Diolates of Dimolybdenum and Ditungsten (M≡M) with Seven-, Eight- and Nine-membered Rings

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The use of the bulky diols, H_2L^1 = 2,5-dimethylhexane-2,5-diol and H_3L^2 = 2,2′-methylenebis(6-*tert*-butyl-*p*-cresol) in reactions with $M_2(NMe_2)_6$ (M≡M) compounds leads to dinuclear diolates $M_2(L^1)_3(HNMe_2)_2$ **1**, $M_2(L^1)_3$ **2**, $Mo_2(NMe_2)_2(HL^2)$ **3** having seven-, eight- and nine-membered rings and $W_2(\mu\text{-H})(\mu\text{-NMe}_2)(NMe_2)(HNMe_2)(HL^2)(L^2)$, **4**, where L^2 is the anionic ligand derived from cyclometallation at the methylene carbon atom; the compounds **1** and **2** where M = W, **3**, and **4** have been structurally characterized.

Chelating ligands have played a remarkable role in the development of coordination chemistry. They may stabilize complexes by either thermodynamic or kinetic means and they may serve in the exploration of reaction mechanisms.[1] We are trying to establish the ground state coordination and reaction chemistries of Mo_2^{6+} and W_2^{6+} containing compounds.[2] We show here that the use of diols in the preparation of dinuclear diolates can lead to some fascinating and unexpected findings.

2,5-Dimethylhexane-2,5-diol H_2L^1 (3 equiv.) and $M_2(NMe_2)_6$ react in hexane–diethyl ether solution at −20 °C

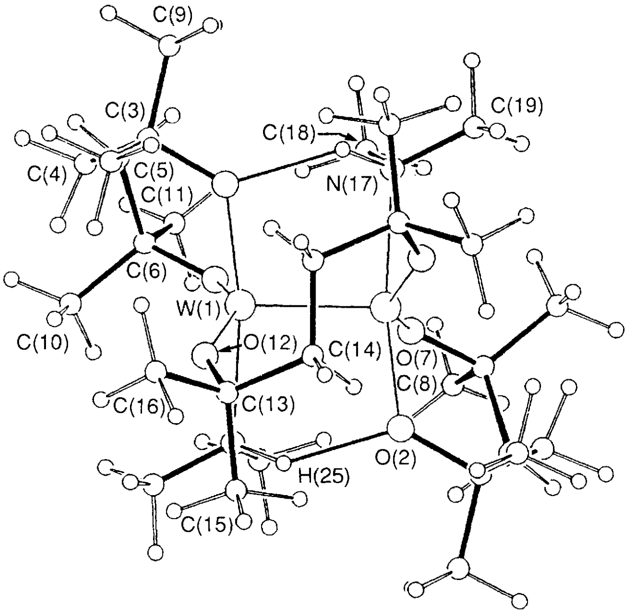

Fig. 1 A ball-and-stick drawing of **1** (M = W) showing the atom numbering scheme. Some pertinent distances (Å) and angles (°) are W–W 2.320(1), W–N 2.29(1), W–O 1.95(2) (av.); W–W–N 92.1(3), W–W–O 97–107. The molecule has a crystallographically imposed C_2 axis of symmetry.

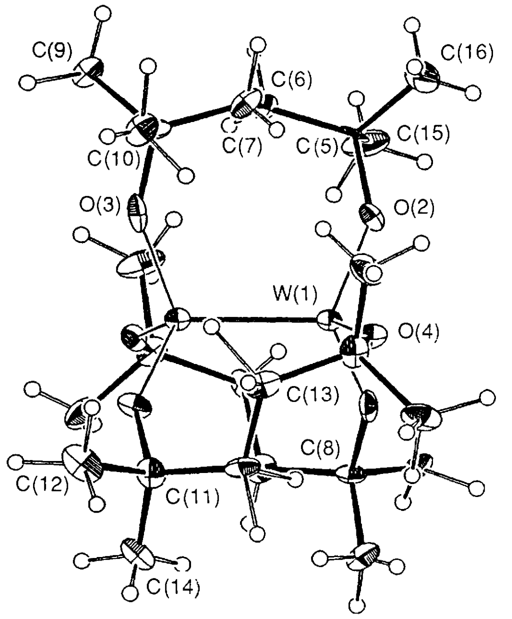

Fig. 2 An ORTEP drawing of **2** (M = W) showing the atom numbering scheme. Some pertinent distances (Å) and angles (°) are: W–W 2.363(1), W–O 1.88(1) (av.); W–W–O = 109(1) (av.). The molecule has a crystallographically imposed C_2 axis of symmetry.

