Dioxododecaisopropoxytetratungsten. Oxygen Atom Abstraction from Acetone in Reactions with Hexaisopropoxyditungsten(*W≡W*)

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$W_2(OPr^i)_6(py)_2$(*W≡W*) (py = pyridine) and acetone (1 equiv.) react in hydrocarbon solvents at ambient temperatures to yield tetramethylethylene and $W_4O_2(OPr^i)_{12}$ the latter of which is shown, by an *X*-ray study, to be an unusual cluster type in which the eight electrons available for M–M bonding are partitioned into an M–M triple and M–M single bond.

Since their discovery the hexa-alkoxides of dimolybdenum[1,2] and ditungsten[3,4] have provided entry into a rich field of reaction chemistry.[5] The metal–metal triple bonds provide a source of electrons for redox reactions and the dinuclear centre may provide a template for the assembly of substrate molecules or eliminate the need for consecutive reduction steps. The reduction of C≡C, C≡N, and C≡O bonds in the reactions involving $W_2(OR)_6$ compounds exemplifies these principles.[5] We describe here a reaction between $W_2(OPr^i)_6(py)_2$ (py = pyridine) and acetone which, by oxygen atom abstraction, leads to a novel tetranuclear cluster $W_4O_2(OPr^i)_{12}$.

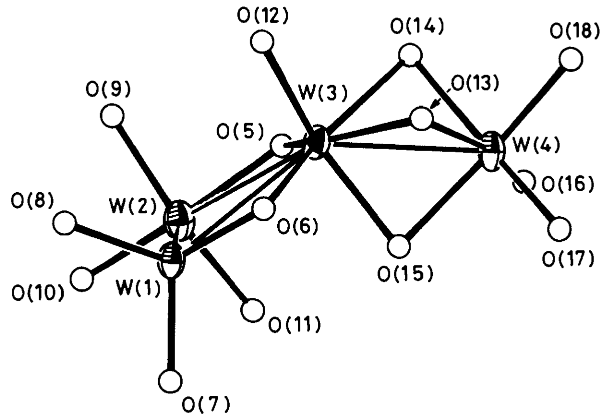

Figure 1. The central W_4O_{14} skeleton of the $W_4O_2(OPr^i)_{12}$ molecule. O(5) and O(6) are oxo oxygen atoms. Some pertinent distances (Å) and angles (°) are: W(1)–W(2) 2.404(2), W(1)–W(3) 2.948(2), W(2)–W(3) 2.950(2), W(3)–W(4) 2.684(2), W(1)–O(6), –O(7), –O(8) 1.845(13), 1.865(14), 1.856(13); W(2)–O(5), –O(9), –O(10), –O(11) 1.942(13), 1.910(16), 1.883(17), 1.951(16); W(3)–O(5), –O(6), –O(12), –O(13), –O(14), –O(15) 1.857(13), 2.008(13), 1.902(14), 2.197(13), 2.125(14), 2.055(13); W(4)–O(13), –O(14), –O(15), –O(16), –O(17), –O(18) 2.016(13), 2.054(14), 2.054(13), 1.888(17), 1.910(15), 1.805(14); W(2)–O(5)–W(3) 101.9(6), W(1)–O(6)–W(3) 99.8(6), W(2)–W(1)–O(6) 108.1(4), W(2)–W(1)–O(7) 105.2(4), W(2)–W(1)–O(8) 106.9(4), W(1)–W(2)–O(5) 103.9(4), W(1)–W(2)–O(9) 101.1(5), W(1)–W(2)–O(10) 99.9(5), W(1)–W(2)–O(11) 102.5(5), W(1)–W(2)–W(3) 65.91(5), W(2)–W(1)–W(3) 65.98(5), W(1)–W(3)–W(2) 48.11(4), W(1)–W(3)–W(4) 137.48(5), W(2)–W(3)–W(4) 131.50(5).

