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A New Structure Type for a 6-Electron Triangulo Tungsten Cluster: $W_3(\mu_3\text{-CMe})(\mu\text{-O-}i\text{-Pr})_3(\text{O-}i\text{-Pr})_6$

Sir:

The early transition elements niobium, molybdenum, and tungsten have recently been found to exhibit an extensive trinuclear chemistry with a variety of ligands.[1,2] Even the Mo(IV) aquo ion has been shown by a variety of spectroscopic techniques to contain the trinuclear unit $Mo_3(\mu_3\text{-O})(\mu\text{-O})_3^{4+}$.[3-5] These complexes have triangulo M_3 units capped by either one or two μ_3-X groups (X may be O, S, CR, etc.). The metal atoms are coordinated to six or seven ligand atoms as shown schematically in Figure 1. We describe here the preparation and structural characterization of a W_3 cluster, namely, $W_3(\mu_3\text{-CMe})(\mu\text{-O-}i\text{-Pr})_3(\text{O-}i\text{-Pr})_6$, in which each tungsten atom is coordinated to only five ligand atoms.

In an attempt to prepare a compound of formula $W_2(\text{O-}i\text{-Pr})_6(\mu\text{-C}_2\text{Me}_2)(\text{py})_n$, where by analogy with known related compounds n could be 1 or 2,[6,7] $W_2(\text{O-}i\text{-Pr})_6(\text{py})_2$[8] and MeC≡CMe (1 equiv) were allowed to react in hexanes solution in the presence of an excess of pyridine (ca. 20 equiv) at 0 °C.[9] By ^{1}H NMR spectroscopy we can determine that this leads to a product mixture containing $W_2(\text{O-}i\text{-Pr})_6(\mu\text{-C}_4\text{Me}_4)(\eta^2\text{-C}_2\text{Me}_2)$,[6,10] $W_3(\mu_3\text{-CMe})(\mu\text{-O-}i\text{-Pr})_3(\text{O-}i\text{-Pr})_6$, and some unreacted $W_2(\text{O-}i\text{-Pr})_6(\text{py})_2$. $W_3(\mu_3\text{-CMe})(\mu\text{-O-}i\text{-Pr})_3(\text{O-}i\text{-Pr})_6$ was obtained by crystallization from hexanes solution in ca. 26% yield based on tungsten. $W_2(\text{O-}i\text{-Pr})_6(\mu\text{-C}_4\text{Me}_4)(\eta^2\text{-C}_2\text{Me}_2)$, which is more soluble in hexanes than $W_3(\mu_3\text{-CMe})(\mu\text{-O-}i\text{-Pr})_3(\text{O-}i\text{-Pr})_6$, can be obtained by crystallization from i-PrOH solutions.

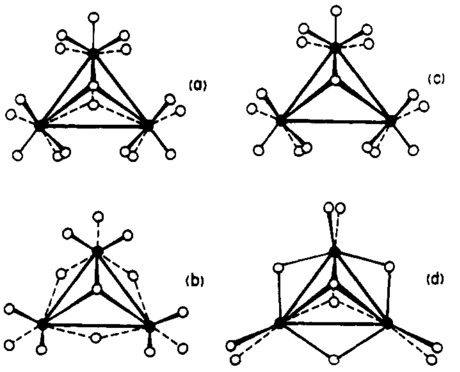

Figure 1. Prototypal representations of the four types of trinuclear cluster structures known for molybdenum and/or tungsten compounds:[1] (a) the bicapped structure found in $[M_3X_2(O_2CR)_6(H_2O)_3]^{n+}$ species; (b) the trigonal M_3O_4 type found in, for example, the Mo(IV) aquo ion; (c) the hemicapped structure found in $[W_3O(O_2CMe)_6(H_2O)_3]ZnBr_4\cdot 8H_2O$; (d) the M_3O_{11} core found in $M_3O(OR)_{10}$ compounds.

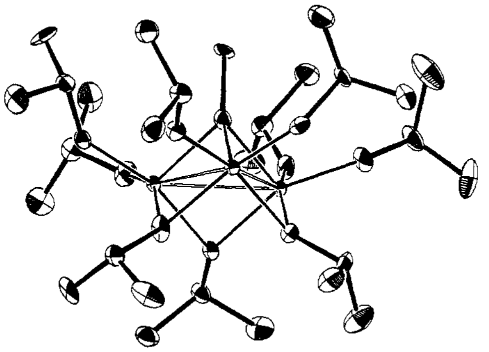

Figure 2. ORTEP view of the $W_3(\mu_3\text{-CMe})(\mu\text{-O-}i\text{-Pr})_3(\text{O-}i\text{-Pr})_6$ molecule showing the square-based pyramidal geometry at each tungsten atom. Pertinent bond distances (Å, averaged) are W–W = 2.75 (1), W–O (terminal) = 1.92 (2), W–O (bridging) = 2.04 (3), and W–C = 2.06 (2).

