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Trishomocubane-Type Methoxide Cluster as a Novel Mediator in the Extension of Cube Size in Organometallic Oxide Clusters: Synthesis and Structures of $[(\text{RhCp}^*)_2\text{Mo}_3\text{O}_9(\text{OMe})_4]\cdot\text{MeOH}$ and a Linear Quadruple Cubane-Type Cluster $[(\text{RhCp}^*)_4\text{Mo}_6\text{O}_{22}]\cdot 4\text{CH}_2\text{Cl}_2$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$)

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In recent years, we have directed our efforts primarily toward the synthesis of integrated cubane-type clusters as potential models for inorganic solid surfaces to understand the chemistry¹ on them and have been reporting novel organometallic oxide clusters that contain soft as well as hard multimetal centers.²⁻⁴ Examples include $[\text{MCp}^*\text{MoO}_4]_2$ and $[(\text{MCp}^*)_4\text{V}_6\text{O}_{19}]$ ($\text{M} = \text{Rh}, \text{Ir}$).³

The cluster $[\text{RhCp}^*\text{MoO}_4]_4$ (**1**) has triply fused cubane character with a central Mo_4O_4 framework. Having noted that the same framework can be recognized as a repeating unit in the infinite layer structure of MoO_3 ,⁵ a heterogeneous catalyst for the oxidation of MeOH to CH_2O and Me_2O ,⁶ we were prompted to investigate the potential utility of **1** in the transformation of methanol. Consequently, the exploitation of the reaction system

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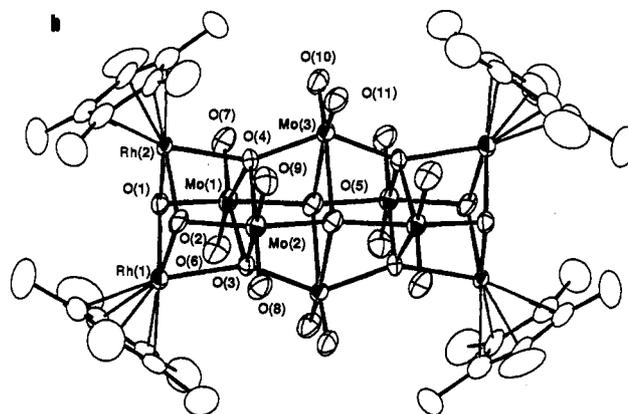
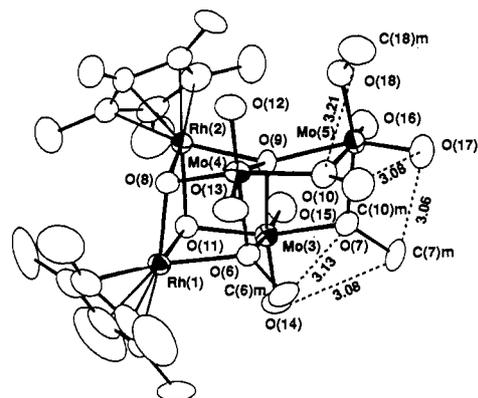
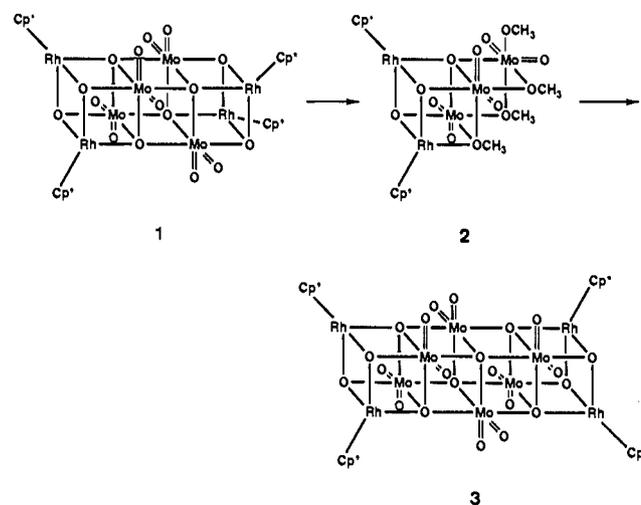


Figure 1. Perspective drawings of (a) $[(\text{RhCp}^*)_2\text{Mo}_3\text{O}_9(\text{OMe})_4]$ (**2**) and (b) $[(\text{RhCp}^*)_4\text{Mo}_6\text{O}_{22}]$ (**3**). Selected interatomic distances and angles have been deposited as supplementary material.

Scheme I



of **1** with MeOH was undertaken to reveal serendipitous conversion, outlined in Scheme I, of the triple cubane-type cluster **1** to a trishomocubane-type⁷ cluster $[(\text{RhCp}^*)_2\text{Mo}_3\text{O}_9(\text{OMe})_4]$ (**2**) and then to a quadruple cubane-type cluster $[(\text{RhCp}^*)_4\text{Mo}_6\text{O}_{22}]$ (**3**). Here, we report brief accounts of novel fragmentation and extension of cube size in the organometallic oxide cluster **1** as well as the structural characterization of **2**· MeOH and **3**· $4\text{CH}_2\text{Cl}_2$.

