Cl<sub>2</sub>, NaCl) [v(CO)]: 2019 s, 1925 vs. – MS (EI), *m/z*: 930 [C<sub>6</sub>H<sub>4</sub>[SeW(CO)<sub>3</sub>cp]<sub>2</sub>]<sup>+</sup>, 824 [cpW(CO)<sub>3</sub>]<sub>2</sub>Se<sup>+</sup>, 666 [cpW(CO)<sub>3</sub>]<sub>2</sub><sup>+</sup> = A, 582 [A – 3 CO]<sup>+</sup>

(100%). – C<sub>24</sub>H<sub>18</sub>O<sub>6</sub>Se<sub>2</sub>W<sub>2</sub> (928.00): calcd. C 31.08, H 1.96; found C 30.50, H 1.93.

**$\mu$ -(Benzylidene)bis[ $\eta^5$ -cyclopentadienyl)(tricarbonyl)tungsten(II)] Dichloromethane Solvate (5):** LiSeWcp(CO)<sub>3</sub> was prepared from cpW(CO)<sub>3</sub>Cl (1.0 g, 2.714 mmol), a 1 M LiBEt<sub>3</sub>H solution in THF (6 ml, 6 mmol), grey Se (0.214 g, 2.714 mmol), and *t*BuOH (1 ml, 10.4 mmol) in 30 ml THF. A solution of  $\alpha,\alpha$ -dibromotoluene PhCHBr<sub>2</sub> (0.35 g, 1.357 mmol) in 10 ml of THF was added dropwise via a syringe to the brown reaction mixture within 30 min. After stirring at ambient temperature for 16 h the resulting deep red solution was evaporated to dryness. Addition of 10 ml of CH<sub>2</sub>Cl<sub>2</sub> and removal of LiBr over Celite afforded a deep red solution, which was reduced to 5 ml. Chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub> as eluent gave first a yellow band of a by-product. The second, deep red band was the main product, which was recrystallised from CH<sub>2</sub>Cl<sub>2</sub>/hexanes. Yield 0.513 g (41%), m.p. 88°C (dec.). – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 4.74 [s, CH], 5.28 [s, CH<sub>2</sub>Cl<sub>2</sub>], 5.35 [s, C<sub>5</sub>H<sub>5</sub>], 7.26 [m, *o*- and *p*-C<sub>6</sub>H<sub>5</sub>], 7.45 [m, *m*-C<sub>6</sub>H<sub>5</sub>]. – <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): 28.0 [s, CH], 92.5 [s, C<sub>5</sub>H<sub>5</sub>], 126.7, 127.9, 128.1 [s, unsubstituted carbon atoms of C<sub>6</sub>H<sub>5</sub>R], 147.2 [s, *ipso* carbon atom of C<sub>6</sub>H<sub>5</sub>R], 211.8, 212.2 [s, CO]. – <sup>77</sup>Se NMR (CDCl<sub>3</sub>): –160.3 s. – C<sub>24</sub>H<sub>18</sub>Cl<sub>2</sub>O<sub>6</sub>Se<sub>2</sub>W<sub>2</sub> (998.93): calcd. C 28.87, H 1.82; found C 28.85, H 1.62. – IR (CH<sub>2</sub>Cl<sub>2</sub>, NaCl) [v(CO)]: 2023 s, 2013 s, 1929 s. – MS (EI), *m/z*: 824 [cpW(CO)<sub>3</sub>]<sub>2</sub>Se<sup>+</sup>, 744 [cpW(CO)<sub>3</sub>]<sub>2</sub>Se<sup>+</sup>.