The molecular structure of the new triangulo tungsten cluster, deduced from a single-crystal X-ray study,[11] is shown in Figure 2. Each tungsten atom is coordinated to five ligand atoms such that the local geometry about each tungsten corresponds to a square-based pyramid. The three square-

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[1] See ref 1–10 in: Ardon, M.; Cotton, F. A.; Dori, Z.; Fang, A.; Kapon, M.; Reisner, G. M.; Shaia, M. *J. Am. Chem. Soc.* **1982**, *104*, 5394.

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[9] Dry and oxygen-free solvents and atmospheres (N_2) were used in all preparations. $W_2(\text{O-}i\text{-Pr})_6(\text{py})_2$ (0.50 g, 0.57 mmol) in hexanes/pyridine (10 mL/1 mL) was frozen at −196 °C and C_2Me_2 (0.57 mmol) was condensed into the flask with use of a calibrated vacuum manifold. The mixture was rapidly warmed to 0 °C and then stirred for 0.5 h at 0 °C and 0.5 h at room temperature. The volatiles were removed, and the solid that remained was redissolved in hexanes (4 mL). Cooling at −20 °C for 48 h produced dark crystals, which were isolated by filtration (yield 0.11 g, 26% based upon W).

[10] Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.*, in press.

[11] Crystal data at −158 °C: a = 18.255 (7) Å, b = 11.396 (4) Å, c = 11.500 (4) Å, α = 110.55 (2)°, β = 72.56 (2)°, γ = 75.16 (2)°, Z = 2, space group $P\bar{1}$. Of the 5243 reflections collected, with use of Mo Kα radiation, 6° ≤ 2θ ≤ 45°, the 4755 having $F > 3\sigma(F)$ were used in the full-matrix least-squares refinement. While most H atoms were visible in a difference Fourier, several failed to properly converge and therefore all were placed in idealized positions (d_{C-H} = 0.95 Å) during the refinement. Final residuals are $R(F)$ = 0.045 and $R_w(F)$ = 0.047.

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pyramidal units are fused together through the agency of a μ_3-CMe ligand and by three basal μ-OR ligands. The 360-MHz ^{1}H NMR spectrum recorded in toluene-d_8 at −1 °C is as expected on the basis of the solid-state structure. Specifically there are two types of O-*i*-Pr ligands in the ratio of 1:2 assignable to bridging and terminal groups, respectively, and the latter, but not the former, show diastereotopic methyl groups.[12] The signal assignable to the μ_3-CMe protons shows coupling to ^{183}W ($I = {}^1/_2$, natural abundance 14.3%), and the satellite intensities are consistent with expectations for a triply bridging group (31.5% of the total signal intensity is due to the isotopomer containing one ^{183}W nucleus).

The W–W distances, 2.75 Å, are notably longer than those seen in $M_3(\mu_3\text{-}O)(\mu_3\text{-}O\text{-}i\text{-}Pr)(\mu\text{-}O\text{-}i\text{-}Pr)_3(O\text{-}i\text{-}Pr)_6$ compounds (M–M = 2.53 Å (M = Mo) and 2.54 Å (M = W)).[13,14] The present structure may be viewed formally as a derivative of the $M_3(\mu_3\text{-}O)(\mu\text{-}O)_3{}^{4+}$ structure in which one of the octahedral sites, that trans to the capping ligand, is vacant.

Of interest, too, is how the new compound is formed in the reaction between $W_2(O\text{-}i\text{-}Pr)_6$ and MeC≡CMe. We believe that all the products can be accounted for in terms of reactions 1–4.

$$W_2(O\text{-}i\text{-}Pr)_6(py)_2 + MeCCMe \rightarrow W_2(O\text{-}i\text{-}Pr)_6(py)_n(\mu\text{-}C_2Me_2) \quad (1)$$

$$n = 0, 1, \text{ or } 2$$

$$W_2(O\text{-}i\text{-}Pr)_6(py)_n(\mu\text{-}C_2Me_2) \rightleftharpoons 2(i\text{-}PrO)_3W{\equiv}CMe + n\,py \quad (2)$$

$$W_2(O\text{-}i\text{-}Pr)_6 + (i\text{-}PrO)_3W{\equiv}CMe \rightarrow W_3(\mu_3\text{-}CMe)(\mu\text{-}O\text{-}i\text{-}Pr)_3(O\text{-}i\text{-}Pr)_6 \quad (3)$$

$$W_2(O\text{-}i\text{-}Pr)_6(py)_n(\mu\text{-}C_2Me_2) + 2MeCCMe \rightarrow W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4Me_4)(\eta^2\text{-}C_2Me_2) + n\,py \quad (4)$$