and below to yield green crystalline compounds, $M_2(L^1)_3(HNMe_2)_2$, **1**, where M = Mo and W.† The compounds **1** are hydrocarbon soluble and in solution liberate $HNMe_2$ at room temperature and above yielding orange $M_2(L^1)_3$ compounds, **2**. Compounds **2** may also be prepared from the addition of the diol H_2L^1 (3 equiv.) to the $M_2(OBu^t)_6$ compounds and by the solid-state conversion of **1** to **2** at temperatures between 110 and 130 °C under a dynamic vacuum. Addition of $HNMe_2$ to hydrocarbon solutions of **2** at room temperature gives an equilibrium mixture as shown in equation 1.

$$\underset{\mathbf{1}}{M_2(L^1)_3(HNMe_2)_2} \rightleftharpoons \underset{\mathbf{2}}{M_2(L^1)_3} + 2HNMe_2 \qquad (1)$$

Rather interestingly the addition of $HNMe_2$ to [$^2H_8$]toluene solutions of **2** (M = W) at −45 °C does not yield **1**. The equilibrium (1) must favour the dimethylamine adduct **1** at low temperatures on thermodynamic grounds [as is seen for reactions between $M_2(OR)_6$ compounds and Lewis bases][3] but the kinetic barrier for adduct formation is too great to allow its formation. Thus, preparation of **1** in the alcoholysis reaction involving $M_2(NMe_2)_6$ compounds at −45 °C provides insight concerning the pathway wherein the alkoxide-metal bond is formed and the amide ligand is transformed to an amine at the dinuclear centre.

The molecular structures of the compounds **1** and **2** (M =

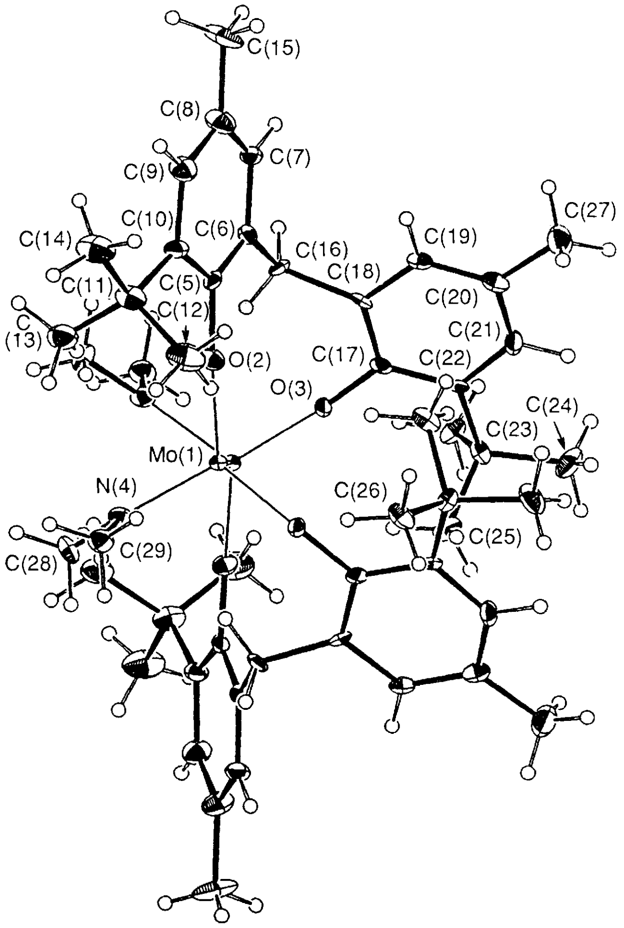

Fig. 3 An ORTEP drawing of **3** giving the atom numbering scheme. Some pertinent bond distances (Å) and angles (°) are: Mo–Mo 2.245(1), Mo–N 1.92(1), Mo–O 1.92(1) (av.); Mo–Mo–N 97.8(1), Mo–Mo–O 110(1) (av.). The molecule has a crystallographically imposed C_2 axis of symmetry.

