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A New Route to Organometallic Selenolate Complexes of Tungsten(II) and Molybdenum(II). Crystal Structure of $[W(\eta^5-C_5H_5)(CO)_3(SeCH_2Ph)]$

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Molybdenum(II) and tungsten(II) organoselenolate complexes were synthesised *via* selenium insertion into the corresponding metal–lithium bonds and subsequent reactions with organohalides.

Transition-metal selenolate complexes have received increasing attention associated with applications such as solar-cell technology.[1] Various syntheses of transition-metal complexes with organoselenolate ligands have been reported, *e.g.* metathetical reactions of metal halogenide complexes with alkali-metal salts of organoselenolates or oxidative-addition reactions of organic diselenides with metal carbonyl complexes.[2,3] Thus the reaction of $[W(\eta^7-C_7H_7)(CO)_2I]$ with $Li[SePh]$ or the reaction of $[\{Cr(\eta^5-C_5H_5)(CO)_3\}_2]$ with Ph_2Se_2 leads to the corresponding organoselenolate complexes.[4,5]

Here we report on the synthesis of alkali-metal salts of organo-tungsten and -molybdenum selenolates *via* an alternative strategy, *viz.* selenium insertion into metal–lithium bonds and the subsequent reactions with Me_3SiCH_2Cl or $PhCH_2Cl$. The required lithium carbonylates are easily accessible through reductive metal–metal bond cleavage of dimeric metal carbonyls and their complexes with $Li[BEt_3H]$.[†,6]

We have found that selenium readily inserts into metal–lithium bonds {*e.g.* $[LiM(\eta^5-C_5H_5)(CO)_3]$ (M = Mo or W); $[LiMn(CO)_5]$, $[LiFe(\eta^5-C_5H_5)(CO)_2]$ in thf solution in a 1:1 molar ratio (Scheme 1). The resulting deep red-brown solutions are less sensitive to air than are the corresponding lithium carbonylates. In the case of molybdenum and tungsten, $[LiSeM(\eta^5-C_5H_5)(CO)_3]$ is formed as the main product, as evidenced by the reaction with the organic electrophiles $PhCH_2Cl$ and Me_3SiCH_2Cl. The new complexes **1**–**4** are formed in good yields. Further studies on the reactivity of alkali-metal salts of organometallic selenolates (*e.g.* reactions with halogeno transition-metal complexes and oxidation reactions) are in progress.

Few crystal structures of monomeric transition-metal complexes with terminal organoselenolate ligands have been determined. In the case of tungsten, only $[W(\eta^7-C_7H_7)(CO)_2(SePh)]$ has been described.[4] The structure of complex **3** was determined by single-crystal X-ray diffraction and consists of two independent molecules per asymmetric unit. One is shown in Fig. 1.[‡] The $W(\eta^5-C_5H_5)(CO)_3$ moiety has a 'piano-stool' arrangement, as in many other $M(C_5H_5)(CO)_x$ fragments. The bond angle at Se is ideal tetrahedral, but the substitution at W(1) with the $PhCH_2Se$ ligand leads to a distortion, with bond angles at W(1) (excluding those to $\eta^5-C_5H_5$) ranging from 73.5(3) to 136.6(3)°. A similar arrangement can be seen in $[Cr(\eta^5-C_5H_5)(CO)_3(SePh)]$.[5] The W–Se bond length is 2.623(1) Å, *cf.* 2.588(2) Å in $[W(\eta^7-C_7H_7)(CO)_2(SePh)]$.[4] In

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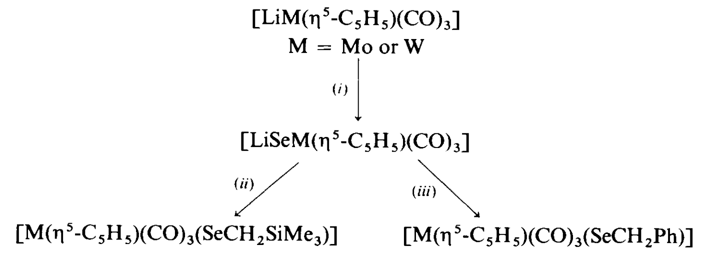
[†] Preparation of $[M(\eta^5-C_5H_5)(CO)_3(SeR)]$ **1**–**4** (M = Mo or W; R = CH_2Ph or CH_2SiMe_3): $[\{M(\eta^5-C_5H_5)(CO)_3\}_2]$ (0.5 mmol) was dissolved in tetrahydrofuran (thf) (30 cm^3) and a 1 mol dm^{-3} solution (1.5 base cm^3) of $Li[BEt_3H]$ (1.5 mmol) in thf was added; after stirring for 0.5 h Bu^tOH (1 cm^3) was added and the solution evaporated to dryness. Grey selenium (1 mmol) and thf (30 cm^3) were added; after stirring for 1 h, RCl (1 cm^3) was added to the dark red-brown solution *via* a syringe. Stirring overnight afforded dark red solutions. After evaporation, addition of CH_2Cl_2 (10 cm^3), removal of LiCl by filtration, addition of light petroleum (b.p. 40–60 °C) and cooling the yields of the resulting black (Mo) or red (W) complexes were 51 (**1**), 67 (**3**) and 56% (**4**). In the case of **2** the reaction residue was extracted with three portions of light petroleum and the resulting deep red solution was cooled to −60 °C. Yield of black crystals 56%. $[Mo(\eta^5-C_5H_5)(CO)_3(SeCH_2Ph)]$ **1**·CH_2Cl_2: m.p. 151 °C (decomp.); ^1H NMR: ($CDCl_3$, external $SiMe_4$): δ 3.69 (s, 2 H, CH_2), 5.22 (s, 2 H, CH_2), 5.29 (s, 5 H, C_5H_5), 7.27 (m, 5 H, Ph) [Found (Calc.): C, 39.25 (38.45); H, 2.75 (2.80)%]. $[Mo(\eta^5-C_5H_5)(CO)_3(SeCH_2SiMe_3)]$ **2**: m.p. 79 °C; ^1H NMR: δ 0.11 (s, 9 H, $SiMe_3$), 1.41 (s, 2 H, CH_2), 5.47 (s, 5 H, C_5H_5) [Found (Calc.): C, 35.15 (35.05); H, 4.00 (3.90)%]. $[W(\eta^5-C_5H_5)(CO)_3(SeCH_2Ph)]$ **3**: m.p. 108 °C; ^1H NMR: δ 3.66 (s, 2 H, CH_2), 5.25 (s, 5 H, C_5H_5), 7.27 (m, 5 H, Ph) [Found (Calc.): C, 35.15 (35.85); H, 2.35 (2.40)%]. $[W(\eta^5-C_5H_5)(CO)_3(SeCH_2SiMe_3)]$ **4**: m.p. 101 °C; ^1H NMR: δ 0.10 (s, 9 H, $SiMe_3$), 1.36 (s, 2 H, CH_2), 5.58 (s, 5 H, C_5H_5) [Found (Calc.): C, 27.85 (28.90); H, 3.10 (3.25)%].

