## Triple Bonds between Molybdenum and Tungsten Atoms supported by Selenolate Ligands: $M_2(SeAr)_6$ and $M_2(OPr^i)_2(SeAr)_4$ (Ar = Mesityl)

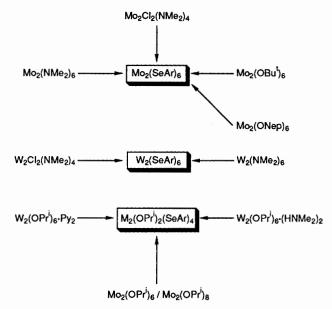
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The reactions between  $M_2(NMe_2)_6$  and mesityl (Ar) selenol (>6 equiv.) in toluene yield  $M_2(SeAr)_6$  compounds as red-brown crystals while related reactions involving  $M_2(OR)_6$  yield  $M_2(SeAr)_6$  and  $M_2(OR)_2(SeAr)_4$  compounds which have been characterized by single-crystal X-ray crystallography and shown to contain a central ( $M\equiv M$ )<sup>6+</sup> unit supported by selenolate ligands, M = Mo or W.

The first homoleptic transition metal selenolate complexes<sup>1</sup> have been prepared and structurally characterized according to the reactions shown in Scheme 1. The use of the mesityl (Ar) group affords sufficient steric pressure to overcome cluster formation; also the presence of the aromatic carbon-

selenium bond obviates facile Se–C bond cleavage. The compounds are very sparingly soluble in hydrocarbon solvents and are relatively inert to the atmosphere at ambient temperature in the light. Under N<sub>2</sub> atmosphere the compounds decompose at elevated temperatures (>160 °C).



Scheme 1. The reactions were carried out at room temperature in toluene and the products crystallized out from the solution on standing for a few days. All the reactions were performed by adding a greater than six-fold excess of the mesityl selenol to the dissolved Mo/W alkoxide or amide. Satisfactory microanalysis and IR data were obtained for all the compounds studied. The insolubility of the products limited the study by <sup>1</sup>H NMR spectroscopy to the mixed selenol/alkoxide cases; the spectra were then consistent with the *anti*-rotamer as observed in the crystal structure. Ar = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>; Py = pyridine; Nep = neopentyl.

The M<sub>2</sub>(SeAr)<sub>6</sub> compounds are isomorphous and isostructural.<sup>†</sup> An ORTEP view of one of the compounds is given in Figure 1 and a view of W<sub>2</sub>(OPr<sup>i</sup>)<sub>2</sub>(SeAr)<sub>4</sub> is given in Figure 2. The M-M distances are typical of triple bond distances in related X<sub>3</sub>M $\equiv$ MX<sub>3</sub> compounds (X = alkyl, amide, alkoxide, and thiolate)<sup>2</sup> and the M-Se distances are relatively short with respect to what may be expected on the basis of the estimated

† *Crystal data* for C<sub>54</sub>H<sub>66</sub>Mo<sub>2</sub>Se<sub>6</sub>: M = 1380.76, triclinic, space group P1, a = 11.747(2), b = 11.725(2). c = 11.139(2) Å,  $\alpha = 95.49(1)$ ,  $\beta = 96.11(1)$ ,  $\gamma = 118.20(1)^\circ$ , V = 1325.59 Å<sup>3</sup>, Z = 1,  $D_c = 1.730$  g cm<sup>-3</sup>,  $\lambda$  (Mo- $K_{\alpha}$ ) = 0.71069 Å.

 $C_{54}H_{66}Se_6W_2$ : M = 1556.58, triclinic, space group  $P\overline{1}$ , a = 11.727(4), b = 11.765(3), c = 11.158(3) Å,  $\alpha = 95.66$ ,  $\beta = 95.93(2)$ ,  $\gamma = 118.27(2)$ , V = 1329.32 Å<sup>3</sup>, Z = 1,  $D_c = 1.944$  g cm<sup>-3</sup>,  $\lambda$ (Mo- $K_{\alpha}$ ) = 0.71069 Å.

C<sub>42</sub>H<sub>58</sub>O<sub>2</sub>Se<sub>4</sub>W<sub>2</sub>: M = 1278.46, triclinic, space group P1, a = 10.805(1), b = 11.434(1), c = 9.428(1) Å,  $\alpha = 98.28(1)$ ,  $\beta = 110.62(1)$ ,  $\gamma = 88.75(1)^{\circ}$ , V = 1078.26 Å<sup>3</sup>, Z = 1,  $D_c = 1.969$  g cm<sup>-3</sup>,  $\lambda$ (Mo- $K_{\alpha}$ ) = 0.71069 Å.

 $C_{42}H_{58}Mo_2O_2Se_4$ : M = 1102.64, monoclinic, space group A2/a, a = 24.971(7), b = 8.692(2), c = 22.001(7) Å,  $\beta = 110.10(1)$ , V = 4484.73 Å<sup>3</sup>, Z = 4,  $D_c = 1.633$  g cm<sup>-3</sup>,  $\lambda$ (Mo- $K_{\alpha}$ ) = 0.71069 Å.

