compound **4**, which had a shorter retention time when passed through an HPLC silica gel column, was designated the *R,R* isomer.[12] The resolved amide **4** was subjected to acid hydrolysis and then hydride reduction, giving (*R*)-(methylenecyclopropyl)-methanol **6** in 63% yield.[13] The stereochemical assignment of this sample was further confirmed by ^{1}H NMR analysis of its Mosher ester, whose methoxyl signal showed a greater lanthanide-induced shift than that of the *S* isomer derived from **5**.[14] Chain elongation converting **6** to **8** via the cyanide intermediate **7** was accomplished in four steps, with an overall yield of 52%.[15] Condensation of **8** with isobutyl chloroformate followed by coupling to coenzyme A in aqueous THF solution (pH 8-8.5)[5,16] afforded the desired (*S*)-MCPA-CoA (**9**).[17] The corresponding *R* epimer was synthesized from compound **5** by an identical sequence. The crude MCPA-CoA was chromatographed on an HPLC Partisil-C_{18} column and eluted with 30% methanol in 50 mM potassium phosphate buffer, pH 5.3.[18] Fractions containing MCPA-CoA gave a negative result to the nitroprusside test[19] and had an A_{223}/A_{256} ratio of 0.45-0.5. After removal of methanol in vacuo, the pooled fractions were desalted by reversed-phase chromatography (eluting with water and then methanol)[18] and then lyophilized.

The effect of the MCPA-CoA isomers on the catalytic activity of GAD was analyzed by the method of successive titration used by Wenz et al.[4a,20] As shown in Figure 1, a plot of the residual activity observed under aerobic conditions versus total equivalents of MCPA-CoA added gave a partition ratio of 4.4 and 5.0 for (*R*)- and (*S*)-MCPA-CoA, respectively. These results unequivocally demonstrated that both stereoisomers of MCPA-CoA are competent inhibitors. Since the racemic mixture gave a partition ratio of 4.4 under identical conditions,[21] the aforementioned results clearly indicated that the inactivation of GAD by either epimer of MCPA-CoA follows the same course. Namely, the inactivation is nonstereospecific. Such a lack of stereospecificity of bond rupture at C_β of MCPA-CoA in the enzyme active site strongly suggests that the ring-opening step leading to inactivation is likely a spontaneous event, induced by an α-cyclopropyl radical. Since the rearrangement of α-cyclopropyl radicals to ring-opened alkyl radicals is extremely rapid, the ring cleavage may bypass the chiral discrimination normally imposed by the enzyme.[22] Thus, the mechanistic insights deduced from this study support our early notion that GAD is capable of mediating one-electron oxidation-reduction.

Note Added in Proof. Similar results were reported in a recent publication by Baldwin et al.[23]

Acknowledgment. We thank the National Institutes of Health (GM 40541) for financial support. H.-w.L. also thanks the National Institutes of Health for a Research Career Development Award. The technical help from Dr. Younan Shih and Li-da Liu was greatly appreciated.

(11) (a) Helmchen, G.; Nill, G.; Flockerzi, D.; Schühle, W.; Youssef, M. S. K. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 62. (b) Helmchen, G.; Volter, H.; Schühle, W. *Tetrahedron Lett.* **1977**, 1417.

(12) Chromatographed on a preparative silica gel column (Spherisorb 5μ, 10 mm × 25 cm) eluting with 10% 2-propanol/CH_2Cl_2 at a flow rate of 4 mL/min, amide **4** and **5** gave a retention time of 4.5 and 5.1 min, respectively. The enantiomeric purity of the resolved **4** and **5** was determined to be greater than 99% based on the integration of the eluted peaks.

(13) This chemically synthesized racemic mixture could also be resolved at the alcohol stage (**6** and its *S* epimer) by the conversion of the alcohols to the corresponding Mosher esters followed by an HPLC separation of the diastereomeric esters with a DAICEL Chiralcel OJ column (10% 2-propanol/hexane). Attempts to resolve the racemic alcohols (**6** and its *S* epimer) by a double resolution sequence based on the lipase-catalyzed esterification and hydrolysis (Ladner, W. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1984**, *106*, 7250. Drueckhammer, D. G.; Barbas, C. F.; Nozaki, K.; Wong, C.-H. *J. Org. Chem.* **1988**, *53*, 1607) were futile.

