A New Structural Type for an Electron-Precise, Six-Electron Triangular Metal Cluster: $W_3O_2(O\text{-}t\text{-}Bu)_8$

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Triangular metal clusters involving molybdenum(IV) and tungsten(IV) have been known for over 30 years, existing both as molecular species and as part of extended lattices, e.g., as in $Zn_2Mo_3O_8$.[1,2] The six electrons provided by the three M(IV) centers make these cluster units electron precise in the sense that they are analogues of cyclopropane. The common structural motif of all known M_3^{12+} oxo containing clusters of molybdenum and tungsten is the presence of either one or two μ_3 ligand caps. We now report the preparation of the compound $W_3O_2(O\text{-}t\text{-}Bu)_8$, which has unprecedented structural features.

The reaction between $W_2(O\text{-}t\text{-}Bu)_6$ ($M{\equiv}M$)[3] and N_2O proceeds according to the stoichiometry shown in eq 1.[4] The compound formulated as $W_2O_3(O\text{-}t\text{-}Bu)_6$ (I) is also formed in the reaction between $W_2(O\text{-}t\text{-}Bu)_6$ and O_2 (>1.5 equiv) in hydrocarbon solvents.[5] The structure of I is not known, and in terms of reactivity and solution behavior, I may be viewed as the sum of two components: $WO(O\text{-}t\text{-}Bu)_4$[6] and $WO_2(O\text{-}t\text{-}Bu)_2$.

$$W_2(O\text{-}t\text{-}Bu)_6 + 3N_2O \xrightarrow[\text{pentane}]{0 \to 23\ ^\circ C} \underset{\text{I}}{\text{“}W_2O_3(O\text{-}t\text{-}Bu)_6\text{”}} + 3N_2 \qquad (1)$$

Red, pentane solutions of $W_2(O\text{-}t\text{-}Bu)_6$ initially turn green upon reaction with N_2O and then fade to the straw color associated with I. When the reaction between $W_2(O\text{-}t\text{-}Bu)_6$ and N_2O (2 equiv) is carried out in pentane at −15 °C, the green crystalline compound $W_3O_2(O\text{-}t\text{-}Bu)_8$ (II) is isolated (15% based on tungsten). The molecular structure of II deduced from a single-crystal X-ray study is shown in Figure 1.[7] The structure is without precedent: (1) There is no capping μ_3 ligand. (2) The metal–metal distances fall into two types: two long (2.93 Å) and one short (2.45 Å). (3) Each tungsten atom is in a unique coordination environment, and within the molecule we see coordination numbers of 5, 4, and 3 with respect to W–O bonding. (4) The two oxo ligands are in the W_3 plane and bridge the two long W–W distances while the short W–W edge of the triangle is not supported by a bridging ligand.

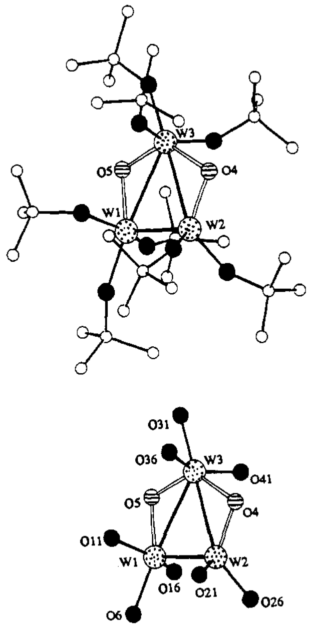

Figure 1. Ball-and-stick drawings of the $W_3O_2(O\text{-}t\text{-}Bu)_8$ molecule. The representation on the top shows the placement of all non-hydrogen atoms, while the representation below has the alkyl groups of the *tert*-butoxy groups omitted for clarity. The atom numbering scheme is the same. Pertinent distances (Å) are as follows: W(1)–W(2) = 2.447 (4); W(1)–W(3) = 2.927 (2); W(2)–W(3) = 2.935 (2); W(1)–O(5) = 1.94 (2); W(2)–O(4) = 1.81 (2); W(3)–O(4) = 1.99 (2); W(3)–O(5) = 1.84 (2). The W–O alkoxide distances span the range 1.85–1.93 Å.

