Organometallic Selenolates. 5.[1] Synthesis and Complexing Properties of 2-Propene- and 2-Methyl-2-propeneselenolato Molybdenum and Tungsten Compounds. Crystal Structures of cp(CO)$_3$WSeCH$_2$C(CH$_3$)=CH$_2$, [cp(CO)$_2$MoSeCH$_2$C(CH$_3$)=CH$_2$]$_2$, [cp(CO)$_3$Mo(μ-SeCH$_2$C(CH$_3$)=CH$_2$)W(CO)$_5$], [cp(CO)$_3$Mo(μ-SeCH$_2$C(CH$_3$)=CH$_2$)Mo(CO)$_5$], and [cp(CO)$_3$Mo(μ-SeCH$_2$CH=CH$_2$)Mo(CO)$_5$]

Peter G. Jones, Jörg Laube, and Carsten Thöne*

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany

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2-Propene- and 2-methyl-2-propeneselenolato complexes of molybdenum(II) and tungsten(II) have been prepared via insertion of gray selenium into alkali-metal−molybdenum and −tungsten bonds and subsequent reaction with allyl and β-methallyl chlorides. The complexes are monomeric in the solid state. The (β-methallyl)molybdenum compound cp(CO)$_3$MoSeCH$_2$C(CH$_3$)=CH$_2$ (**2**) decomposes slowly in solution with CO loss and formation of the corresponding dimer [cp(CO)$_2$MoSeCH$_2$C(CH$_3$)=CH$_2$]$_2$ (**3**), whose crystal structure has been determined (C$_{22}$H$_{24}$Mo$_2$O$_4$Se$_2$, monoclinic, $P2_1/c$, $a = 11.151(2)$ Å, $b = 13.436(3)$ Å, $c = 16.872(3)$ Å, $\beta = 102.42(2)°$, $Z = 4$). A monomeric structure has been found for cp(CO)$_3$WSeCH$_2$C(CH$_3$)=CH$_2$ (**5**) (C$_{12}$H$_{12}$O$_3$SeW, triclinic, $P\bar{1}$, $a = 7.592(3)$ Å, $b = 7.700(3)$ Å, $c = 12.296(5)$ Å, $\alpha = 98.31(4)°$, $\beta = 104.24(2)°$, $\gamma = 108.49(3)°$, $Z = 2$). Additionally, the complexing properties of the selenolato complexes have been investigated. The reactions of the molybdenum complexes cp(CO)$_3$MoSeCH$_2$CH=CH$_2$ (**1**) and (**2**) with the metal(0)−carbonyl complexes W(CO)$_5$(THF), (CH$_3$CN)$_3$Mo(CO)$_3$, and (η^6-C$_7$H$_8$)Mo(CO)$_3$ (C$_7$H$_8$ = cycloheptatriene) led to the formation of [cp(CO)$_3$Mo(μ-SeCH$_2$C(CH$_3$)=CH$_2$)M(CO)$_5$] (M = W (**6**), Mo (**7**)) and [cp(CO)$_3$Mo(μ-SeCH$_2$CH=CH$_2$)Mo(CO)$_5$] (**8**), respectively. **6** and **7** are isostructural and crystallize in the monoclinic space group $P2_1/n$ (**6**, C$_{17}$H$_{12}$MoO$_8$SeW, $a = 14.708(2)$ Å, $b = 9.837(2)$ Å, $c = 14.958(2)$ Å, $\beta = 103.030(10)°$, $Z = 4$; **7**, C$_{17}$H$_{12}$Mo$_2$O$_8$Se, $a = 14.712(2)$ Å, $b = 9.8670(10)$ Å, $c = 14.982(2)$ Å, $\beta = 103.100(10)°$, $Z = 4$), whereas [cp(CO)$_3$Mo(μ-SeCH$_2$CH=CH$_2$)Mo(CO)$_5$] (**8**) crystallizes in the noncentrosymmetric orthorhombic space group $Pna2_1$ (C$_{16}$H$_{10}$Mo$_2$O$_8$Se, $a = 18.638(4)$ Å, $b = 9.707(2)$ Å, $c = 11.169(3)$ Å, $Z = 4$). Furthermore, ^{77}Se-NMR spectra displayed chemical shifts consistent with earlier results on related complexes.

Introduction

The chemistry of metal selenolate complexes is a growing area of current interest, associated with unusual structural aspects, new synthetic methods, and novel applications.[2] Important syntheses of organoselenolate complexes are metatheses of alkali-metal organoselenolates with appropriate transition-metal halo complexes and oxidative additions of diorgano diselenides to unsaturated metal complexes.[3] These routes require the accessibility of the corresponding organoseleno compounds, the syntheses of which are only straightforward in the case of simple organic groups (*e.g.* Me, Ph, and their substituted derivatives) or sterically hindered groups such as −E(SiMe)$_3$; E = C, Si,[4] or 2,6-*i*-Pr$_2$C$_6$H$_3$ and related aryls.[2,5]

We have employed oxidative addition to synthesize *Se,N*-complexes of the pyridineselenolate anion,[6] which are also in some cases accessible via proton transfer from pyridineselenol.[7]

Recent studies in our laboratory have shown that (organoselenolato)metal complexes can be synthesized via selenium insertion into alkali-metal−transition-metal bonds of carbonylates and subsequent reactions with organohalides.[8] These reactions can be performed under mild conditions, and the intermediate, usually malodorous organoseleno compounds need not be isolated. Additionally, this method allows the substitution of organodi- and tetrahalides, whereas the straightforward transformation of these halides into the corresponding selenolates is not always possible.

Here we report the extension of this method to the allyl halides CH$_2$=CHCH$_2$X and CH$_2$=C(CH$_3$)CH$_2$Cl; (X = Cl, Br), together with studies on the complexing properties of the new allylic selenolato complexes.