(14) (a) Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512. (b) Yasuhara, F.; Yamaguchi, S. *Tetrahedron Lett.* **1977**, 4085.

(15) The optical rotations of compound **8** and the corresponding *R* epimer were +0.86 ($CHCl_3$, *c* 1.6) and −0.82 ($CHCl_3$, *c* 1.5), respectively.

(16) Belcher, M. *Methods Enzymol.* **1981**, *72*, 404.

(17) It should be noted that the configuration assignment at the chiral center was reversed when compound **6** was converted to **7**/**8**/**9** due to the change of the priority sequence of the substituents at the chiral center.

(18) Eberhard, A. *Chromatogram* **1987**, *8*, 10.

(19) Stadtman, E. R. *Methods Enzymol.* **1957**, *3*, 931.

(20) The GAD used in this study was purified from pig kidney to homogeneity based on a procedure described by Thorpe (Thorpe, C. *Methods Enzymol.* **1981**, *71*, 366).

(21) The partition ratio of this inactivation found in our early study was slightly lower than the value reported here.[5] Since the early racemic MCPA-CoA sample was only purified by conventional chromatography, it might still contain impurities that could inhibit GAD.

(22) It is worth noting that the inactivation caused by (*R*)-MCPA-CoA is faster than that observed for the *S* isomer. Such a rate distinction may arise from the rate difference of the α-proton abstraction step which is expected to be more sensitive to the steric environment around C_α and the binding orientation of substrate in the enzyme active site.

(23) Baldwin, J. E.; Ostrander, R. L.; Simon, C. D.; Widdison, W. C. *J. Am. Chem. Soc.* **1990**, *112*, 2021.

Asymmetric Tandem Claisen-Ene Strategy for Steroid Total Synthesis: An Efficient Access to (+)-9(11)-Dehydroestrone Methyl Ether

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The concept of the "tandem reaction sequence"[1] has currently stimulated interest as an efficient strategy for the stereocontrolled synthesis of complex molecules. Steroids have played vital roles as synthetic targets in the development of new strategies because their well-defined structures provide an opportunity to test new methods and explore their stereochemistry.[2,3] Herein we report a conceptually new, efficient strategy for the asymmetric total synthesis of (+)-9(11)-dehydroestrone methyl ether (**1**), a key intermediate for estrogens.[2,4] The key transformation is the asymmetric Claisen-ene sequence (I → II → III), which proceeds in tandem[1,5] and in a highly stereocontrolled fashion (Scheme I).

Our total synthesis starts with the preparation of the requisite *S*-*Z* allylic alcohol **2**[6] from (*R*)-glyceraldehyde acetonide **3**. Thus, the Wittig olefination[7] of methyl ketone **6**[8] derived from **3** was carried out in THF at −78 °C using [5-(trimethylsilyl)-4-pentynyl]phosphonium salt and butyllithium to afford, after desilylation (n-Bu_4NF), (*Z*)-enyne **7** exclusively[9] (Chart I). Methoxy-

(1) For the terminology of "tandem" and recent examples: (a) Ziegler, F. E. *Chem. Rev.* **1988**, *88*, 1423. (b) Nakai, T.; Mikami, K. *Ibid.* **1986**, *86*, 885.

(2) Reviews: (a) Blickenstaff, R. T.; Ghosh, A. C.; Wolf, G. C. *Total Synthesis of Steroids*; Academic Press: New York, 1974. (b) Taub, D. In *The Total Synthesis of Natural Products*; ApSimon, J., Ed.; John Wiley: New York, 1984; Vol. 6. (c) Groen, M. B.; Zeelen, F. J. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 465.