Compound II is fluxional and labile in solution at room temperature as noted by ^1H NMR spectroscopy and a visual color change of the solution from green to red-brown upon warming. However, when green crystals of II are dissolved in toluene-d_8 at −72 °C, a low-temperature (less than −20 °C) limiting ^1H NMR spectrum of the *tert*-butoxy resonances in the ratio 1:1:2:2:2 is observed.[8] This is consistent with expectations based on the molecular structure shown in Figure 1, where a virtual mirror plane contains the atoms W(1), W(2), W(3), O(4), O(5), O(6), and O(31).

Upon warming this sample to 10 °C, a resonance associated with $W_2(O\text{-}t\text{-}Bu)_6$ is readily identified by ^1H NMR spectroscopy and becomes more intense as the sample is warmed to 45 °C. Thus, compound II dissociates according to eq 2.

$$W_3O_2(O\text{-}t\text{-}Bu)_8 \rightarrow W_2(O\text{-}t\text{-}Bu)_6 + WO_2(O\text{-}t\text{-}Bu)_2 \qquad (2)$$

The reaction in eq 2 is not reversible. After the sample is heated at 45 °C for 48 h, the ^1H NMR signals associated with II are not restored upon recooling the solution. Thus, the kinetic route to II in the reaction between $W_2(O\text{-}t\text{-}Bu)_6$ and N_2O may not involve $WO_2(O\text{-}t\text{-}Bu)_2$.[9] Nevertheless it is instructive to consider that II represents a product of a redox comproportionation reaction involving a d^0 WO_2 fragment to a $(W{\equiv}W)^{6+}$ moiety. Perhaps for steric reasons a more symmetrical structure involving μ_3-oxo groups is not viable, and redox disproportionation (eq 2) is thus favored.[10]

Supplementary Material Available: VERSORT drawings and stereoviews and a complete listing of bond distances and angles

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(4) All operations were carried out with dry and oxygen-free solvents and atmospheres by employing Schlenk and vacuum-line techniques.

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(7) Crystal data at −170 °C: a = 17.886 (2) Å, b = 12.374 (1) Å, c = 19.586 (3) Å, β = 99.80 (1)°, Z = 4, d_{calcd} = 1.817 g cm^{-3}, and space group $P2_1/a$. Of the 9785 reflections collected (Mo Kα, 6° < 2θ < 45 °C), 5598 were unique, and the 3874 having $F > 3\sigma(F)$ were used in the refinement. The final $R(F)$ value for 3874 reflections was 0.074, and the total number of parameters varied was 197 (including the scale factor and an overall isotropic extinction parameter), giving a ratio of observations to parameters of 19.66. The $R(F)$ for the complete data set was 0.087. The W atoms were refined anisotropically and the non-H atoms isotropically. The H atoms were introduced into fixed calculated positions during the final cycles of the full-matrix refinement. They were assigned isotropic thermal parameters equal to 1.0 + the isotropic thermal parameter of the parent C atom.

(8) ^1H NMR (360 MHz, −50 °C) (δ, C_7D_8) for $W_3O_2(O\text{-}t\text{-}Bu)_8$: 1.89, 1.87, 1.53, 1.45, 1.42 (all singlets with intensity ratio 1:1:2:2:2, respectively).

(9) The compound $WO_2(O\text{-}t\text{-}Bu)_2$ is probably oligomeric. It could be that in the reaction between $W_2(O\text{-}t\text{-}Bu)_6$ and N_2O a reactive monomeric species $WO_2(O\text{-}t\text{-}Bu)_2$ is formed and is kinetically trapped by reaction with unreacted $W_2(O\text{-}t\text{-}Bu)_6$ in preference to association with itself. This matter remains for further investigation.

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and isotropic and anisotropic thermal parameters (15 pages); listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

Methanolic C–O Bond Activation on Pd{111}: A Coverage-Dependent Reaction

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We find that the previously reported methanolic C–O bond activation on Pd{111} to form adsorbed methyl and hydroxyl at 225 K[1] occurs only for initial methanol coverages near 1 monolayer. At lower and higher coverages, methanol decomposes via the more traditional methoxy intermediate. Moreover, when methyl is formed, it is not observed to decompose until the temperature is raised to 400 K. This thermal behavior is quite unusual since CH_3 has been observed to combine with H to desorb as CH_4 below 300 K,[2-5] dimerize to produce C_2H_6 below 200 K,[6,7] or dehydrogenate to form CH_2 and H below 200 K.[8] In addition, we find that methyl undergoes sequential dehydrogenation as the temperature is increased to form CH_2 at 400 K, CH at 500 K, and C at >500 K. We speculate that the coverage dependency is connected with the thermal stability of CH_3 by a site-blocking mechanism, probably involving CO.