**$\alpha,\alpha$ -Dichlorobenzylselenolato( $\eta^5$ -cyclopentadienyl)(tricarbonyl)tungsten(II) (6):** The synthesis was performed as described above, but required a 1 M NaBEt<sub>3</sub>H solution in THF. Four different bands were separated from the column (silica gel, CH<sub>2</sub>Cl<sub>2</sub> as eluent). The first (yellow) band contained 50 mg of a by-product. – <sup>1</sup>H NMR ([D<sub>6</sub>]acetone):  $\delta$  = 7.26 [s, C<sub>5</sub>H<sub>5</sub>], 7.27 [m, *m*-C<sub>6</sub>H<sub>5</sub>], 7.32 [m, *p*-C<sub>6</sub>H<sub>5</sub>], 7.46 [m, *o*-C<sub>6</sub>H<sub>5</sub>]. – The second deep blue band contained the title compound. Yield 0.631 g (41%), m.p. 128°C (dec.). – <sup>1</sup>H NMR ([D<sub>6</sub>]acetone):  $\delta$  = 5.87 [s, C<sub>5</sub>H<sub>5</sub>], 7.35 [dt, *m*-C<sub>6</sub>H<sub>5</sub>, <sup>3</sup>J<sub>H-H</sub> 7 Hz], 7.66 [dt, *p*-C<sub>6</sub>H<sub>5</sub>, <sup>3</sup>J<sub>H-H</sub> 7 Hz], 7.82 [m, *o*-C<sub>6</sub>H<sub>5</sub>]. – <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 90.8 [s, C<sub>5</sub>H<sub>5</sub>], 92.3 [s, CCl<sub>2</sub>], 120.1 [s, unsubstituted carbon atoms of C<sub>6</sub>H<sub>5</sub>], 150.7 [s, *ipso*-carbon of C<sub>6</sub>H<sub>5</sub>], 204.6, 214.3 [s, CO]. – <sup>77</sup>Se NMR (CDCl<sub>3</sub>):  $\delta$  = +782, s. – C<sub>15</sub>H<sub>10</sub>Cl<sub>2</sub>O<sub>3</sub>SeW (571.96): calcd. C 31.50, H 1.76; found C 30.83, H 1.80. – IR (CH<sub>2</sub>Cl<sub>2</sub>, NaCl) [v(CO)]: 1952 s, br, 1878 s. – MS (EI), *m/z*: 572 [M]<sup>+</sup>, 498 [cpW(CO)<sub>3</sub>]<sub>2</sub> – 6 CO]<sup>+</sup> (100%). After a brown band, which consisted of a small amount of several inseparable by-products, a green band of [cpW(CO)<sub>3</sub>]<sub>2</sub>Se<sub>2</sub> occurred. Yield 0.100 g (9%).

**$\mu$ -(*m*-Xylylidene)tetrakis[ $\eta^5$ -cyclopentadienyl)(tricarbonyl)tungsten(II)] (7):** The synthesis was the same as described for **6**, but a 1 M LiBEt<sub>3</sub>H solution in THF was used. Two bands were separated from the column (CH<sub>2</sub>Cl<sub>2</sub>, silica gel); the first (yellow) band (50 mg) contained one by-product, whereas the second (deep red) band contained the title compound. Yield 0.230 g (20%), m.p. 160°C. – <sup>1</sup>H NMR ([D<sub>6</sub>]acetone):  $\delta$  = 4.82 [s, CH], 5.70 [s, C<sub>5</sub>H<sub>5</sub>], 7.28 [m, 3 H, C<sub>6</sub>H<sub>4</sub>], 7.61 [m, 1 H, C<sub>6</sub>H<sub>4</sub>]. – <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 29.6 [s, CH], 93.0 [s, C<sub>5</sub>H<sub>5</sub>], 126.3, 127.7, 134.6 [s, unsubstituted carbon atoms, C<sub>6</sub>H<sub>4</sub>], 147.6 [s, *ipso* carbon atoms of C<sub>6</sub>H<sub>4</sub>R<sub>2</sub>], 212.5, 212.7, 223.4 [s, CO]. – <sup>77</sup>Se NMR (CDCl<sub>3</sub>): –159.5 s. – C<sub>40</sub>H<sub>26</sub>O<sub>12</sub>Se<sub>4</sub>W<sub>4</sub> (1749.87): calcd. C 27.46, H 1.50; found C 27.25, H 1.66. – IR (CH<sub>2</sub>Cl<sub>2</sub>, NaCl) [v(CO)]: 2021 s, 2011 vs, 1928 s. – MS (EI), *m/z*: 1312 [M, – CO, – SeW(CO)<sub>3</sub>cp]<sup>+</sup>, 1088 [M, – 9 CO, – SeW(CO)<sub>3</sub>cp]<sup>+</sup> (100%).

**Crystal Structure Determination:** Suitable crystals of compounds **1**, **3**, **4**, and **5** were grown from CH<sub>2</sub>Cl<sub>2</sub>/hexanes (**1**, **3**, and **4**; ambient temperature) or EtOH (**5**; –30°C), mounted on glass fibers in