(3) For leading recent examples: (a) Johnson, W. S.; Lindell, S. D.; Steele, J. *J. Am. Chem. Soc.* **1987**, *109*, 5852. (b) Stork, G.; Saccomano, N. A. *Tetrahedron Lett.* **1987**, *28*, 2087. (c) Ziegler, F. E.; Wang, T. F. *J. Am. Chem. Soc.* **1984**, *106*, 718. (d) Takahashi, T.; Shimizu, K.; Doi, T.; Tsuji, J. *Ibid.* **1988**, *110*, 2674. (e) Horiguchi, Y.; Nakamura, E.; Kuwajima, I. *Ibid.* **1989**, *111*, 6257.

(4) (a) Ziegler, F. E.; Lim, H. *J. Org. Chem.* **1982**, *47*, 5230. (b) Posner, G. H.; Switzer, C. *J. Am. Chem. Soc.* **1986**, *108*, 1239. (c) Posner, G. H.; Mallamo, J. P.; Black, A. Y. *Tetrahedron* **1981**, *37*, 3921. (d) Quinkert, G.; Weber, W. D.; Schwartz, U.; Duerner, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1027. Quinkert, G.; Schwartz, U.; Stark, H.; Weber, W. D.; Baier, H.; Adam, F.; Duerner, G. *Ibid.* **1980**, *19*, 1029.

(5) The tandem Claisen-ene reaction has previously been reported on racemic cyclopentenol systems: Ziegler, F. E.; Mencel, J. J. *Tetrahedron Lett.* **1984**, *25*, 127. Ziegler, F. E.; Mikami, K. *Tetrahedron Lett.* **1984**, *25*, 131.

(6) To introduce the 14*S* chirality in the Claisen product II, either (*S*)-(*Z*)-**2** or (*R*)-(*E*)-**2** is required. We employed the former in view of the easy availability of (*R*)-glyceraldehyde **3** and the high *Z* selectivity in the Wittig olefination of α-alkoxy ketones (ref 7).

(7) Streekumar, C.; Durst, K. P.; Still, W. C. *J. Org. Chem.* **1980**, *45*, 4260.

(8) The ketone **6** was prepared from **3** via the standard method [MeMgI; DMSO, $(COCl)_2$, Et_3N]; $[\alpha]^{28}_D$ +74.1°; lit. $[\alpha]^{20}_D$ +53.3°: Dumont, R. *Helv. Chim. Acta* **1983**, *66*, 814.

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Scheme I

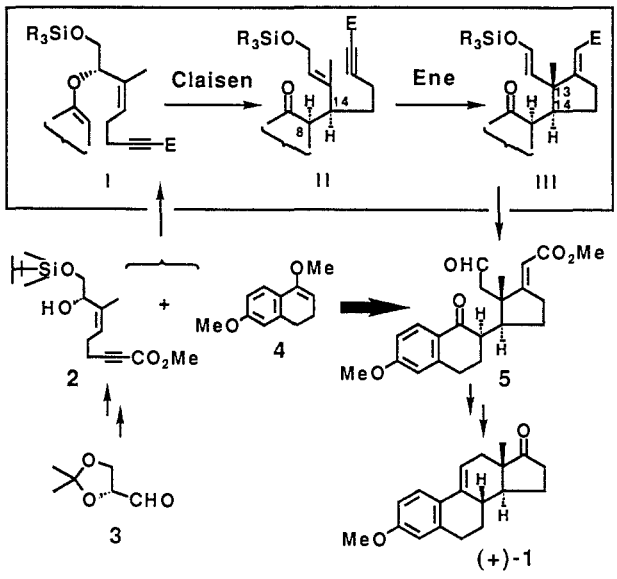
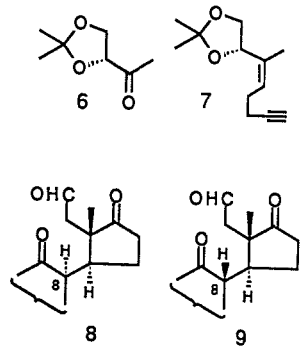


