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Supplementary Material Available: Procedures for the preparation of **2**, the tandem Claisen–ene process, and the transformation of **5** to (+)-**1** (5 pages). Ordering information is given on any current masthead page.

Arsaoxanes as Reversible, Ligating Oxygen-Transfer Agents in the Synthesis of Neutral Metal–Oxo Clusters. The X-ray Structures of $Cp^*_2W_6O_{17}$ and $Cp^*_6Mo_8O_{16}$

James R. Harper and Arnold L. Rheingold*

Department of Chemistry and the Center for Catalytic Science and Technology University of Delaware, Newark, Delaware 19716

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Methylarsaoxanes, $(CH_3AsO)_n$, are heterocyclic oligomers of alternating methylarsenic groups and oxygen atoms where n = 2–5.[1,2] We form them by oxidation (under controlled conditions with dioxygen) of homocyclic pentamethylcyclopentaarsine, c-$(CH_3As)_5$ (eq 1). We find that these heterocycles are reversible, ligating oxygen-transfer agents in their reactions with group 6 organometallic substrates. What distinguishes these systems from other oxygen-transfer agents reviewed by Holm[3] is their ability to act simultaneously as controlled, reversible oxidants and to ligate in both reduced and oxidized forms using the same ligating atom. Throughout, As remains trivalent, retains its "soft" ligand properties, and ligates regiospecifically.

We report the use of methylarsaoxanes as a new class of oxygen-transfer agent for the synthesis of novel, neutral, high-nuclearity M–oxo (M = Mo, W) clusters illustrated by $(C_5Me_5)_2W_6O_{17}$ (**1**) and $(C_5Me_5)_6Mo_8O_{16}$ (**2**) (Figures 1 and 2). There exists extensive knowledge about anionic oxomolybdate and oxotungstate clusters.[4] Neutral organometallic analogues of these polymetalates have not previously been isolated, but would be of high interest as a means of studying their reactivity in organic media. **1** is the first example of a neutral, organically soluble organometallic tungstate and as such compliments the work of Day and Klemperer[5] in the chemistry of homonuclear and substituted heteronuclear polyoxoanions. **2** is the largest neutral organomolybdenum oxide characterized and the first example of an oxide containing two distinct molybdenum oxidation states.

Compounds **1** and **2** are formed as the major oxidation products from the sealed-tube reactions of the corresponding triply bonded pentamethylcyclopentadienyl metal carbonyl dimers $[Cp^*M(CO)_2]_2$ (M = Mo, W)[6] and either the cyclic polyarsine c-$(AsCH_3)_5$ containing 15–25% (NMR integration) of the arsaoxane or, additionally, in the case of **2**, with isolated crystalline $(CH_3AsO)_4$.[7,8] Other products accompanying the formation of **1** and **2** include the oxo dimers, Mo^{VI} $\{[Cp^*Mo(O)_2]_2(\mu\text{-}O)\}^9$ and Mo^V *cis*-$[Cp^*Mo(O)(\mu\text{-}O)]_2{}^{10}$ (eq 2), the tetrahedrane-analogue