Table 2. X-ray structure analyses, details of solution and refinement

	1	3	4	5
Empirical formula	C <sub>15</sub> H <sub>12</sub> O <sub>3</sub> W	C <sub>24</sub> H <sub>18</sub> O <sub>6</sub> Se <sub>2</sub> W <sub>2</sub>	C <sub>24</sub> H <sub>18</sub> O <sub>6</sub> Se <sub>2</sub> W <sub>2</sub>	C <sub>23</sub> H <sub>22</sub> O <sub>7</sub> Se <sub>2</sub> W <sub>2</sub>
Mol. mass [g mol <sup>-1</sup> ]	424.10	928.00	928.00	960.05
Crystal system	orthorhombic	triclinic	monoclinic	monoclinic
Space group (no.)	<i>Pbca</i> (61)	<i>P</i> $\bar{1}$ (2)	<i>C2/c</i> (15)	<i>P2<sub>1</sub>/m</i> (11)
<i>a</i> [Å]	16.657(2)	6.5200(10)	10.615(3)	8.488(2)
<i>b</i> [Å]	8.7697(12)	6.7051(12)	8.067(2)	16.743(3)
<i>c</i> [Å]	17.850(2)	14.548(2)	28.842(7)	9.434(2)
$\alpha$ [°]	90	80.609(12)	90	90
$\beta$ [°]	90	84.286(8)	96.47(2)	98.99(2)
$\gamma$ [°]	90	75.953(12)	90	90
<i>V</i> [Å <sup>3</sup> ]	2607.4(6)	607.5(2)	2453.9(10)	1324.3(5)
$\rho_{\text{calc}}$ [g cm <sup>-3</sup> ]	2.16	2.54	2.51	2.41
<i>Z</i>	8	1	4	2
<i>F</i> (000) [e]	1600	426	1704	888
$\mu$ [cm <sup>-1</sup> ]	88.6	124.9	123.7	114.7
Crystal size [mm]	0.36×0.18×0.08	0.20×0.15×0.10	0.40×0.30×0.10	0.53×0.13×0.13
$2\theta_{\text{max}}$ [°]	50	50	50	55
<i>T</i> [°C]	-100	-100	-100	-130
Measured refl.	4488	3465	3535	9971
Unique refl.	2294	2137	2145	3139
<i>R</i> <sub>int</sub>	0.0548	0.0202	0.0421	0.0245
No. of param.	172	154	155	179
No. of restraints	115	85	93	133
Transm. (min./max.)	0.62/0.69	0.66/0.93	0.19/0.63	0.52/0.82
<i>R</i> ( <i>F</i> ), <i>F</i> > 4 $\sigma$ ( <i>F</i> ) <sup>[a]</sup>	0.0283	0.0302	0.0290	0.0234
<i>R</i> <sub>w</sub> ( <i>F</i> <sup>2</sup> ), all refl. <sup>[b]</sup>	0.0564	0.0745	0.0688	0.0571
Weight. param. ( <i>a</i> , <i>b</i> )	0.0175, 0	0.0464, 0	0.05115, 0	0.0288, 2.547
$S$ <sup>[c]</sup>	0.82	1.04	0.99	1.10
max. $\Delta/\sigma$	< 0.001	< 0.001	< 0.001	< 0.001
$\rho_{\text{diff}}$ (max./min.) [e Å <sup>-3</sup> ]	1.72/-1.04	3.34/-1.31	1.12/-1.43	1.20/-0.88

[a]  $R(F) = \frac{\sum \|F_o\| - |F_c|}{\sum \|F_o\|} \times 100$ ,  $wR(F^2) = \frac{\sum \{w(F_o^2 - F_c^2)^2\}}{\sum \{w(F_o^2)^2\}}^{0.5}$ ;  $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ , where  $P = [F_o^2 + 2F_c^2]/3$  and *a* and *b* are constants adjusted by the program. - [c]  $S = \frac{\sum \{w(F_o^2 - F_c^2)^2\}}{\sum \{w(F_o^2)^2\}}^{0.5}$ , where *n* is the number of data and *p* the number of parameters.

inert oil and transferred to the cold gas stream of the diffractometers (1, 3, and 4 Siemens P4, -100°C; 5 Stoe STADI 4, -130°C), both equipped with an LT-2 low-temperature attachment. Mo-*K* $\alpha$  radiation ( $\lambda = 0.71073$  Å, graphite monochromator) was used to collect the intensity data (1, 3, and 4  $\omega$ -scans; 5  $\omega/\theta$ -scans). Cell constants were refined from setting angles of 62 reflections in the  $2\theta$  range 8–23° (1, 3, and 4; Siemens), or from  $\pm\omega$  values of 60 reflections in the  $2\theta$  range 20–23° (5; Stoe). Absorption corrections based on  $\Psi$ -scans were applied.

The crystallographic program system used was SHELXL-93<sup>[21]</sup>. All structures were solved by direct methods and refined by full-matrix least-squares procedures on *F*<sup>2</sup>. All non H atoms were refined anisotropically; hydrogen atoms were included by using a riding model. The final difference Fourier maps were featureless; in the case of 3, the highest peak of 3.34 e Å<sup>-3</sup> is located near the

carbonyl carbon atom C7 and many be associated with unidentified disorder or twinning phenomena. Additional crystallographic data are presented in Table 2. Selected bond lengths and angles are listed in the Figure captions<sup>[22]</sup>.

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[96099]