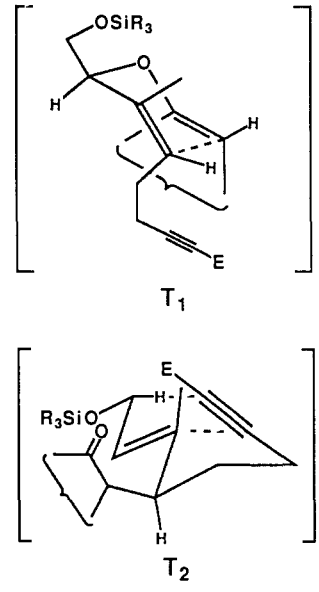
Chart I



carbonylation (*n*-BuLi/$ClCO_2CH_3$, THF, −78 °C) of **7** followed by deacetonization (*p*-TsOH, MeOH) and selective protection of the primary hydroxyl group with dimethylthexylsilyl chloride (DMF, imidazole, −40 °C) gave **2** in stereochemically pure form[10] in 86% overall yield from **3**.

Now, the stage was set for the one-pot Claisen–ene sequence. A toluene solution of **2** and cyclic enol ether **4**[11] (the A,B-ring component) in the presence of 2,6-dimethylphenol (10 mol %)[12] was heated in a sealed tube at 180 °C for 60 h. The "tandem Claisen–ene" product **5** was isolated in 76% yield after hydrolysis (1 N HCl, THF). A careful NMR analysis (500 MHz) of **5** showed that the 13,14-configuration was exclusively trans and the 8,14-configuration was 90% syn.[13] The transformation of the tandem product to the estrogen skeleton was accomplished by following Ziegler's procedure. Ozonolysis (O_3, MeOH,[14] −35 °C, Me_2S) of **5** afforded Ziegler's diketo aldehyde **8** and **9**[4a] (4:1) in 67% yield. The isomeric mixture was subjected to epimerization at C-8 (NaOMe/MeOH, 25 °C)[4a] to give an anti-rich mixture (**8**:**9** = 1:4).[15] The desired $8H_\beta$-isomer **9** was isolated in 69% yield. Application of the modified McMurry coupling reaction ($TiCl_3$–Zn(Ag), DME)[4a,b,16] to **9** for the C-ring construction furnished the desired compound **1** in 56% isolated yield. Its physical and spectral data were in accord with the literature values:[4] $[\alpha]^{21}_D$ +258° (*c* 0.70, $CHCl_3$), mp 144–145 °C (EtOAc–EtOH); lit.[4b] $[\alpha]^{25}_D$ +247.2° (>97.3% ee) (*c* 0.50, $CHCl_3$), mp 144–145 °C. The optical purity of **1** was 100% ee as judged from the reported $[\alpha]_D$ value.[4b] The overall yield of **1** from (*R*)-glyceraldehyde **3** was 17% in 11 steps.

Chart II



The key feature of the present strategy is the successful development of the asymmetric tandem Claisen–ene sequence for the double carbocyclization of D and C rings that allows for the relatively short construction of the estrogen framework in a highly stereocontrolled fashion. Particularly noteworthy is the stereochemical consequence of the asymmetric tandem sequence. The cyclic enol ether Claisen rearrangement[12] proceeds through the chair-like transition state (T_1) (Chart II). Thus, the *S*-*Z* chirality of alcohol **2** is completely transmitted to the 14*S* chirality in the Claisen product II, along with a high 8,14-syn selectivity. The subsequent ene–cyclization of II proceeds via the bicyclic-endo transition state (T_2) with the A,B ring at the sterically favorable pseudoequatorial position[17] to eventually establish the 13,14*S*-trans configuration in the ene product III, along with the formation of the silyl enol ether side chain.