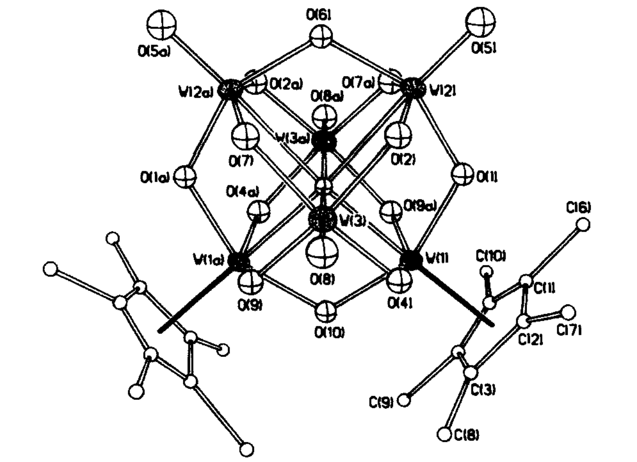

Figure 1. Molecular structure of $Cp^*_2W_6O_{17}$. The μ_6-O atom is O(3). Distances (Å): W(1)–CNT(1), 2.11 (4); W(1)–O(1), 1.941 (16); W(1)–O(4), 1.966 (16); W(1)–(O10), 1.928 (12); W(1)–O(9a), 1.921 (16); W(1)–O(3), 2.204 (13); W(2)–O(5), 1.692 (20); W(2)–O(1), 1.886 (16); W(2)–O(2), 1.930 (16); W(2)–O(6), 1.924 (11); W(2)–O(7a), 1.924 (17); W(2)–O(3), 2.502 (15); W(3)–O(8), 1.694 (17); W(3)–O(2), 1.939 (18); W(3)–O(4), 1.923 (18); W(3)–O(7), 1.937 (19); W(3)–O(9), 1.926 (18); W(3)–O(3), 2.355 (2).

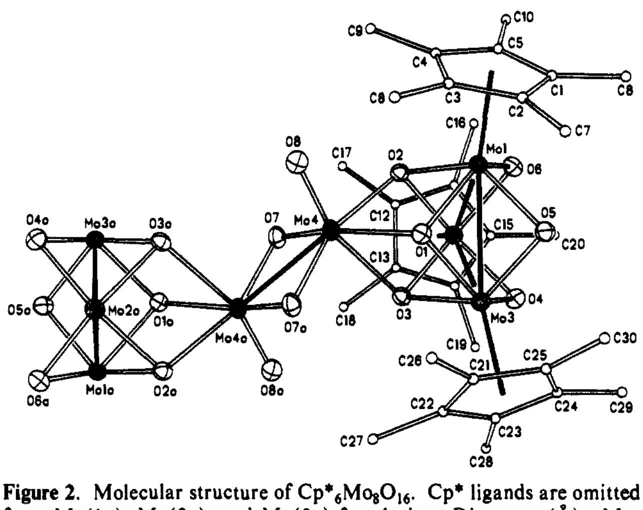

Figure 2. Molecular structure of $Cp^*_6Mo_8O_{16}$. Cp* ligands are omitted from Mo(1a), Mo(2a), and Mo(3a) for clarity. Distances (Å): Mo(1)–Mo(2), 2.751 (1); Mo(1)–Mo(3), 2.748 (1); Mo(2)–Mo(3), 2.734 (1); Mo(1)–CNT(1), 2.046 (4); Mo(1)–O(1), 2.040 (2); Mo(1)–O(2), 2.035 (2); Mo(1)–O(5), 1.946 (2); Mo(1)–O(6), 1.958 (1); Mo(2)–CNT(2), 2.052 (2); Mo(2)–O(2), 2.027 (2); Mo(2)–O(3), 2.022 (2); Mo(2)–O(4), 1.940 (2); Mo(2)–O(6), 1.969 (3); Mo(3)–CNT(3), 2.055 (3); Mo(3)–O(1), 2.041 (2); Mo(3)–O(3), 2.021 (2); Mo(3)–O(4), 1.953 (1); Mo(3)–O(5), 1.957 (2); Mo(4)–Mo(4a), 2.572 (1); Mo(4)–O(1), 2.137 (2); Mo(4)–O(2), 2.150 (2); Mo(4)–O(3), 2.260 (2); Mo(4)–O(7), 1.949 (2); Mo(4)–O(7a), 1.943 (2); Mo(4)–O(8), 1.691 (3).

Scheme I. Reaction Summary

$$\text{c-}(CH_3As)_5 + O_2 \rightarrow \text{c-}(CH_3AsO)_n \quad n = 2\text{–}5 \qquad (1)$$

$$[Cp^*M(CO)_2]_2 + \text{c-}(CH_3AsO)_n \xrightarrow[-CO]{} \left\{\begin{array}{l} Cp^*_2W_6O_{17}\ (M = W)\ (\mathbf{1}) \\ Cp^*_6Mo_8O_{16}\ (M = Mo)\ (\mathbf{2}) \\ [Cp^*M(O)_2]_2(\mu\text{-}O)^9 \\ [Cp^*M(O)(\mu\text{-}O)]_2{}^{10} \end{array}\right. + \text{c-}(CH_3As)_5 \qquad (2)$$
$$M = Mo, W$$