Although methylidyne, methylene, and methyl have been proposed to be the fundamental building units in catalytic methanation and Fischer–Tropsch synthesis,[9,10] direct evidence of such radicals on a well-defined single crystal under ultrahigh vacuum conditions is sparse.[1,8,11-13] Using X-ray photoelectron spectroscopy (XPS) and secondary-ion mass spectrometry (SIMS), we previously reported direct evidence for CH_3 and OCH_3 formation on Pd{111} during CH_3OH decomposition after initial exposures of ~1.25 L (1 L = 10^{-6} Torr s),[1] where 1 monolayer corresponds to ~1.3-L exposure. These conclusions were questioned in subsequent work from data produced by a series of isotope scrambling experiments which showed that the CO bond remained intact during methanol decomposition.[14] Many other confusing reports concerning the reactivity of simple hydrocarbons abound in the literature,[15-18] and it is important to establish the experimental parameters which allow the critical mechanistic pathways to emerge.

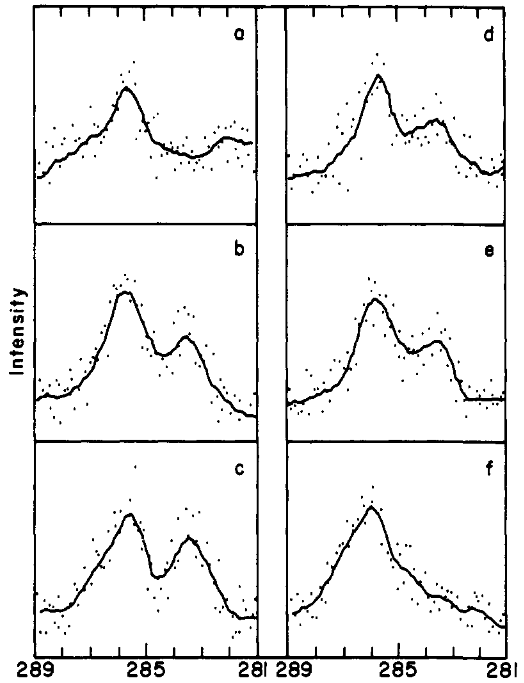

Figure 1. Carbon 1s XPS spectra for Pd{111} exposed to (a) 0.75 L, (b) 1.00 L, (c) 1.25 L, (d) 1.50 L, (e) 1.75 L, and (f) 2.00 L of methanol at 105 K and then heated to 300 K. The spectra are reported without normalization.

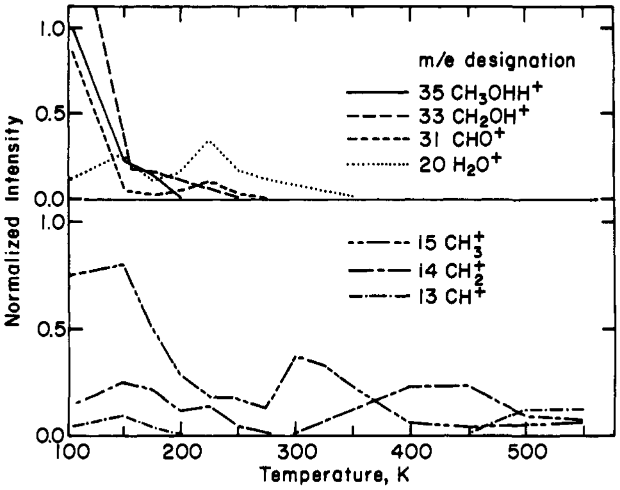

Figure 2. Intensity of selected positive secondary ions versus surface temperature for Pd{111} exposed to 1.25 L of $CH_3{}^{18}OH$ initially at 105 K. The ion intensities are determined from peak heights and reported relative to the $CH_3{}^{18}OHH^+$ ion signal at 105 K. Spectra were recorded with an Ar^+ ion beam energy of 3.0 KeV and an ion beam current density of 2 nA/cm^2.

Experiments were conducted in a multitechnique surface analysis system described previously.[19] The procedures for cleaning a Pd{111} crystal and purifying methanol and the spectroscopic protocols involving binding-energy referencing, peak deconvolution, and static SIMS measurements have been described in detail.[1] Methanol exposures are corrected by an ion gauge sensitivity factor of 1.9.[20] All spectra were recorded after the sample was warmed to the desired temperature at ~1 K/s and recooled to near the adsorption temperature of 105 K.

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