Finally, the present approach to the $\Delta^{9(11)}$-steroidal skeleton permits easy access to 11-oxygenated estrogens of pronounced biological activity[18] as well as 19-norcorticoids through the utilization of the 17-side chain of **5**.[2,19]

(9) When the reaction was done at −30 °C, ca. 5% of the *E* isomer was formed: $\delta_{3\text{-Me}}$ 1.73 ppm for (*Z*)-**7** and 1.63 ppm for (*E*)-**7**.

(10) **2**: $[\alpha]^{24}_D$ +23.9° (*c* 2.01, $CHCl_3$); ^1H NMR δ 0.10 (s, 6 H), 0.80 (s, 8 H), 0.88 (s, 6 H), 1.5–1.8 (m, 1 H), 1.70 (br s, 3 H), 2.0–2.4 (m, 4 H), 3.49 (d, 2 H, *J* = 8.1 Hz), 3.80 (s, 3 H), 4.52 (t, 1 H, *J* = 8.1 Hz), 5.2–5.4 Hz (m, 1 H) ppm; ^{13}C NMR δ 154.0, 136.5, 125.5, 89.0, 73.1, 70.4, 65.2, 52.4, 34.2, 25.6, 25.2, 20.3, 19.8, 18.5, 3.5 ppm.

(11) Prepared according to the literature procedure: Miller, R. B.; Guerres, C. G. *J. Org. Chem.* **1978**, *43*, 1569.

(12) We have already reported that 2,6-dimethylphenol is an efficient catalyst for cyclic enol ether Claisen rearrangement: Mikami, K.; Takahashi, K.; Nakai, T. *Tetrahedron Lett.* **1987**, *28*, 5879.

(13) The aldehyde protons of $8H_\alpha$-**5** and $8H_\beta$-**5** were observed at δ 9.70 and 9.45 ppm, respectively. 8,14-*syn*,13,14-*trans*-**5**: $[\alpha]^{19}_D$ +77.1° (*c* 2.31, $CHCl_3$); mp 129 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 1.16 (s, 3 H), 1.6–1.8 (m, 2 H), 2.0–2.4 (m, 3 H), 2.5–3.0 (m, 6 H), 3.2–3.3 (m, 1 H), 3.69 (s, 3 H), 3.85 (s, 3 H), 5.73 (t, 1 H, *J* = 2.5 Hz), 6.67 (d, 1 H, *J* = 2.2 Hz), 6.82 (dd, 1 H, *J* = 8.85, 2.4 Hz), 7.95 (d, 1 H, *J* = 8.85 Hz), 9.70 (t, 1 H, *J* = 1.2 Hz) ppm; ^{13}C NMR δ 201.4, 197.8, 174.1, 167.0, 163.6, 145.6, 130.0, 126.2, 113.5, 112.4, 111.3, 55.4, 53.3, 51.0, 48.8, 47.7, 44.3, 31.6, 27.9, 27.4, 26.8, 23.4 ppm. 8,14-*anti*,13,14-*trans*-**5**: ^1H NMR δ 1.16 (s, 3 H), 1.6–3.3 (m, 12 H), 3.69 (s, 3 H), 3.85 (s, 3 H), 5.65 (m, 1 H), 6.67 (d, 1 H, *J* = 2.5 Hz), 6.82 (m, 1 H), 7.95 (d, 1 H), 9.45 (m, 1 H).

(14) The use of CH_2Cl_2 or CH_2Cl_2–MeOH as the solvent was found to afford a complex mixture.

(15) The aldehyde protons of **8** and **9** were observed at δ 9.76 ppm as a doublet and at δ 9.35 ppm as a singlet, respectively.

(16) Note that McMurry has recently reported an improved procedure for the carbonyl coupling: McMurry, J. E.; Lectka, T.; Rico, J. G. *J. Org. Chem.* **1989**, *54*, 3748. Review: Lenoir, D. *Synthesis* **1989**, 883.

(17) We have reported the high trans-diastereofacial selectivity in the ene–carbocyclization of related 1,6-enyne systems and proposed the bicyclic endo transition state model for explaining the trans selectivity: Mikami, K.; Takahashi, K.; Nakai, T. *Chem. Lett.* **1987**, 2347.