Experimental Section

All preparations were performed under dry nitrogen atmosphere. Solvents were dried by standard methods and distilled under nitogen

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prior to use. Allyl chloride, allyl bromide, β-methallyl chloride (Aldrich), gray selenium (Jansen), 1 m LiBEt$_3$H in THF (Fluka), Mo-(CO)$_6$, and W(CO)$_6$ (Acros) were used as received. [cpMo(CO)$_3$]$_2$, [(CH$_3$CN)$_3$Mo(CO)$_3$], [W(CO)$_5$(THF)], and cpW(CO)$_3$Cl were prepared according to literature methods.[9−12]

All NMR spectra were recorded in C$_6$D$_6$ on a Bruker AC 200 spectrometer: ^{1}H at 200.1 MHz, TMS internal; ^{13}C at 50.3 MHz, TMS internal; ^{77}Se at 38.2 MHz, Me$_2$Se external. Heteronuclear NMR spectra were recorded proton-decoupled. IR spectra were measured on a Bio-Rad FTS 165 spectrometer as CH$_2$Cl$_2$ solutions between KBr plates. For mass spectra, a Finnigan MAT 8430 device was used. The elemental analyses were carried out by the analytical laboratory of the Chemical Institutes of this university.

cp(CO)$_3$MoSeCH$_2$CH=CH$_2$ (1) and cp(CO)$_3$MoSeCH$_2$C-(CH$_3$)=CH$_2$ (2). LiSeMo(CO)$_3$cp solutions in 40 mL of THF were prepared from [cpMo(CO)$_3$]$_2$ (1 g, 2.04 mmol), 1 m LiBEt$_3$H solution in THF (4.1 mL, 4.1 mmol), and gray selenium (0.315 g, 4.08 mmol) according to the published method.[8a] The deep red-brown reaction mixtures were treated with an excess of allyl chloride (0.5 mL, 6.1 mmol) (1) or β-methallyl chloride (0.5 mL, 5.1 mmol) (2) via a syringe. The color changed to deep red immediately. After 15 h of stirring with exclusion of light, the solvent was removed in vacuo and the remaining residue was extracted with 30 mL of CH$_2$Cl$_2$. The mixture was filtered over Celite to remove LiCl. Chromatographic workup on silica gel (20 × 3 cm; 1:1 CH$_2$Cl$_2$/hexanes as eluent) afforded 1 and 2 as deep red second fractions. The first, also deep red, fractions were identified as small quantities of [cpMo(CO)$_3$]$_2$ in both cases. Products were obtained by recrystallization from toluene/hexanes at −60 °C. In case of the 2-methyl-2-propeneselenolato complex, a small quantity of a red decomposition product crystallized when a solution of 2 in CH$_2$Cl$_2$ was layered with diethyl ether and left to stand for 2 weeks. This product was identified as the dimeric complex [cp(CO)$_2$MoSeCH$_2$C-(CH$_3$)=CH$_2$]$_2$ (3) by X-ray crystallography (*vide infra*).

Physical Data for 1. Yield: 465 mg (31%), dark-red crystals. Mp: 37 °C. ^{1}H-NMR: δ 3.16 (d, 2H, −CH$_2$−, $^3J_{H-H}$ 7.7 Hz), 4.62 (s, 5H, C$_5$H$_5$), 4.83 (d, 1H, *cis* H$_2$C=CH−, $^3J_{H-H}$ 9.7 Hz), 5.05 (d, 1H, *trans* H$_2$C=CH−, $^3J_{H-H}$ 16.7 Hz), 5.90 (ddt, 1H, =CH−). ^{13}C-NMR: δ 22.74 (−CH$_2$−), 93.66 (C$_5$H$_5$), 114.58 (=CH$_2$), 139.01 (=CH−), 223.35, 236.31 (CO). ^{77}Se-NMR: δ −354.8 s. IR [ν(CO)], cm^{-1}: 2051 s, 1978 s, 1960 s. MS (EI), m/z (%): 366 (15) [M]$^+$, 338 (10) [M − CO]$^+$, 282 (19) [M − 3CO]$^+$. Anal. Calcd for C$_{11}$H$_{10}$MoO$_3$Se: C, 36.19; H, 2.76. Found: C, 35.92; H, 2.75.

Physical Data for 2. Yield: 1.066 g (69%), dark-red crystals. Mp. 70 °C. ^{1}H-NMR: δ 1.91 (dd, 3H, CH$_3$, $^4J_{H-H}$ 0.8 Hz, *trans* H$_2$C=C-(CH$_3$)−, 1.4 Hz, *cis* H$_2$C=C(CH$_3$)−), 3.19 (d, 2H, −CH$_2$−, $^4J_{H-H}$ 0.9 Hz, *trans* H$_2$C=C(CH$_3$)−, $^2J_{Se-H}$ 9.4 Hz from ^{77}Se satellites), 4.64 (s, 5H, C$_5$H$_5$), 4.76 (dq, 1H, *cis* CH$_2$=, $^2J_{H-H}$ 1.7 Hz), 4.98 (dtq, 1H, *trans* CH$_2$=). ^{13}C-NMR: δ 21.80 (−CH$_2$−), 28.16 (CH$_3$), 93.55 (C$_5$H$_5$), 111.98 (=CH$_2$), 146.14 (C−CH$_3$), 223.34, 236.50 (CO). ^{77}Se-NMR: δ −363.5 s. IR [ν(CO)], cm^{-1}: 2023 s, 1931 s, br. MS (EI), m/z (%): 380 (12) [M]$^+$, 352 (11) [M − CO]$^+$, 298 (77) [M − 3CO]$^+$. Anal. Calcd for C$_{12}$H$_{12}$MoO$_3$Se: C, 38.02; H, 3.19. Found: C, 38.25; H, 3.27.

cp(CO)$_3$WSeCH$_2$CH=CH$_2$ (4) and cp(CO)$_3$WSeCH$_2$C(CH$_3$)=CH$_2$ (5). The synthetic and workup procedure was the same as for the corresponding molybdenum complexes. cpW(CO)$_3$Cl (1 g, 2.71 mmol), 1 m LiBEt$_3$H solution in THF (5.5 mL, 5.5 mmol), gray selenium (213 mg, 2.71 mmol), and allyl chloride (0.5 mL, 6.1 mmol) (4) or β-methallyl chloride (0.5 mL, 5.1 mmol) (5) were employed. After elution of small quantities of a yellow byproduct, 4 and 5 were eluted as deep-red main fractions.