Cluster **1** is very soluble and stable in MeOH at ambient temperature. In the presence of excess *p*-hydroquinone (HQ),

(7) Introduction of three methylene groups into the C_8H_8 cubane skeleton results in the class of $\text{C}_{11}\text{H}_{14}$ trishomocubanes: Marchand, A. P. *Chem. Rev.* **1989**, *89*, 1011. In order to describe the 11-vertex skeleton of cluster **2**, the term "trishomocubane-type" was adopted.

however, a solution of **1** in MeOH generates the orange adduct, 1·2HQ.⁸ Reflux of either a solution of this adduct in MeOH or an equimolar solution of **1** and HQ in MeOH for 3–4 h results in the formation of the methoxide cluster **2**. The composition of 2·MeOH, established by X-ray study, is consistent with other data.⁸

The crystal structure consists of well-separated **2** and MeOH. The molecular structure of **2**, displayed in Figure 1a along with selected metrical data, contains an 11-vertex Rh₂Mo₃O₆ framework which can be viewed as an inorganic analogue of organic trishomocubanes.⁷ The Rh₂Mo₂O₄ cubic fragment is similar to, but more distorted than, that observed in **1**. Another intriguing structural feature of **2** is the spatial arrangement of the four methoxy groups. Three groups engaged in bridging interactions encompass the vacant vertex. One terminal methoxy group is situated in such a way that C₁ molecular symmetry results. The overall methoxy conformation leads to close proximities (3.05–3.12 Å) between doubly bridged methoxy carbons and terminal Mo=O oxygens (O(13), O(14), and O(17)), indicating possibly short C—H···O intramolecular contacts.⁹ Similar close proximities (3.13–3.21 Å) are also found between one of the doubly bridging methoxy oxygens (O(7) and O(10)) and a methoxy carbon of a triply bridged or terminal methoxy group. These indicate a possible path for nonredox methyl transfers between methoxy groups involved in the MeOH/MoO₃ reaction system.^{6a,b}

The solid-state trishomocubane framework of **2** is quite stable in air at room temperature, but its integrity does not remain intact upon dissolution in most organic solvents such as CH₂Cl₂, MeCN, MeNO₂, etc. A 20-min-old solution of 2·MeOH in CD₂Cl₂ reveals extra peaks in addition to signals⁸ assigned to **2** in the ¹H NMR spectrum. Over a period of 12 h, orange microcrystals precipitate and the ¹H NMR spectrum does not contain any features of **2** but mainly reveals peaks ascribable to **1** and MeOH. In a separate experiment, a solution of **2** (100 mg) in 5 cm³ of CH₂Cl₂ was kept at room temperature for 2–3 days, affording orange crystalline 3·4CH₂Cl₂, whose structure and composition were established by a single-crystal X-ray diffraction study.⁸ Consistent with the ¹H NMR observation is the isolation of **1** from the filtrate obtained by removing crystalline 3·4CH₂Cl₂.

The linear quadruple cubane type of **3** is depicted in Figure 1b. Two trishomocubane-type Rh₂Mo₃O₆ framework share two oxygen vertices, forming an unprecedented organometallic oxide cluster with a center of symmetry at the centroid of a planar Mo₂O₂ rhombus. The overall molecular symmetry of **3** deviates from the ideal D_{2h}. Because of the linearly extended Mo₄O₄ cubic unit in **3** relative to the triple cubane-type cluster **1**, the former might be a better congruent representation of the infinite layer lattice⁵ of MoO₃ recovered in the catalytic cycle of oxidation of MeOH. The structure of **3** also can be viewed as four Cp*Rh²⁺ cations being bound to a central Mo₆O₂₂⁸⁻ anion which constitutes a new member to the family of Mo(VI) hexametalates¹⁰ along with Mo₆O₁₉²⁻.¹¹ The Mo₆ core forms a rather regular octahedron whose four peripherally situated Mo₃ triangular faces are capped with oxygens. Two other oxygens in the Mo₆O₆ polyhedral core of the Mo₆O₂₂⁸⁻ anion are located at the extremely distorted tetrahedral interstices defined by two sets of two equatorial and two axial Mo atoms.

The clusters described here provide a novel synthetic example of extending the topological equivalent of a recognizable unit in the infinite lattice. The stoichiometric expressions for the conversions outlined in Scheme I remain to be established. Currently, other chemical products associated with the formation of **2** and

3, as well as the reactivities of these clusters, are under investigation.

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Supplementary Material Available: ORTEP diagrams, crystallographic data, bond distances and angles, listings of fractional coordinates with equivalent isotropic thermal parameters, and anisotropic thermal parameters for **2** and **3** and selected analytical, spectroscopic, and other data to characterize 1·2HQ, **2**, and **3** (16 pages); listings of observed and calculated structure factors for **2** and **3** (58 pages). Ordering information is given on any current masthead page.

Direct Insertion of Alkali (Alkaline-Earth) Metals into Allylic Carbon-Halogen Bonds Avoiding Stereorandomization

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An allylmetal is one of the most useful reagents in organic synthesis.¹ The reason for its synthetic importance is that there exist a straightforward way of generating it and regio- and stereoselective methods for controlling its subsequent reactions. In the realm of stereoselectivity, however, one great challenge that had not previously been met was the preparation of stereochemically homogeneous alkali allylmetals directly from allylic halides.² This is not a simple problem, since γ -substituted allylmetal, crotylmagnesium bromide, for example, is known to isomerize rapidly between the *Z* and *E* isomers even at -80 °C.³ Our interest in the structural and mechanistic aspects of these species has led us to undertake a careful investigation of these well-known organometallics.

Our initial assumption was that stereoisomerization of the allylmetal was due to the rapid isomerization through metallotropic rearrangements that were temperature dependent. Thus geranyl or neryl chloride⁴ was transformed to the corresponding Grignard reagent at low temperature, advantage being taken of the pioneering work of Rieke.⁵ The mixture was stirred for 30 min at each temperature⁶ and quenched by methanol. The isomerization

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