$$[Cp^*M(CO)_2]_2\ (\text{or } [Cp^*M(CO)_3]_2) + \text{c-}(CH_3As)_5 \rightarrow [Cp^*M(CO)_2]_aAs_b{}^{11} \quad a + b = 4 \qquad (3)$$

$$[Cp^*M(CO)_2]_2 + CO \rightarrow [Cp^*M(CO)_3]_2{}^{13} \qquad (4)$$

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clusters $[Cp^*M(CO)_2]_aAs_b$[11] ($a + b = 4$), the π-allyl analogue dimethyltriarsinidene complex $\{Cp^*W(CO)_2[\eta^3\text{-}(MeAsAsAsMe)]\}$[12] (eq 3), and the single-bonded carbonylated metal dimer $[Cp^*M(CO)_3]_2$[13] (eq 4) (see reaction summary, Scheme I).[14]

The structures of **1** and **2** were determined by single-crystal X-ray diffraction.[15] **1** is a neutral organometallic analogue of the well-known hexatungstate $W_6O_{19}^{2-}$ structure,[5a] in which two O^{2-} have been replaced (formally) by two Cp^{*-}. Bond distances for **1** reveal extensive distortion of the prototype $W_6O_{19}^{2-}$ structure; the W–μ_6O distances occur in three sets: Cp*W–O(3), 2.204 (13) Å; W(3)–O(3), 2.355 (2) Å; and W(2)–O(3), 2.502 (15) Å. This compares to the W–μ_6O bond distances of ca. 2.33 Å in several $W_6O_{19}^{2-}$ structures.[16] The variations in the W–μ_6O distances in **1** are comparable to those seen in the heteropolytungstate $[CpTiW_5O_{18}]^{3-}$, in which the bond trans to the substituted metal atom is lengthened.[5b] **1** is sparingly soluble in polar solvents; the Cp* ^{1}H NMR signal (δ 2.611 ppm) is unusually deshielded and in keeping with the abnormally long average W–C_{ring} distance, 2.41 (3) Å.

The octamolybdenum cluster **2** is joined about its inversion center by two d^1 molybdenum(V) atoms which are each capped by three μ_3-O bridges to a trigonal base of equivalent Cp*-coordinated molybdenum atoms. Assignment of oxidation state for Mo(4) was made by comparison of bond distances in **2** to other Mo^V and Mo^{VI} structures.[9,10] The Cp*-coordinated molybdenum atoms are assigned an average formal oxidation state of $4^2/_3$; an absence of charge localization is suggested by the close similarities in the three Cp*Mo coordination spheres. The structure of **2** is unlike the open network of the large anionic polymolybdates that have been studied as either thermal or photolytic oxidation catalysts.[17] A closer structural analogy is that of the oxo-bridged condensed vanadium clusters (e.g., $[Cp_5V_6(\mu_3\text{-}O)_8]_2(\mu\text{-}O)$ and $[Cp_5V_6(\mu_3\text{-}O)_8]_2[(\mu_2\text{-}O_8)V_4Cp_4]$) synthesized by Bottomley and co-workers.[18]

The synthesis of **2** from crystalline $(CH_3AsO)_4$ implicates the arsaoxane as the oxidant in these reactions. Following initial arsaoxane coordination, rapid cleavage of the heterocyclic ring and transfer of oxygen to the metal center occur to form Mo^{VI} and Mo^V–oxo clusters. Evidence for initial arsaoxane coordination comes in reactions of both $Mo(CO)_6$[19] and $Mn_2(CO)_{10}$[20] systems, in which intact, but expanded, arsaoxane systems coordinate as 12- and eight-membered rings, respectively. Reduction of the arsaoxanes to the precursor cycloorganopolyarsines allows for further reaction with either $[Cp^*M(CO)_2]_2$ or $[Cp^*M(CO)_3]_2$ to produce the tetrahedrane-analogue and π-allyl-analogue compounds.

Synthetic routes to, and the structure and bonding modes of, high-oxidation-state metal clusters are generally not well-developed,[21] and further reactions are planned to assess the applicability of this system to other transition metals.