Physical Data for 4. Yield: 509 mg (42%), red crystals. Mp: 43 °C. ^{1}H-NMR: δ 3.13 (d, 2H, −CH$_2$−, $^3J_{H-H}$ 8.1 Hz), 4.64 (s, 5H, C$_5$H$_5$), 4.83 (d, 1H, *cis* H$_2$C=CH−, $^3J_{H-H}$ 9.9 Hz), 5.01 (d, 1H, *trans* H$_2$C=CH−, $^3J_{H-H}$ 16.7 Hz), 5.83 (ddt, 1H, =CH−). ^{13}C-NMR: δ 22.69 (−CH$_2$−), 92.35 (C$_5$H$_5$), 114.85 (=CH$_2$), 138.99 (=CH−),

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212.45, 224.42 (CO). ^{77}Se-NMR: δ − 401.8 s. IR [ν(CO)], cm^{-1}: 2020 s, 1941 vs, 1922 s. MS (EI), m/z (%): 454 (26) [M]$^+$, 385 (100) [M − CO − CH$_2$CH=CH$_2$]$^+$. Anal. Calcd for C$_{11}$H$_{10}$O$_3$SeW: C, 29.16; H, 2.22. Found: C, 28.56; H, 2.20.

Physical Data for 5. Yield: 807 mg (64%), dark-red crystals. Mp: 90 °C. ^{1}H-NMR: δ 1.87 (s, 3H, CH$_3$), 3.16 (s, 2H, −CH$_2$−), 4.64 (s, 5H, C$_5$H$_5$), 4.67 (s, 1H, *cis* H$_2$C=C(CH$_3$)−), 4.98 (s, 1H, *trans* H$_2$C=C(CH$_3$)−). ^{13}C-NMR: δ 21.79 (−CH$_2$−), 28.19 (CH$_3$), 92.27 (C$_5$H$_5$), 111.91 (=CH$_2$), 146.04 (=C(CH$_3$)−), 212.54, 224.63 (CO). ^{77}Se-NMR: δ −411.4 s. IR [ν(CO)], cm^{-1}: 2020 vs, 1925 vs, br. MS (EI), m/z (%): 468 (21) [M]$^+$, 384 (100) [M − 3 CO]$^+$. Anal. Calcd for C$_{12}$H$_{12}$O$_3$SeW: C, 30.86; H, 2.59. Found: C, 30.51; H, 2.56.

Reaction of LiSe$_x$W(CO)$_3$cp (x = 1, 2) with Allyl Bromide. The use of freshly distilled allyl bromide, instead of the chloride, as the organic electrophile for the reaction with LiSe$_x$W(CO)$_3$cp led to the formation of [cpW(CO)$_3$]$_2$Se$_2$ (x = 1) and [cpW(CO)$_3$]$_2$Se$_3$ (x = 2), respectively. The detailed workup procedure for this reaction is as published.[8c] The oligoselenido complexes thus obtained were identified from comparison with the corresponding ^{1}H-NMR data. The yields are lower than for the published oxidation procedure with O$_2$/SiO$_2$, and several unidentifiable byproducts were obtained.

[cp(CO)$_3$Mo(μ-SeCH$_2$C(CH$_3$)=CH$_2$)W(CO)$_5$] (6). W(CO)$_5$(THF) was prepared from a solution of W(CO)$_6$ (300 mg, 0.85 mmol) in 300 mL of THF according to the literature method. Solid cp(CO)$_3$-MoSeCH$_2$C(CH$_3$)=CH$_2$ (2) was added, and the resulting red solution was stirred for 1 h at room temperature. The chromatographic workup procedure (SiO$_2$, 20 × 3 cm, 1:1 CH$_2$Cl$_2$/hexanes) yielded complex 6 as the red main fraction after traces of green W(CO)$_5$(THF). A red crystalline product was obtained by recrystallization from CH$_2$Cl$_2$/hexanes at −60 °C. Yield: 315 mg (78%). Mp 118−120 °C. ^{1}H-NMR: δ 1.69 (s, 3H, CH$_3$), 3.24 (s, 2H, −CH$_2$−), 4.42 (s, 5H, C$_5$H$_5$), 4.85 (s, 1H, *cis* H$_2$C=C(CH$_3$)), 5.05 (s, 1H, *trans* H$_2$C=C(CH$_3$)). ^{13}C-NMR: δ 21.44 (−CH$_2$−), 42.20 (CH$_3$), 93.70 (C$_5$H$_5$), 116.34 (=CH$_2$), 142.56 (=C(CH$_3$)), 199.15 (W-CO), 200.0 (W−CO), 225.97 (Mo−CO), 234.20 (Mo−CO). ^{77}Se-NMR: δ −384.2 s. IR [ν(CO)], cm^{-1}: 2068 s, 2033 s, br, 1960 s, br, 1927 s, br, 1898 s. MS (EI), m/z (%): 704 (4) [M]$^+$, 620 (38) [M − 3CO]$^+$. Anal. Calcd for C$_{17}$H$_{12}$MoO$_8$SeW: C, 29.04; H, 1.72. Found: C, 28.56; H, 1.59.

[cp(CO)$_3$Mo(μ-SeCH$_2$C(CH$_3$)=CH$_2$)Mo(CO)$_5$] (7). Route A. Solutions of [cp(CO)$_3$MoSeCH$_2$C(CH$_3$)=CH$_2$] (2) (350 mg, 0.92 mmol) in 20 mL of toluene and (C$_7$H$_8$)Mo(CO)$_3$ (C$_7$H$_8$ = η^6-cycloheptatriene) (153 mg, 0.92 mmol) in 20 mL of toluene were combined and stirred for 3.5 h at room temperature. The solvent was removed in vacuo, and the chromatographic workup (SiO$_2$, 20 × 3 cm, 2:3 CH$_2$Cl$_2$/hexane) yielded first an orange band of (C$_7$H$_8$)Mo(CO)$_3$ and second the deep-red main fraction of complex 7. Recrystallization using CH$_2$Cl$_2$/hexanes at −60 °C afforded deep-red crystals. Yield: 111 mg (32%).