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Acknowledgment. We thank Professor F. E. Ziegler for providing authentic spectra of **1**, **8**, and **9**. This work was supported in part by the foundation "Hattori-Hokokai" and the Asahi-Kasei Award in Synthetic Organic Chemistry, Japan.

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 $Cp^*_6Mo_8O_{16}$

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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

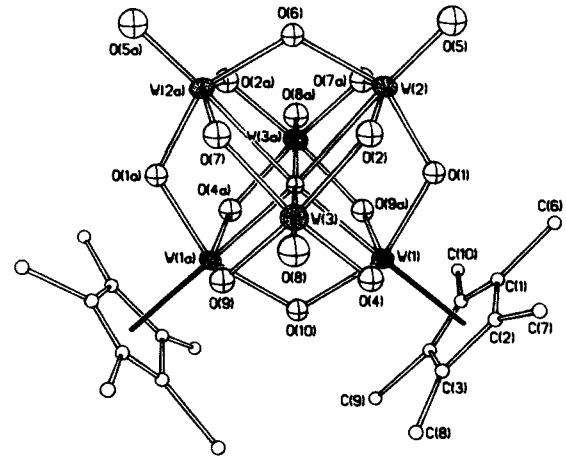

Figure 1. Molecular structure of $Cp^*_2W_6O_{17}$. The μ_6-O atom is O(3). Distances (Å): W(1)–CNT(1), 2.11 (4); W(1)–O(1), 1.941 (16); W(1)–O(4), 1.966 (16); W(1)–(O10), 1.928 (12); W(1)–O(9a), 1.921 (16); W(1)–O(3), 2.204 (13); W(2)–O(5), 1.692 (20); W(2)–O(1), 1.886 (16); W(2)–O(2), 1.930 (16); W(2)–O(6), 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).

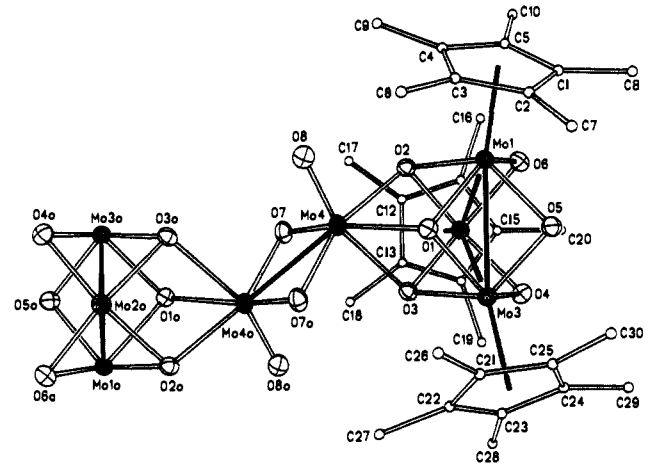

Figure 2. Molecular structure of $Cp^*_6Mo_8O_{16}$. Cp* ligands are omitted from Mo(1a), Mo(2a), and Mo(3a) for clarity. Distances (Å): Mo(1)–Mo(2), 2.751 (1); Mo(1)–Mo(3), 2.748 (1); Mo(2)–Mo(3), 2.734 (1); Mo(1)–CNT(1), 2.046 (4); Mo(1)–O(1), 2.040 (2); Mo(1)–O(2), 2.035 (2); Mo(1)–O(5), 1.946 (2); 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

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

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

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

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

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

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(7) c-$(CH_3As)_5$ synthesis: Rheingold, A. L. In *Organometallic Synthesis*; King, R. B., Eisch, J. J., Ed.; Elsevier: Amsterdam, 1986; Vol. 3, p 618. Arsaoxane NMR spectrum (n = 2 to 5) in accord with ref 3 and integrated against c-$(CH_3As)_5$. Crystalline $(CH_3AsO)_4$ is isolated from the reaction of c-$(CH_3As)_5$ and atmospheric oxygen in the presence of $Mn_2(CO)_{10}$.[20]

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