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)

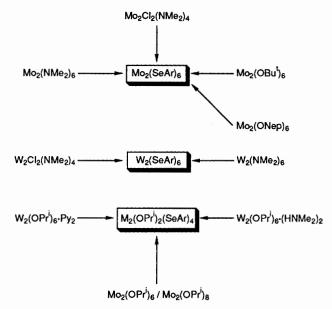**Malcolm H. Chisholm, Ivan P. Parkin, John C. Huffman, and William B. Streib**

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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 $(M{\equiv}M)^{6+}$ unit supported by selenolate ligands, M = Mo or W.

The first homoleptic transition metal selenolate complexes[1] 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_2 atmosphere the compounds decompose at elevated temperatures (>160 °C).

$$Mo_2Cl_2(NMe_2)_4$$

$$Mo_2(NMe_2)_6 \longrightarrow \boxed{Mo_2(SeAr)_6} \longleftarrow Mo_2(OBu^t)_6$$

$$\nwarrow Mo_2(ONep)_6$$

$$W_2Cl_2(NMe_2)_4 \longrightarrow \boxed{W_2(SeAr)_6} \longleftarrow W_2(NMe_2)_6$$

$$W_2(OPr^i)_6 \cdot Py_2 \longrightarrow \boxed{M_2(OPr^i)_2(SeAr)_4} \longleftarrow W_2(OPr^i)_6 \cdot (HNMe_2)_2$$

$$Mo_2(OPr^i)_6 / Mo_2(OPr^i)_8$$

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 ^1H 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-$Me_3C_6H_2$; Py = pyridine; Nep = neopentyl.

The $M_2(SeAr)_6$ compounds are isomorphous and isostructural.† An ORTEP view of one of the compounds is given in Figure 1 and a view of $W_2(OPr^i)_2(SeAr)_4$ is given in Figure 2. The M–M distances are typical of triple bond distances in related $X_3M{\equiv}MX_3$ compounds (X = alkyl, amide, alkoxide, and thiolate)[2] and the M–Se distances are relatively short with respect to what may be expected on the basis of the estimated
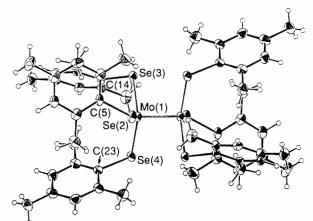
Figure 1. An ORTEP drawing of the $Mo_2(SeAr)_6$ molecule (Ar = 2,4,6-$Me_3C_6H_2$; selected bond lengths (Å) and angles (°) [$W_2(SeAr)_6$ in brackets]: M–M 2.2175(13) [2.3000(11)], M(1)–Se(2) 2.4324(11) [2.4214(15)], M(1)–Se(3) 2.4385(11) [2.4278(14)], M(1)–Se(4) 2.4568(12) [2.4457(16)], Se(2)–C(5) 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) 120.04(4) [120.13(5)], Se(3)–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) 105.82(21) [105.6].
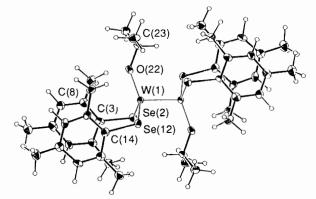

Figure 2. An ORTEP drawing of the $W_2(OPr^i)_2(SeAr)_4$ molecule; selected bond lengths (Å) and angles (°) [$Mo_2(OPr^i)_2(SeAr)_4$ in brackets]: M(1)–M(1') 2.3077 [2.2180(24)], M(1)–Se(2) 2.4303(10) [2.4281(21)], M(1)–Se(12) 2.4410(10) [2.4427(19)], M(1)–O(22) 1.858(6) [1.872(9)], Se(2)–C(3) 1.955(9) [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_π–M d_π bonding.

References

1 G. Wilkinson, R. D. Gillard, and J. A. McCleverty, 'Comprehensive Coordination Chemistry,' Pergamon, Oxford, 1987, p. 663.
2 M. H. Chisholm, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 21 (*Angew. Chem.*, 1986, **98**, 21).