Route B. Mo(CH$_3$CN)$_3$(CO)$_3$ was prepared from Mo(CO)$_6$ (244 mg, 0.92 mmol) according to the literature method and dissolved in 40 mL of THF. 4 (350 mg, 0.92 mmol) in 20 mL of THF was added via a syringe, and the resulting deep-red solution was stirred for 4 h at room temperature. The chromatographic workup and results were the same as for route A except for the first green band, which contained a small amount of Mo(CH$_3$CN)$_3$(CO)$_3$. Yield: 241 mg (43%). Mp: 107 °C. ^{1}H-NMR: δ 1.69 (s, 3H, CH$_3$), 3.13 (s, 2H, −CH$_2$−), 4.43 (s, 5H, C$_5$H$_5$), 4.81 (s, 1H, *cis* H$_2$C=C(CH$_3$)), 5.03 (s, 1H, *trans* H$_2$C=C-(CH$_3$)). ^{13}C-NMR: δ 21.52 (−CH$_2$−), 40.63 (CH$_3$), 93.61 (C$_5$H$_5$), 115.88 (=CH$_2$), 147.70 (=C(CH$_3$), 206.26, 213.34, 225.38, 234.47 (CO). ^{77}Se-NMR: δ −301.5 s. IR [ν(CO)], cm^{-1}: 2070 s, 2062 m, 2033 s, 1960 s, br, 1937 s, br, 1902 s, br. MS (EI), m/z (%): 616 (20) [M]$^+$, 532 (45) [M − 3 CO]$^+$. Anal. Calcd for C$_{17}$H$_{12}$Mo$_2$O$_8$Se: C, 33.19; H, 1.97. Found: C, 33.15; H, 1.91.

[cp(CO)$_3$Mo(μ-SeCH$_2$CH=CH$_2$)Mo(CO)$_5$] (8). The preparation and workup procedure is the same as route B for complex 7. Mo-(CO)$_6$ (269 mg, 1.02 mmol) and cp(CO)$_3$MoSeCH$_2$CH=CH$_2$ (1) (372 mg, 1.02 mmol) were employed. Yield: 211 mg (35%). Mp: 89 °C. ^{1}H-NMR: δ 3.06 (d, 2H, −CH$_2$−, $^3J_{H-H}$ 7.7 Hz), 4.44 (s, 5H, C$_5$H$_5$), 4.97 (d, 1H, *cis* H$_2$C=CH, $^3J_{H-H}$ 9.9 Hz), 5.11 (d, 1H, *trans* H$_2$C=CH, $^3J_{H-H}$ 16.7 Hz), 5.67 (ddt, 1H, =CH−). ^{13}C-NMR: δ 34.26 (−CH$_2$−), 93.77 (C$_5$H$_5$), 119.05 (=CH$_2$), 136.18 (=CH−), 206.26, 212.24, 217.29, 225.41, 234.30 (CO). ^{77}Se-NMR: δ −326.6 s. IR [ν(CO)], cm^{-1}: 2072 s, 2033 s, 1958 s, br, 1939 s, br, 1900 s, br. MS (EI) (%)

Table 1. Crystallographic Data for Complexes **3** and **5−8**

	3	**5**	**6**	**7**	**8**
empirical formula	$C_{22}H_{24}Mo_2O_4Se_2$	$C_{12}H_{12}O_3SeW$	$C_{17}H_{12}MoO_8SeW$	$C_{17}H_{12}Mo_2O_8Se$	$C_{16}H_{10}Mo_2O_8Se$
fw	702.21	467.03	703.02	615.11	601.08
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$Pna2_1$ (No. 33)
a (Å)	11.151(2)	7.592(3)	14.708(2)	14.712(2)	18.638(4)
b (Å)	13.436(3)	7.700(3)	9.837(2)	9.8670(10)	9.707(2)
c (Å)	16.872(3)	12.296(5)	14.958(2)	14.982(2)	11.169(3)
α (deg)	90	98.31(4)	90	90	90
β (deg)	102.42(2)	104.24(2)	103.030(10)	103.100(10)	90
γ (deg)	90	108.49(3)	90	90	90
V (Å^3)	2468.7(9)	641.1(4)	2108.4(6)	2118.2(5)	2020.8(8)
Z	4	2	4	4	4
T (°C)	−130	−100	−100	−100	−130
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
ρ_{calc} (g cm^{-3})	1.889	2.419	2.215	1.929	1.976
μ (cm^{-1})	39.89	118.40	78.11	29.41	30.80
R1^a [$I > 2\sigma(I)$]	0.0349	0.0506	0.0206	0.0195	0.0360
wR2^b (all data)	0.0873	0.1450	0.0429	0.0416	0.0915

^{a} R1 $= \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} wR2 $= [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

m/z: 600 (9) [M]$^+$, 362 (18) [M − Mo(CO)$_5$]$^+$. Anal. Calcd for $C_{16}H_{10}Mo_2O_8Se$: C, 31.97; H, 1.68. Found: C, 32.22; H, 1.66.