[‡] Compound **3**: $C_{15}H_{12}O_3SeW$, $M_r = 503.1$, triclinic, space group $P\bar{1}$, $a = 9.783(3)$, $b = 11.706(3)$, $c = 12.628(4)$ Å, $\alpha = 91.99(3)$, $\beta = 95.01(3)$, $\gamma = 90.08(3)°$, $U = 1440$ Å^3, $Z = 4$, $D_c = 2.321$ Mg m^{-3}, λ(Mo-Kα) = 0.710 73 Å, $\mu = 10.55$ mm^{-1}, $F(000) = 936$, $T = -130$ °C. Orange prism 0.4 × 0.4 × 0.3 mm, Stoe Stadi4 diffractometer, 6390 intensities to 2θ 50° (absorption corrected, 4885 unique, R_{int} 0.0395). Refinement on F^2 for all reflections (SHELXL 93 [7]), hydrogen atoms with riding model. The final $wR(F^2)$ was 0.172, conventional $R(F)$ 0.061, for 361 parameters and 480 restraints; weighting scheme $w^{-1} = [\sigma^2(F_o)^2 + (aP)^2 + bP]$ with $P = (F_o^2 + 2F_c^2)/3$, $a = 0.1189$, $b = 8.5932$; $S = 1.09$, maximum $\Delta/\sigma < 0.001$, maximum $\Delta\rho$ 4.3 e Å^{-3}. Details of the structure determination have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote the full literature citation and the reference number CSD 401232.



Scheme 1 (*i*) Grey Se, thf; (*ii*) Me_3SiCH_2Cl (excess); (*iii*) $PhCH_2Cl$ (excess)

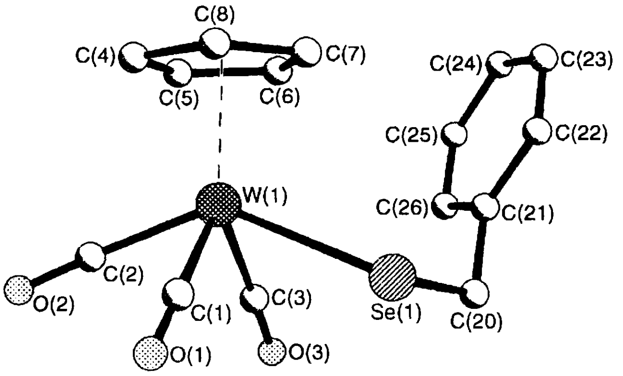


Fig. 1 One of the two independent molecules of complex **3** in the crystal. Radii are arbitrary; hydrogen atoms are omitted. Selected bond lengths (Å) and angles (°) (values for the second molecule in square brackets): W(1)–Se(1) 2.623(1) [2.619(1)], W(1)–ring centre (C_5H_5) 2.013(5) [2.006(5)], W(1)–C(1) 1.983(12) [1.970(20)], W(1)–C(2) 1.962(12) [1.993(13)], W(1)–C(3) 1.978(12) [1.986(12)], Se(1)–C(20) 1.961(11) [1.965(11)]; C(1)–W(1)–Se(1) 73.5(3) [73.8(4)], C(2)–W(1)–Se(1) 136.6(3) [136.2(4)], C(3)–W(1)–Se(1) 77.6(3) [76.4(4)], C(2)–W(1)–C(1) 76.9(5) [77.6(5)], C(1)–W(1)–C(3) 78.3(5) [78.2(5)], C(3)–W(1)–C(1) 102.1(5) [102.6(5)], C(20)–Se(1)–W(1) 109.8(4) [109.8(4)], C(21)–C(20)–Se(1) 114.7(7) [115.1(8)], O(1)–C(1)–W(1) 179.0(10) [177.6(13)], O(2)–C(2)–W(1) 178.1(11) [180.0(13)], O(3)–C(3)–W(1) 178.1(10) [179.6(11)]

dimeric tungsten complexes with terminal organoselenolates the W–Se bond lengths are considerably shorter, *e.g.* 2.438(2), 2.461(2) Å in $[W_2(\mu-Se)_2(PPh_2Me)_2(SePh)_4]$ and 2.421(2)–2.446(2) Å in $[\{W(SeC_6H_2Me_3-2,4,6)_3\}_2]$.[8]

Acknowledgements

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