## **Dalton Communications**

# 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.<sup>1</sup> 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.<sup>2,3</sup> 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<sub>2</sub>Se<sub>2</sub> leads to the corresponding organoselenolate complexes.<sup>4,5</sup>

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].†.<sup>6</sup>

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)<sub>5</sub>], [LiFe( $\eta^5-C_5H_5$ )(CO)<sub>2</sub>] 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)<sub>3</sub>] is formed as the main product, as evidenced by the reaction with the organic electrophiles PhCH<sub>2</sub>Cl and Me<sub>3</sub>SiCH<sub>2</sub>Cl. The new complexes 1–4 are formed in good yields. Further studies on the reactivity of alkalimetal 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.<sup>4</sup> 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.<sup>‡</sup> 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<sub>2</sub>Se 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

 $Compound 3: C_{15}H_{12}O_3SeW, M_r = 503.1$ , triclinic, space group  $P\overline{1}$ ,  $a = 9.783(3), b = 11.706(3), c = 12.628(4) \text{ Å}, \alpha = 91.99(3), \beta = 95.01(3), \gamma = 90.08(3)^\circ, U = 1440 \text{ Å}^3, Z = 4, D_c = 2.321 \text{ Mg m}^{-3},$  $\lambda$ (Mo-K $\alpha$ ) = 0.71073 Å,  $\mu$  = 10.55 mm<sup>-1</sup>, F(000) = 936, T = -130 °C. Orange prism 0.4 × 0.4 × 0.3 mm, Stoe Stadi4 diffractometer, 6390 intensities to  $2\theta$  50° (absorption corrected, 4885 unique,  $R_{int}$ 0.0395). Refinement on  $F^2$  for all reflections (SHELXL 93<sup>7</sup>), 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  $\Delta (r^{-1}) = [\sigma^2(F_o)^2 + (aP)^2 + bP]$  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<sup>-3</sup>. 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.

<sup>†</sup> Preparation of  $[M(\eta^5-C_5H_5)(CO)_3(SeR)]$  1-4 (M = Mo or W;  $R = CH_2Ph \text{ or } CH_2SiMe_3$ : [{ $M(\eta^5 - C_5H_5)(CO)_3$ }] (0.5 mmol) was dissolved in tetrahydrofuran (thf) (30 cm<sup>3</sup>) and a 1 mol dm<sup>-3</sup> solution (1.5 base cm<sup>3</sup>) of Li[BEt<sub>3</sub>H] (1.5 mmol) in thf was added; after stirring for 0.5 h Bu<sup>1</sup>OH (1 cm<sup>3</sup>) was added and the solution evaporated to dryness. Grey selenium (1 mmol) and thf (30 cm<sup>3</sup>) were added; after stirring for 1 h, RCl (1 cm<sup>3</sup>) was added to the dark red-brown solution via a syringe. Stirring overnight afforded dark red solutions. After evaporation, addition of CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>), 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<sub>5</sub>H<sub>5</sub>)-(CO)<sub>3</sub>(SeCH<sub>2</sub>Ph)] 1·CH<sub>2</sub>Cl<sub>2</sub>: m.p. 151 °C (decomp.); <sup>1</sup>H NMR: (CDCl<sub>3</sub>, external SiMe<sub>4</sub>):  $\delta$  3.69 (s, 2 H, CH<sub>2</sub>), 5.22 (s, 2 H, CH<sub>2</sub>), 5.29 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 7.27 (m, 5 H, Ph) [Found (Calc.): C, 39.25 (38.45); H, 2.75 (2.80)%]. [Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>(SeCH<sub>2</sub>SiMe<sub>3</sub>)] 2: m.p. 79 °C; <sup>1</sup>H NMR:  $\delta 0.11$  (s, 9 H, SiMe<sub>3</sub>), 1.41 (s, 2 H, CH<sub>2</sub>), 5.47 (s, 5 H, C<sub>5</sub>H<sub>3</sub>) [Found (Calc.): C, 35.15 (35.05); H, 4.00 (3.90)%]. [W( $\eta^{5}$ -C<sub>5</sub>H<sub>3</sub>)-(CO)<sub>3</sub>(SeCH<sub>2</sub>Ph)] 3: m.p. 108 °C; <sup>1</sup>H NMR:  $\delta$  3.66 (s, 2 H, CH<sub>2</sub>), 5.25 (s, 5 H, C<sub>5</sub>H<sub>3</sub>), 7.27 (m, 5 H, Ph) [Found (Calc.): C, 35.15 (35.85); H, 2.35 (2.40)%]. [W(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>(SeCH<sub>2</sub>SiMe<sub>3</sub>)] 4: m.p. 101 °C; <sup>1</sup>H NMR:  $\delta$  0.10 (s, 9 H, SiMe<sub>3</sub>), 1.36 (s, 2 H, CH<sub>2</sub>), 5.58 (s, 5 H, C<sub>5</sub>H<sub>5</sub>) [Found (Calc.): C, 27.85 (28.90); H, 3.10 (3.25)%].

## $[LiM(\eta^{5}-C_{5}H_{5})(CO)_{3}]$ M = Mo or W(i)[LiSeM( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>] (*ii*) (iii)

 $[M(\eta^{5}-C_{5}H_{5})(CO)_{3}(SeCH_{2}SiMe_{3})]$ 

 $[M(\eta^{5}\text{-}C_{5}H_{5})(CO)_{3}(SeCH_{2}Ph)]$ 

Scheme 1 (i) Grey Se, thf; (ii) Me<sub>3</sub>SiCH<sub>2</sub>Cl (excess); (iii) PhCH<sub>2</sub>Cl (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(2)  $\begin{array}{l} 1.961(11) \begin{bmatrix} 1.965(11) \\ 1.961(11) \end{bmatrix}; C(1)-W(1)-Se(1) \\ 73.5(3) \begin{bmatrix} 73.8(4) \\ 1.961(11) \end{bmatrix}; C(2)-W(1)-Se(1) \\ 136.6(3) \begin{bmatrix} 136.2(4) \\ 1.962(11) \end{bmatrix}; C(3)-W(1)-Se(1) \\ 77.6(3) \begin{bmatrix} 76.4(4) \\ 1.962(11) \\ 1.962(11) \end{bmatrix}; C(3)-W(1)-Se(1) \\ 77.6(3) \begin{bmatrix} 76.4(4) \\ 1.962(11)$ Se(1) C(2)-W(1)-C(1) 76.9(5) [77.6(5)], C(1)-W(1)-C(3) 78.3(5) [78.2(5)], 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 [{ $W(SeC_6H_2Me_3-2,4,6)_3$ }\_].<sup>6</sup>

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