X-ray Structure Determinations. The crystal structures of the compounds **3** and **5−8** were determined on four-circle diffractometers (**3**, **8**: Stoe STADI4; −130 °C, ω/θ-scan mode. **5−7**: Siemens P4; −100 °C, ω-scan mode) equipped with an LT-2 low-temperature attachment, using monochromated Mo Kα radiation (λ = 0.710 73 Å). Cell constants were refined from setting angles (Siemens) or ±ω angles (Stoe) of ca. 60 reflections in the 2θ range 6−25° (Siemens) or 20−23° (Stoe). Appropriate absorption corrections based on ψ scans were applied for all complexes.
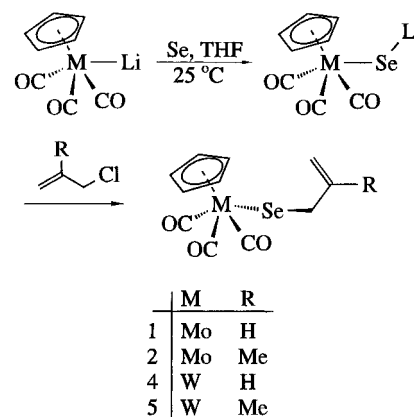
The structures of **3** and **5−8** were solved by direct methods, whereas the structure of **6** was solved by the heavy-atom method. All non-hydrogen atoms were refined anisotropically using full-matrix least-squares methods based upon F^2 (SHELXL-93).[13] Hydrogens were included using a riding model. For **6** and **7**, extinction corrections of the form $F_{cor} = F_c/[1 + 0.001xF_c^2\lambda^3/\sin 2\theta]^{0.25}$ were applied, where x is the refined extinction coefficient (1.27(4) × 10^{-3}, **6**; 1.47(5) × 10^{-3}, **7**). In the crystal structure of **5**, the residual electron density is 3.46 × 10^{-6} e pm^{-3} near the W atom, associated with poor crystal quality. Complex **8** crystallizes in the noncentrosymmetric space group $Pna2_1$ with a corresponding Flack parameter of 0.109(12); the small but significant difference from zero may indicate enantiomeric twinning. Crystallographic data and final R values are given in Table 1.
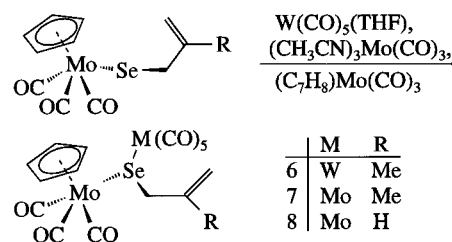
Results and Discussion

When solutions of LiSeM(CO)$_3$cp (M = Mo, W) in THF are treated with allyl or β-methallyl chloride, the brown color of the solutions changes to deep-red within a few hours and the corresponding allylic selenolato complexes are formed in moderate to good yields as deep-red crystalline solids (Scheme 1). In contrast to formerly published derivatives, the solutions of the molybdenum complexes seem to be more stable than those of tungsten, but recrystallization of the (2-methyl-2-propeneselenolato)molybdenum complex **2** from CH$_2$Cl$_2$/hexanes by the diffusion method resulted in formation of the dimeric complex [cp(CO)$_2$MoSeCH$_2$C(CH$_3$)CH$_2$]$_2$ (**3**), whose crystal structure was determined (*vide infra*). Furthermore, the 2-methyl-2-propeneselenolato compounds are more stable than the 2-propeneselenolato complexes. However, the solid complexes are stable over an indefinite period when stored in the dark.

A similar reaction of LiSe$_x$W(CO)$_3$cp (x = 1, 2) with allyl bromide led to the formation of [cpW(CO)$_3$]$_2$Se$_2$ and [cpW(CO)$_3$]$_2$Se$_3$, respectively. These oxidations are not caused by small amounts of free bromine, since the allyl bromide was

(13) Sheldrick, G. M. SHELXL-93, a program for refining crystal structures. University of Göttingen, 1993.

Scheme 1

	M	**R**
1	Mo	H
2	Mo	Me
4	W	H
5	W	Me

Scheme 2

	M	**R**
6	W	Me
7	Mo	Me
8	Mo	H

freshly distilled under inert gas prior to use. However, several inseparable byproducts appeared, and the yields were unsatisfactory. A better method for the synthesis of organotungsten oligoselenides via oxidation of LiSe$_x$W(CO)$_3$cp with O$_2$/SiO$_2$ was published recently.[8c]

The simple 2-propene- and 2-methyl-2-propeneselenolato complexes **1**, **2**, **4**, and **5** can be used as ligands for other metal complex fragments. In order to determine which donor function in these compounds can coordinate to other metals, reactions with (η^7-C$_7$H$_8$)Mo(CO)$_3$, W(CO)$_5$(THF), and (CH$_3$CN)$_3$Mo(CO)$_3$ have been performed (Scheme 2). Thus cp(CO)$_3$-MoSeCH$_2$C(CH$_3$)CH$_2$ (**2**) reacts with W(CO)$_5$(THF) under mild conditions to form the corresponding Mo(II)−W(0) complex cp(CO)$_3$Mo(μ-SeCH$_2$C(CH$_3$)CH$_2$)W(CO)$_5$ (**6**) in high yield. If metal carbonyl compounds with more labile ligands or coordinatively unsaturated fragments are used for the complexation, the reaction mechanism is somewhat different. Interestingly, the reactions of the molybdenum complexes **1** and **2** with (η^7-C$_7$H$_8$)Mo(CO)$_3$ or (CH$_3$CN)$_3$Mo(CO)$_3$ resulted in the formation

of the corresponding $Mo(CO)_5$-substituted complexes [cp-$(CO)_3Mo(\mu\text{-}SeCH_2CRCH_2)Mo(CO)_5$] (R = H (**7**), Me (**8**) in moderate yields. The chromatographic workup of **7** and **8** showed several other inseparable species in the reaction mixtures, suggesting a more complicated mechanism.

^{1}H- and ^{77}Se-NMR data for the new complexes are in accordance with their formulation. For **1**, **2**, **4**, and **8**, the ^{1}H–^{1}H coupling pattern for the allylic sites is well resolved and shows typical $^3J_{H-H}$ and $^4J_{H-H}$ coupling constants. The chemical shifts in the ^{77}Se-NMR spectra are typical of organomolybdenum and organotungsten selenolato complexes. Simple selenolato complexes of molybdenum(II) and tungsten-(II) with two-coordinate selenium usually show a chemical shift in the range −250 to −550 ppm, referred to Me_2Se. The observed shifts for the new complexes also lie in this range and can be explained by different electronic effects of the corresponding organoselenolato group. Thus the 2-propeneselenolato complexes **1** and **4** are shifted 10 ppm downfield compared to the 2-methyl-2-propeneselenato complexes **2** and **5**, because the latter contain electron-richer double bonds. A high-field shift of 50 ppm can be observed when the tungsten complexes **4** and **5** are compared with the corresponding molybdenum complexes **1** and **2**. A shift of this magnitude generally appears when the organic groups are the same or at least comparable with respect to their electronic influences and is due to the electron-richer nucleus of tungsten. For the dinuclear derivatives **6**–**8**, which contain three-coordinate selenium, the relative shift compared to the mononuclear starting materials **1** and **2** is dependent on the electron density of the added metal fragment for the same reason.