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† All reactions were carried out under a dry and oxygen-free N_2 atmosphere with purified solvents. Satisfactory elemental analyses have been obtained. Selected ^1H NMR characterization data (300 MHz, [$^2H_8$]toluene) for **1**: δ 5.21 (s, 2 H), 3.62 (s, 2 H), 3.10 (m, 4 H), 2.21 (m, 4 H), 1.78 (m, 4 H), 1.70 (d, 12 H), 1.45 (m, 18 H), 1.23 (s, 3 H), 0.97 (s, 3 H). For **2**: δ 2.78 (s, 6 H), 1.92 (s, 6 H), 1.62 (s, 18 H), 1.23 (s, 18 H) (temperature invariant −90 °C to + 105 °C). For **3**: δ 7.32 (s, 4 H), 7.22 (s, 2 H), 7.04 (s, 2 H), 6.02 (d, 2 H), 4.23 (s, 6 H), 3.44 (d, 2 H), 2.87 (s, 6 H), 2.39 (s, 6 H), 2.20 (s, 6 H), 1.25 (s, 18 H), 1.06 (s, 18 H). For **4**: δ 11.54 (s, $^1J_{W-H}$ 129 and 95 Hz), 7.80 (s, 2 H), 7.20 (s, 2 H), 7.12 (s, 2 H), 6.98 (m, 2 H), 5.1 (d, 1 H), 4.8 (m, 1 H), 4.7 (s, 3 H), 4.45 (s, 3 H), 4.12 (d, 1 H), 3.86 (m, 3 H), 3.31 (s, 3 H), 3.26 (q, 4 H), 3.15 (s, 3 H), 2.32 (s, 6 H), 2.13 (s, 3 H), 2.16 (s, 6 H), 1.58 (m, 36 H), 1.13 (t, 6 H).

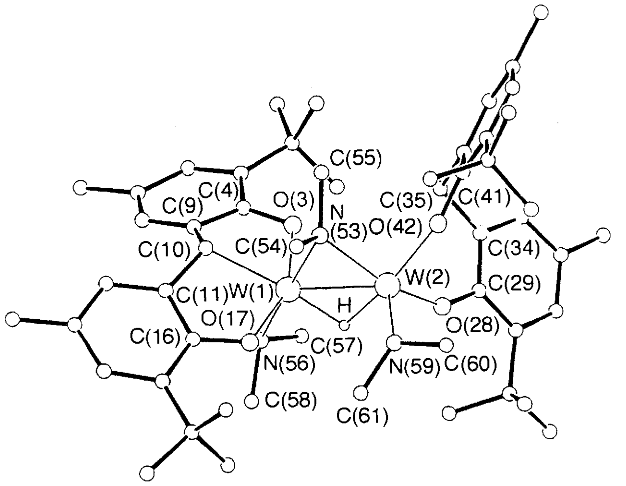

Fig. 4 A ball-and-stick drawing of **4** showing the atom numbering scheme. Selected bond distances (Å) are: W–W 2.4946(6), W(1)–O(3) 1.984(7), W(1)–O(17) 1.967(7), W(1)–N(53) 2.132(8), W(1)–N(56) 2.262(9), W(1)–C(10) 2.209(10), W(2)–O(28) 1.939(7), W(2)–O(42) 1.998(7), W(2)–N(53) 2.090(9), W(2)–N(59) 1.901(8). The hydride atom was refined isotropically and completes octahedral coordination about W(1).