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Supplementary Material Available: Details of the structural characterizations of **1** and **2**, including tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates (10 pages); tables of observed and calculated structure factors for **1** and **2** (56 pages). Ordering information is given on any current masthead page.

(8) Preparation of **1**: $[Cp^*W(CO)_2]_2$ (0.30 g, 0.40 mmol) was dissolved in 15 mL of a dry, degassed toluene solution containing 0.217 g (0.48 mmol) of pentamethylcyclopentaarsine (containing 25% arsaoxane) in a sealed tube and heated at 170 °C for 22 h. Yellow-brown, needle-shaped crystals were separated by filtration: 42% yield; mp = 300–305 °C; ^{1}H NMR (CD_3CN) Cp* 2.611 ppm; IR (KBr) ν 984 (s), 853 (m, sh), 816 (vs, br), 785 (vs), 436 (m) cm^{-1}. Anal. Calcd for $C_{20}H_{30}O_{17}W_6$: C, 14.60; H, 1.84. Found: C, 14.99; H, 2.10. Preparation of **2**: $[Cp^*Mo(CO)_2]_2$ (0.50 g, 0.87 mmol) and $(CH_3As)_5$ (0.78 g, 1.74 mmol) were reacted as described above at 150 °C. Dark green insoluble crystals were separated by filtration: 22% yield; mp = 437–440 °C; IR (KBr) ν 1025 (s), 1013 (m, sh), 930 (vs), 911 (sh), 733 (m), 656 (m), 608 (vs, br), 525 (m) cm^{-1}. Alternate preparation of **2**: $[Cp^*Mo(CO)_2]_2$ (0.458 g, 0.797 mmol) and $(CH_3AsO)_4$ (0.065 g, 0.154 mmol) were reacted as described above at 150 °C. Anal. Calcd for $C_{60}H_{90}O_{16}Mo_8$: C, 39.28; H, 4.94. Found: C, 38.20; H, 4.76.

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(15) **1**: $C_{20}H_{30}O_{17}W_6$; monoclinic, $C2/c$, $a = 8.905$ (3) Å, $b = 18.285$ (8) Å, $c = 18.638$ (7) Å, $\beta = 98.97$ (3)°, $V = 2998$ (2) Å^3, $Z = 4$, D(calcd) = 3.65 g cm^{-3}, $T = 23$ °C, $R(F) = 5.95\%$, $R(wF) = 6.21\%$. **2**: $C_{60}H_{90}O_{16}Mo_8$; triclinic, $P\bar{1}$, $a = 11.240$ (2) Å, $b = 11.349$ (3) Å, $c = 15.598$ (3) Å, $\alpha = 70.31$ (2)°, $\beta = 82.19$ (2)°, $\gamma = 60.05$ (1)°, $V = 1622.0$ (6) Å^3, $Z = 1$, D(calcd) = 1.88 g cm^{-3}, $T = 23$ °C, $R(F) = 2.71\%$, $R(wF) = 3.15\%$.

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Unusual C,O-Bridging Coordination of Acetate and Acetylacetonate Ligands in the Platinum Clusters $[Pt^{III}_2(\mu\text{-}CH_2COO\text{-}C,O)_2(\mu\text{-}CH_3COO\text{-}O,O')_2Cl_2]^{2-}$ and $Pt^{II}_4(\mu\text{-}CH_3COO\text{-}O,O')_4(\mu\text{-}CH_3COCHCOCH_3\text{-}O,C^3)_4$

Tadashi Yamaguchi, Yoichi Sasaki,* and Tasuku Ito*

Department of Chemistry, Faculty of Science
Tohoku University, Aramaki, Aoba-ku, Sendai 980, Japan
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While studying the preparation and properties of platinum cluster compounds with acetate as a ligand,[1] we have found two new compounds, given in the title. These Pt–Pt-bonded compounds have acetate or acetylacetonate ligands which bridge between two platinum ions through an oxygen and a carbon atom. Although platinum ions tend to take on a Pt–C-bonded structure, such C,O-bridging modes are to the best of our knowledge unprecedented for these ligands.[2,3]

Platinum(III) dimers with a Pt–Pt single bond are known for various bridging ligands including sulfate and phosphate,[4-6] but

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