X-ray Crystal Structures

Crystal structures of metal complexes containing allylic selenolato functions were not known[14] until now, and even for the corresponding sulfur analogues, only five structures have been published, of which four contain allylic thiolato groups as bridging or cyclic ligands.[15] We present here the first crystal structures of allylic selenolato metal complexes, namely the dimeric structure of **3**, the mononuclear 2-methyl-2-propeneselenolato complex **5**, and the M(CO)$_5$-substituted complexes **6**–**8**.

The crystal structure of **3** is shown in Figure 1, with bond lengths and angles in Table 2. The central moiety is a folded four-membered Mo_2Se_2 ring (angles between Se–Mo–Se planes 43.9°, Mo–Se–Mo planes 56.6°; torsion angles Mo-(1)–Se(2)–Mo(2)–Se(1) 35.33(2)°, Mo(1)–Se(1)–Mo(2)–Se-(2) −35.21(2)°). A similar structural unit was found in [cp(CO)$_2$MoSePh]$_2$, with corresponding angles of 48 and 37.9°, respectively.[16] The bent structure unit causes relatively short nonbonding Se···Se distances of 3.001 Å (3.127 Å in [cp-(CO)$_2$MoSePh]$_2$), associated with small Se–Mo–Se angles (69.44(2) and 69.54(2)°). In analogous manganese selenolato complexes, the Mn_2Se_2 rings are planar and therefore the Se···Se

(14) Only two structures of organic allylic selenolato compounds have been published: (a) Dyachenko, V. D.; Sharanin, Y. A.; Litvinov, V. P.; Nesterov, V. N.; Shklover, V. E.; Struchkov, Y. T.; Promonenkov, V. K.; Turov, A. V. *Zh. Obshch. Khim.* **1991**, *61*, 747. (b) Nesterov, V. N.; Dyachenko, V. D.; Sharanin, Y. A.; Struchkov, Y. T. *Russ. Chem. Bull.* **1994**, *43*, 118.

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(16) Rakoczy, H.; Schollenberger, M.; Nuber, B.; Ziegler, M. L. *J. Organomet. Chem.* **1994**, *467*, 217.
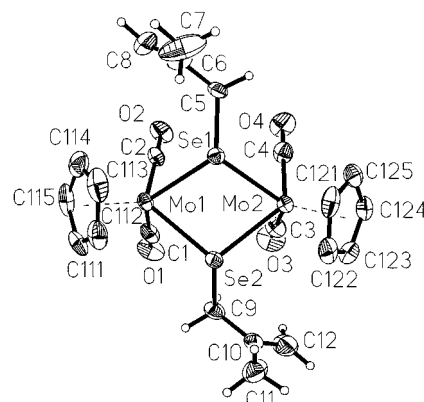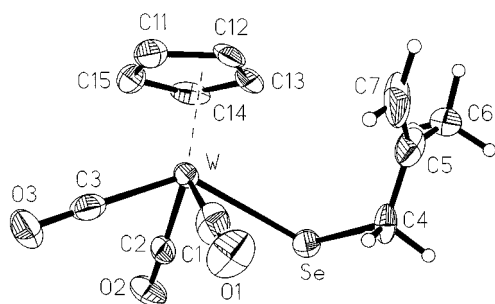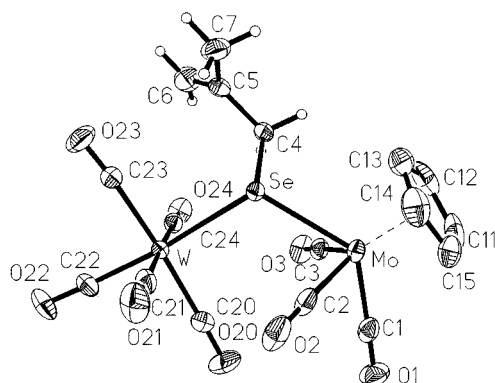

Figure 1. Molecular structure of **3** in the crystal (ellipsoids with 50% probability level). Cp hydrogens are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **3**

Mo(1)−C(2)	1.941(5)	Mo(1)−C(1)	1.950(6)
Mo(1)−cp	2.006	Mo(1)−Se(2)	2.6308(9)
Mo(1)−Se(1)	2.6379(8)	Se(1)−C(5)	1.992(5)
Se(1)−Mo(2)	2.6294(8)	C(5)−C(6)	1.482(8)
C(6)−C(8)	1.323(8)	C(6)−C(7)	1.476(9)
Se(2)−C(9)	1.991(5)	Se(2)−Mo(2)	2.6325(8)
C(9)−C(10)	1.482(7)	C(10)−C(12)	1.329(8)
C(10)−C(11)	1.500(9)	Mo(2)−C(3)	1.937(6)
Mo(2)−C(4)	1.954(6)	Mo(2)−cp	2.006
C(2)−Mo(1)−C(1)	74.4(2)	C(2)−Mo(1)−Se(2)	119.1(2)
C(1)−Mo(1)−Se(2)	81.2(2)	C(2)−Mo(1)−Se(1)	81.6(2)
C(1)−Mo(1)−Se(1)	126.0(2)	Se(2)−Mo(1)−Se(1)	69.44(2)
C(5)−Se(1)−Mo(2)	110.8(2)	C(5)−Se(1)−Mo(1)	111.2(2)
Mo(2)−Se(1)−Mo(1)	99.26(2)	C(6)−C(5)−Se(1)	110.3(4)
C(8)−C(6)−C(7)	122.9(6)	C(8)−C(6)−C(5)	120.4(6)
C(7)−C(6)−C(5)	116.6(6)	C(9)−Se(2)−Mo(1)	112.1(2)
C(9)−Se(2)−Mo(2)	110.7(2)	Mo(1)−Se(2)−Mo(2)	99.36(3)
C(10)−C(9)−Se(2)	109.9(4)	C(12)−C(10)−C(9)	120.8(6)
C(12)−C(10)−C(11)	122.2(6)	C(9)−C(10)−C(11)	117.0(5)
C(3)−Mo(2)−C(4)	73.8(2)	C(3)−Mo(2)−Se(10	119.5(2)
C(4)−Mo(2)−Se(1)	80.9(2)	C(3)−Mo(3)−Se(2)	83.1(2)
C(4)−Mo(2)−Se(2)	126.4(2)	Se(1)−Mo(2)−Se(2)	69.54(2)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **5**