Hydrocarbon solutions (hexane, benzene, or toluene) of $W_2(OPr^i)_6(py)_2$ and acetone (1 equiv.) react† according to equation (1) at ambient temperatures.

$$2W_2(OPr^i)_6(py)_2 + 2Me_2C{=}O \rightarrow W_4O_2(OPr^i)_{12} + 4py + Me_2C{=}CMe_2 \quad (1)$$

Analyses of the volatile products of the reaction by ^1H n.m.r. spectroscopy and g.c.–mass spectroscopy showed only pyridine, tetramethylethylene, and traces of acetone and propan-2-ol. The tungsten-containing residue was obtained as black crystals from toluene and was shown to be $W_4O_2(OPr^i)_{12}$ by single crystal *X*-ray studies.‡ The central W_4O_{14} skeleton of the molecule is shown in Figure 1.

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† Dry and oxygen-free atmospheres (N_2) and solvents were used throughout.

‡ *Crystal data* for $W_4O_2(OPr^i)_{12}$ at −140 °C: a = 13.386(7), b = 19.426(15), c = 10.250(6) Å, α = 99.28(4), β = 104.20(3), γ = 94.52(3)°, Z = 2, D_c = 1.938 g cm^{-3}, triclinic, space group $P\bar{1}$. Of the 6658 unique reflections collected using Mo-K_α radiation (6° ≤2θ ≤45°), the 5423 having $F > 3\sigma(F)$ were used in the full-matrix least-squares refinement, using anistropic thermal parameters for the W atoms, while O and C atoms were isotropic. The hydrogen atoms were located in fixed positions. No absorption or extinction corrections were used. There was no evidence of solvent molecules being present. Final residual values are R 0.065 and R_w 0.065. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Although molybdenum and tungsten are known to form a wide variety of tetranuclear clusters including M_4 tetrahedra,[6] butterflies,[7,8] squares,[7] rectangles,[9] parallelograms,[10,11] and even *chains*,[12] the W_4 skeleton seen here is unique. The average oxidation state of tungsten is +4 yielding eight electrons for M–M bonding. Based on W–W distances,[5,13] these are evidently used to form one W–W triple bond, W(1)–W(2) 2.404(2) Å, and one W–W single bond, W(3)–W(4) 2.684(2) Å. Any direct M–M bonding at a distance of 2.95 Å must be weak by comparison. The molecule may thus be viewed as a dimer of two different dinuclear species. Note the W≡W bond is unbridged by any atom and the two tungsten atoms, W(1) and W(2), are three- and four-co-ordinate, respectively. The latter observation is very unusual and has only been seen recently in $(Pr^iO)_3Mo\equiv Mo(OPr^i)(CH_2Ph)_2(PMe_3)$.[14] The oxo bridges may be partitioned: O(6) as O^- to W(1), *i.e.* O(6) is like an alkoxy group in which W(3) substitutes for a carbon atom, and O(5) as an oxygen dative bond to W(2). Consistent with this line of reasoning the bond distances W(3)–O(5), 1.86(2), and W(3)–O(6), 2.01(1) Å, represent formally W–O double and single bonds, respectively. The other half of the molecule involving W(3) and W(4) is a confacial bioctahedron, $(RO)(O^-)(O^{2-})W(\mu\text{-}OR)_3W(OR)_3$, containing a W_2^{10+} core: (*W–W*).

The oxygen atom abstraction reaction and coupling of ketonic carbon atoms in equation (1) has an obvious parallel with the McMurry reagent[15] which employs reduced titanium, probably finely divided Ti metal or at least clusters.[16] In this instance it is probable that C–C bond formation occurs to give a diolate, akin to the reactions reported by Cotton, Walton and their co-workers[17] involving W=W bonds. The reaction could then proceed to give C–O bond cleavage and the alkene followed by cluster formation, or alternatively $W_2(OPr^i)_6$ could act as a reducing agent, giving a W_4-cluster from which alkene is released.

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