W) are shown in Figs. 1 and 2, respectively.‡ In **1** each tungsten is four-coordinate; one diolate ligand spans the M–M triple bond forming an eight-membered ring while the other two are chelates, one to each metal, forming seven-membered rings. In **2** the diolates span the M–M triple bond yielding an inorganic [6.6.6]propellane having three eight-membered rings. The central W_2O_6 core is staggered and evidently rigid on the NMR timescale since the methyl groups form a diastereotopic pair and the methylene protons form an AA′MM′ spectrum.† The interconversion of **1** and **2** involves not only the formation and rupture of M–N(amine) bonds but also metal–oxygen terminal and bridge exchange. Presumably it is the kinetic barrier to the latter process that is responsible for the inability of **2** to react with $HNMe_2$ at low temperatures.

2,2′-Methylenebis(6-*tert*-butyl-*p*-cresol), H_3L^2 (3 equiv.) and $Mo_2(NMe_2)_6$ in hexane–diethyl ether react to give the yellow, hydrocarbon soluble crystalline compound $Mo_2(HL^2)_2(NMe_2)_2$ **3** that adopts the *gauche*-bridged structure shown in Fig. 3 wherein two diolate ligands span the Mo–Mo triple bond forming nine-membered rings.[3] This structure is evidently also present in solution since the methylene protons are diastereotopic and there are two types of *tert*-butyl and *p*-Me ^1H NMR signals (−70 to +105 °C in [$^2H_8$]toluene).[3] Rotations about the Mo–N bonds are also frozen out on the NMR time scale at 105 °C. It is likely that steric factors impede further amide replacement and formation of a $Mo_2(HL^2)_3$ compound.

The analogous reaction involving $W_2(NMe_2)_6$ and H_3L^2 (3 equiv.) yields an entirely different product of formula $W_2(\mu\text{-}H)(\mu\text{-}NMe_2)(NMe_2)(HNMe_2)(HL^2)(L^2)$ **4** where L^2 represents a cyclometallated diolate HL^2.[3] Compound **4** is a black hydrocarbon soluble crystalline material that has been structurally characterized by X-ray crystallography with Et_2O as a solvent of crystallization. The molecular structure of **4**, shown in Fig. 4, involves five- and six-coordinate tungsten atoms united by bridging hydride and amide ligands. The W–W distance of 2.49 Å is typical of a W=W bond[4] and is consistent with the presence of the oxidized W_2^{8+} centre. One tungsten is supported by a chelating diolate that forms an eight-membered ring together with an amide ligand. The other tungsten is coordinated by $HNMe_2$ and the metallated diolate ligand that now forms two five-membered rings as a result of W–C bond formation to the former methylene carbon. The hydride ligand occurs at δ 11.5 and shows coupling to two inequivalent ^{183}W nuclei.

Further studies are clearly warranted.

We thank the National Science Foundation for support of this research. I. P. P. is a NATO SERC postdoctoral fellow.

Received, 27th June 1991; Com. 1/03208I

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‡ *Crystal data* for **1** (M = W) at −170 °C: $a = b = 20.188(3)$, $c = 17.819(3)$ Å, $Z = 8$ and space group $P4/ncc$. $R(F) = 0.0439$ and $R_w(F) = 0.0421$ using 1785 observed data; for **2** (M = W) at −171 °C: $a = b = 12.568(2)$, $c = 37.075(8)$ Å, $Z = 8$ and space group $I4_1/a$. $R(F) = 0.0384$ and $R_w(F) = 0.0372$ using 1490 observed data; for **3** at −173 °C: $a = 24.999(4)$, $b = 11.283(1)$, $c = 17.551(2)$ Å, $Z = 4$ and space group $C2/c$. $R(F) = 0.0478$ and $R_w(F) = 0.0584$ using 2873 observed data; for **4** at −170 °C: $a = 23.285(3)$, $b = 25.800(3)$, $c = 18.364(2)$ Å, $Z = 8$ and space group $Pbca$. $R(F) = 0.0485$ and $R_w(F) = 0.0444$ using 5745 observed data. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1. 1991.

References

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3 M. H. Chisholm, *Polyhedron*, 1983, **2**, 681.
4 For a listing of (W=W)$^{8+}$ distances see ref. 3 and F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Atoms*, Wiley, New York, 1982.