W−C(1)	1.98(2)	W−C(2)	1.95(2)
W−C(3)	1.96(2)	W−cp	2.001
W−Se	2.63(2)	Se−C(4)	1.985(12)
C(4)−C(5)	1.43(2)	C(5)−C(7)	1.36(2)
C(5)−C(6)	1.49(2)		
C(2)−W−C(1)	106.9(6)	C(2)−W−C(3)	78.2(6)
C(3)−W−C(1)	77.0(6)	C(2)−W−Se	74.6(4)
C(3)−W−Se	132.4(4)	C(1)−W−Se	74.6(4)
C(4)−Se−W	108.9(4)	C(5)−C(4)−Se	116.3(9)
C(7)−C(5)−C(4)	120(2)	C(7)−C(5)−C(6)	123(2)
C(4)−C(5)−C(6)	116.4(12)		

distances are longer than 3.3 Å.[8b] The observed Mo−Se bond lengths are approximately the same (average 2.6327(8) Å) and comparable to those in [cp(CO)$_2$MoSePh]$_2$ (average 2.652(1) Å). In complexes with Mo−Mo bonds, the Mo−Se bond lengths are considerably shorter ([cpMo(μ-Se)(μ-SePh)]$_2$ (Mo=Mo), 2.460(2)−2.507(2) Å;[16] [cpMo(μ-Se)(μ-SeEt)]$_2$ (Mo=Mo), 2.4816(5)−2.5943(5) Å;[17] [(η^7-C$_7$H$_7$)Mo(μ-SePh)$_3$-Mo(CO)$_3$ (Mo−Mo), 2.563(1)−2.675(2) Å[18]). If the organic substituent is taken into account, the geometry at both selenium atoms is almost tetrahedral with corresponding angles from 110.7(2) to 112.1(2)°. The bond lengths in the allylic group will be discussed in connection with those of the other complexes (*vide infra*).

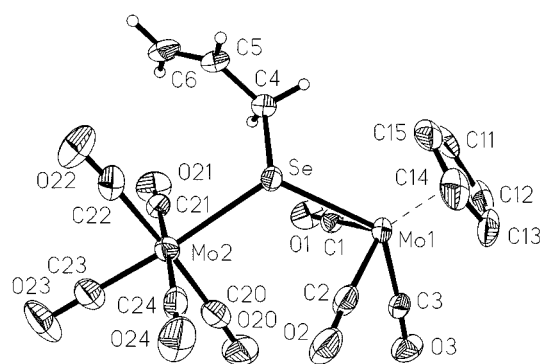(17) Jones, P. G.; Thöne, C. Unpublished results.

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Table 4. Selected Bond Lengths (Å) and Angles (deg) for **6** (M = W; Column 1) and **7** (M = Mo; Column 2)

Mo−C(1)	1.984(4)	1.984(3)	Mo−C(2)	1.992(4)	1.997(2)
Mo−C(3)	2.009(3)	2.008(2)	Mo−cp	2.000	2.003
Mo−Se	2.6708(5)	2.6679(4)	Se−C(4)	1.999(3)	1.996(2)
Se−M	2.6881(6)	2.7014(4)	C(4)−C(5)	1.496(5)	1.497(3)
C(5)−C(6)	1.317(5)	1.318(5)	C(5)−C(7)	1.501(5)	1.492(3)
M−C(22)	1.966(3)	1.971(2)	M−C(21)	2.036(3)	2.040(2)
M−C(20)	2.039(4)	2.045(2)	M−C(23)	2.044(4)	2.049(2)
M−C(24)	2.051(3)	2.051(2)			
C(1)−Mo−C(2)	77.1(2)	77.11(10)	C(1)−Mo−C(3)	76.60(13)	76.69(9)
C(2)−Mo−C(3)	109.09(14)	109.03(9)	C(1)−Mo−Se	129.88(10)	129.78(7)
C(10)−Mo−Se	74.48(9)	74.43(6)	C(3)−Mo−Se	74.95(9)	74.75(6)
C(4)−Se−Mo	103.85(9)	103.93(6)	C(4)−Se−M	105.41(9)	105.43(6)
Mo−Se−M	115.857(14)	115.731(10)	C(5)−C(4)−Se	111.2(2)	111.13(14)
C(6)−C(5)−C(4)	120.6(4)	122.6(2)	C(6)−C(5)−C(7)	122.6(4)	120.5(2)
C(4)−C(5)−C(7)	116.8(3)	116.9(2)	C(22)−M−C(21)	88.86(14)	88.43(9)
C(22)−M−C(20)	90.3(2)	90.13(10)	C(21)−M−C(20)	90.10(14)	90.00(9)
C(22)−M−C(23)	86.9(14)	86.53(9)	C(21)−M−C(23)	89.49(14)	89.63(9)
C(20)−M−C(23)	176.94(13)	176.66(9)	C(22)−M−C(24)	90.93(13)	90.76(9)
C(21)−M−C(24)	178.52(14)	178.34(9)	C(20)−M−C(24)	88.43(14)	88.55(9)
C(23)−M−C(24)	91.96(13)	91.77(9)	C(22)−M−Se	173.95(11)	173.88(7)
C(21)−M−Se	88.97(10)	89.26(7)	C(20)−M−Se	95.39(10)	95.53(7)
C(23)−M−Se	87.64(9)	87.79(6)	C(24)−M−Se	91.39(9)	91.68(6)

Figure 2. Molecular structure of **5** in the crystal (ellipsoids with 50% probability level). Cp hydrogens are omitted for clarity.