Reaction 1 has parallels in the synthesis of other alkyne adducts of ditungsten hexaalkoxides.[6,7] The equilibrium (2) has been found[7] for $W_2(O\text{-}t\text{-}Bu)_6(\mu\text{-}C_2H_2)(py)$ and $(t\text{-}BuO)_3W{\equiv}CH$, and dialkylacetylenes are known to react with $W_2(O\text{-}t\text{-}Bu)_6$ to give $(t\text{-}BuO)_3W{\equiv}CR$ compounds.[15] The comproportionation reaction (3) has a direct analogy to the synthesis of $M_3O(O\text{-}i\text{-}Pr)_{10}$ clusters from $MO(O\text{-}i\text{-}Pr)_4$ and $M_2(O\text{-}i\text{-}Pr)_6$ compounds[13,14] and is similar to (1). The coupling of the alkyne units in (4) is also now well documented.[10,16]

If the proposed reaction sequence is correct, it should be possible to synthesize an extensive class of related compounds including perhaps μ-nitrido clusters by the comproportionation of M≡N- and M≡M-containing compounds. Further studies are in progress.[17]

Registry No. $W_3(\mu_3\text{-}CMe)(\mu\text{-}O\text{-}i\text{-}Pr)_3(O\text{-}i\text{-}Pr)_6$, 92054-28-9; $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4Me_4)(\eta^2\text{-}C_2Me_2)$, 87654-13-5; $W_2(O\text{-}i\text{-}Pr)_6(py)_2$, 70178-75-5; MeC≡CMe, 503-17-3.

Supplementary Material Available: Listing of fractional coordinates and isotropic thermal parameters (1 page). Ordering information is given on any current masthead page.

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[12] ^{1}H NMR data from a toluene-d_8 solution at −1 °C (360 MHz): δ = 4.99, septet, J_{HH} = 6 Hz (6 H); δ = 4.12, J_{WH} = 6.9 Hz (3 H); δ = 3.64, septet, J_{HH} = 6 Hz (3 *H*); δ = 1.47, doublet, J_{HH} = 6 Hz (18 H); δ = 1.41, doublet, J_{HH} = 6 Hz (18 H); δ = 1.26, doublet, J_{HH} = 6 Hz (18 H). δ is relative to Me_4Si.

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Olefin Coordination with Rhodium(II) Trifluoroacetate

Sir:

Rhodium(II) carboxylates are being employed with increasing frequency as catalysts for carbenoid reactions of diazo compounds with unsaturated substrates,[1,2] for olefin hydrogenation,[3] and for autooxidation of alkenes.[4] Extensive structural information is available for these diamagnetic complexes that possess one coordination site per metal,[5] and their formation of 1:1 and 1:2 adducts with Lewis bases is well documented. Recently, Drago and co-workers have concluded that the filled, essentially π^* orbitals of rhodium(II) carboxylates are very effective at π back-donation into π-acceptor ligands.[6,7] However, complexes with olefins have not been observed, and rhodium(II) carboxylates are generally regarded as incapable of such coordination.[8]

We now report the first demonstration of olefin coordination with a rhodium(II) carboxylate and equilibrium constants for the 1:1 adducts of $Rh_2(OOCCF_3)_4$ with a representative series of alkenes. Sequential addition of aliquots of 2,5-dimethyl-2,4-hexadiene to $Rh_2(OOCCF_3)_4$ in anhydrous dichloromethane under nitrogen produces the spectral changes described in Figure 1. A spectral shift from the initial λ_{max} of 610 nm to a limiting value of 590 nm is observed. A plot of $1/\Delta A$ vs. 1/[diene] and/or ΔA vs. ΔA/[diene][9] shows a linear correlation (correlation coefficient >0.99) that describes a 1:1 complex between $Rh_2(OOCCF_3)_4$ and 2,5-dimethyl-2,4-hexadiene. Results obtained with concentrations of $Rh_2(OOCCF_3)_4$ only half that reported in Figure 1 confirm this interpretation. In contrast, the absorption spectrum of $Rh_2(OOCCH_3)_4$ is unaffected by 2,5-dimethyl-2,4-hexadiene or any other olefin employed in this investigation.

Table I reports equilibrium constants for adduct formation of a representative series of olefins with $Rh_2(OOCCF_3)_4$. Equilibrium constants were calculated from absorbance/concentration data by the procedure previously described for 2,5-dimethyl-2,4-hexadiene. A minimum of two separate determinations was made for each olefin, and K_{eq} values were reproducible to within ±7%. Comparison of K_{eq} values in Table I for 1-hexene, *trans*-3-hexene or *trans*-4-octene, and 2-methyl-2-butene shows that increasing alkyl substitution of the carbon–carbon double bond favors coordination. Complex formation with trans olefins is favored over that with cyclohexene, and vinyl ethers form the strongest adducts. Qualitatively, these results are consistent with π-donor stabilization

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