Data were measured on a Picker four-circle diffractomer with graphite-monochromater and Mo- $K_{\alpha}$  radiation using  $\omega$  scans. The structures were solved by a combination of direct methods (Multan 78) and Fourier techniques and refined anisotropically using absorption corrected data to give for  $C_{54}H_{66}Mo_2Se_6R = 0.0417$ ,  $R_w = 0.0415$  for 2936 independent observed reflections with  $|F_0| > 2.33\sigma(|F_o|)$  ( $\theta \le 45^{\circ}$ ); for  $C_{54}H_{66}Se_6W_2R = 0.443$ ,  $R_w = 0.0436$  for 3142 independent observed reflections with  $|F_0| > 2.33\sigma(|F_o|)$  ( $\theta \le 45^{\circ}$ ); for  $C_{42}H_{58}O_2Se_4W_2R = 0.0330$ ,  $R_w = 0.0357$  for 2714 independent reflections with  $|F_0| > 3.0\sigma(|F_o|)$  ( $\theta \le 45^{\circ}$ ); for  $C_{42}H_{58}Mo_2O_2Se_4R = 0.0703$ ,  $R_w = 0.0634$  for 2302 independent reflections with  $|F_0| > 2.33\sigma(|F_o|)$  ( $\theta \le 45^{\circ}$ ). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue 1.

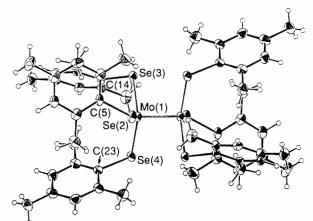


Figure 1. An ORTEP drawing of the  $Mo_2(SeAr)_6$  molecule (Ar = 2,4,6-Me\_3C\_6H\_2); selected bond lengths (Å) and angles (°) [W<sub>2</sub>(SeAr)\_6 in brackets]: M-M 2.2175(13) [2.3000(11)], M(1)-Se(2) 2.4324(11) [2.4214(15)], M(1)-Se(3) 2.4385(11) [2.4278(14)], M(1)-Se(4) 2.4568(12) [2.4457(16)], Se(2)-C(5) 1.938(7) [1.951(11)], Se(3)-C(14) 1.956(7) [1.956(11)], Se(4)-C(23) 1.956(7) [1.957(11)]; M(1)-M(1')-Se(2) 96.56(5) [96.46(5)], M(1)-M(1')-Se(3) 97.18(5) [96.92(4)], M(1)-M(1')-Se(4) 98.17(5) [97.68(5)], Se(2)-M(1)-Se(3) 116.70(4) [116.91(5)], Se(2)-M(1)-Se(4) 118.48(4) [118.54(5)], M(1)-Se(2)-C(5) 104.64(22) [104.3(3)], M(1)-Se(3)-C(14) 106.57(22) [106.1(3)], M(1)-Se(4)-C(23) 105.6].

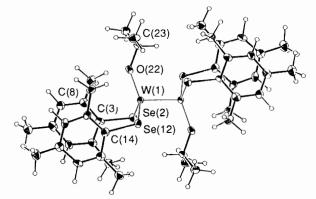


Figure 2. An ORTEP drawing of the  $W_2(OPr^i)_2(SeAr)_4$  molecule; selected bond lengths (Å) and angles (°)  $[Mo_2(OPr^i)_2(SeAr)_4$  in brackets]: M(1)-M(1') 2.3077 [2.2180(24)], M(1)-Se(2) 2.4303(10)[2.4281(21)], M(1)-Se(12) 2.4410(10) [2.4427(19)], M(1)-O(22), 1.858(6) [1.872(9)], Se(2)-C(3) 1.955(9) [1.954(13)], Se(12)-C(13)1.959(9) [1.947(13)], O(22)-C(23) 1.449(10) [1.441(16)]; M(1')-M(1)-Se(2) 100.27(3) [99.39(9)], M(1')-M(1)-Se(12) 93.85(3)[94.71(8)], M(1')-M(1)-O(22) 108.41(17) [107.55(28)], Se(2)-M(1)-Se(12) 120.14(3) [118.59(7)], Se(2)-M(1)-O(22) 111.32(18)[113.8(3)], Se(12)-M(1)-O(22) 118.43(18) [117.9(3)], M(1)-Se(12)-C(13) 107.72(25) [106.0(4)], M(1)-Se(2)-C(3) 90.07(25) [94.6(4)], M(1)-O(22)-C(23) 140.5(5) [140.2(8)], Se(2)-C(3)-C(4) 121.2(6)[119.0(10)], Se(2)-C(3)-C(8) 118.5(6) [119.0(10)].

covalent radii for M and Se in the  $M_2(SeAr)_6$  molecules. It is possible that shortening of the M-Se bonds reflects Se  $p_{\pi}$ -M  $d_{\pi}$  bonding.

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