Figure 4. Molecular structure of **8** in the crystal (ellipsoids with 50% probability level). Cp hydrogens are omitted for clarity.

Figure 3. Molecular structure of **6** in the crystal (ellipsoids with 50% probability level). Cp hydrogens are omitted for clarity.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **8**

Mo(1)−cp	1.995	Mo(1)−C(1)	2.006(6)
Mo(1)−C(2)	1.973(7)	Mo(1)−C(3)	1.977(6)
Mo(1)−Se	2.6606(9)	Se−C(4)	1.999(6)
Se−Mo(2)	2.6762(9)	C(4)−C(5)	1.474(9)
C(5)−C(6)	1.331(10)	Mo(2)−C(23)	1.915(6)
Mo(2)−C(20)	2.001(8)	Mo(2)−C(21)	2.009(6)
Mo(2)−C(24)	2.014(7)	Mo(2)−C(22)	2.024(7)
C(2)−Mo(1)−C(3)	77.0(3)	C(2)−Mo(1)−C(1)	110.1(3)
C(3)−Mo(1)−C(1)	76.7(2)	C(2)−Mo(1)−Se	76.9(2)
C(3)−Mo(1)−Se	132.1(2)	C(1)−Mo(1)−Se	75.6(2)
C(4)−Se−Mo(1)	104.2(2)	C(4)−Se−Mo(2)	105.7(2)
Mo(1)−Se−Mo(2)	116.94(2)	C(5)−C(4)−Se	108.6(5)
C(6)−C(5)−C(4)	122.8(7)	C(23)−Mo(2)−C(20)	90.1(3)
C(23)−Mo(2)−C(21)	88.7(3)	C(20)−Mo(2)−C(21)	88.7(3)
C(23)−Mo(2)−C(24)	88.9(3)	C(20)−Mo(2)−C(24)	89.6(3)
C(23)−Mo(2)−C(22)	88.1(3)	C(21)−Mo(2)−C(22)	93.9(3)
C(24)−Mo(2)−C(22)	87.8(3)	C(20)−Mo(2)−Se	94.7(2)
C(21)−Mo(2)−Se	92.2(2)	C(24)−Mo(2)−Se	90.3(2)
C(22)−Mo(2)−Se	87.1(2)		

The crystal structure of the (2-methyl-2-propeneselenolato)-tungsten complex **5** is shown in Figure 2, with bond lengths and angles in Table 3. Because of the poor crystal quality, standard deviations of bond lengths and angles are rather high. Notwithstanding, the X-ray structure determination of **5** represents the first monomeric structure of an allylic selenolato metal complex. The W−Se bond length of 2.63(2) Å matches the W(II)−Se bond lengths of 2.506(1) and 2.583(1) Å in [W(SeC$_6$H$_3$Pr$^i_2$-2,6)$_2$(CO)$_2$(PMe$_2$Ph)$_2$],[19] 2.588(2) Å in (η^7-C$_7$H$_7$)(CO)$_2$WSePh,[18] and 2.623(1) Å in cp(CO)$_3$WSeCH$_2$Ph.[8a] The coordination geometry at selenium is essentially tetrahedral with an angle of 108.9(4)°.

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Since the M(CO)$_5$-substituted 2-methyl-2-propeneselenolato complexes **6** (M = W) and **7** (M = Mo) are isostructural and the 2-propeneselenolato complex **8** only differs in the organic substituent, they are discussed together. The crystal structure of **6** is shown in Figure 3 (**7** is not shown separately), whereas Figure 4 shows the structure of **8**. The corresponding bond lengths and angles are given in Tables 4 and 5. The three structures contain the cp(CO)$_3$MoSe fragment, in which the selenium can be regarded as the tip of a distorted trigonal pyramid with angles at selenium ranging from 103.85(9) to

116.94(2)°. The Mo(II)−Se bond lengths are 2.6708(5) Å for **6**, 2.6679(4) Å for **7,** and 2.6606(9) Å for **8** and therefore ca. 0.03 Å longer than in cp(CO)$_3$MoSeCH$_2$Ph (2.6294(4) Å).[20] These observations can be explained by the electron-withdrawing character of three-coordinate selenium, which bears a formal positive charge. This electronic effect also influences the M(0)−Se bonds in these complexes, leading to bond lengths of nearly the same value [**6**, W−Se 2.6881(1) Å; **7**, Mo−Se 2.7014(7) Å; **8**, Mo−Se 2.6762(9) Å]. Several structures of W(CO)$_5$-substituted organoseleno compounds have been determined and the W(0)−Se bond lengths are in the range 2.619(3)−2.696(1) Å,[21] whereas crystal structures of the Mo(CO)$_5$-substituted derivatives are not known. In the cyclic bis(selenolato) complex **3**, the corresponding Mo(II)−Se bond lengths are shorter (average 2.6327(8) Å), because the formal positive charges on the selenium can be delocalized into the Mo$_2$Se$_2$ ring, reducing the electronic repulsion between the Mo and Se atoms.

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The bonding parameters in the organoselenolato moieties differ only slightly in all structures discussed. The Se−C bond lengths are essentially the same value (average 1.994(1) Å) and are typical of (organoselenolato) metal complexes with Se−C single bonds.[2] Apart from the less precisely determined structure of **5**, all C−C bond lengths are clearly attributable to single and double bonds in allylic structures.[22]

Conclusion

Selenium insertion into alkali-metal−molybdenum and −tungsten bonds of the corresponding carbonylates and subsequent reaction with allylic chlorides provides a convenient synthesis of selenolato complexes with two donor functions. The monomeric products can act as ligands for unsaturated metal complex fragments, in which further coordination at selenium is observed. The allylic moieties in the products remain intact, and studies on complexing the double bonds to suitable metal centers are in progress.

Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **3** and **5**−**8** are available on the Internet only. Access information is given on any current masthead page.

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