Direct Observation by Electrospray Ionization Mass Spectrometry of $[Cp^*RhMo_3O_8(OMe)_5]^-$, a Key Intermediate in the Formation of the Double-Bookshelf-Type Oxide Cluster $[(Cp^*Rh)_2Mo_6O_{20}(OMe)_2]^{2-}$**

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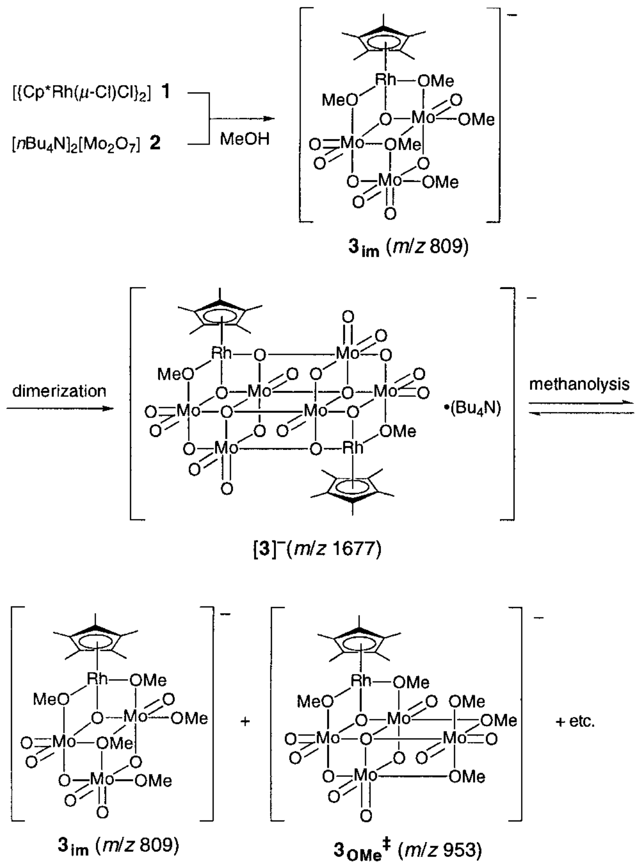
Organometallic oxide clusters with cubic and incomplete cubic frameworks are very useful as homogeneous and heterogeneous catalysts in the oxidation and metathesis of unsaturated hydrocarbons.[1] Recently, we found that the reaction of $[\{Cp^*Rh(\mu\text{-}Cl)Cl\}_2]$ (**1**, $Cp^* = \eta^5\text{-}C_5Me_5$) with four equivalents of $[nBu_4N]_2[Mo_2O_7]$ (**2**) in MeOH quantitatively yields the double-bookshelf-type oxide cluster $[nBu_4N]_2[(Cp^*Rh)_2Mo_6O_{20}(OMe)_2]$ (**3**) with an incomplete cubic framework in which many of the vertices are lacking (Scheme 1).[2] Furthermore, **3** is converted into the face-sharing triple-cubane-type cluster $[(Cp^*Rh)_4Mo_4O_{16}]$, the incomplete double-cubane-type cluster $[(Cp^*Rh)_2Mo_3O_9(OMe)_4]$, and the face-sharing quadruple-cubane-type cluster $[(Cp^*Rh)_4Mo_6O_{22}]$ under different conditions.[2, 3] Understanding the mechanism of formation for these clusters may provide strategies for the synthesis of desired oxide cluster catalysts for hydrocarbon transformations.

We have investigated the formation mechanism of **3** by electrospray ionization mass spectrometry (ESI-MS),[4] which allows us to detect unstable species generated in solution.[5] Herein, we report a direct observation by ESI-MS of $[Cp^*RhMo_3O_8(OMe)_5]^-$ ($\mathbf{3_{im}}$: *m/z* 809), a key intermediate in the formation of **3** from the reaction of **1** and **2** in MeOH at −78 °C.

The ^{95}Mo NMR spectrum of **2** in MeOH showed one broad signal ($\delta = -15$, reference: Na_2MoO_4) even at −50 °C because of the rapid exchange of Mo centers between several species in equilibrium.[6] As shown in Figure 1a, the negative-ion ESI mass spectrum of a cooled solution (−78 °C in an acetone/dry ice bath) of **2** in MeOH in the range of *m/z* 1200 to 250 confirmed that **2** exists as an equilibrium mixture of di- ($[nBu_4NMo_2O_7]^-$: *m/z* 546; $[Mo_2O_4(OMe)_5]^-$: *m/z* 412;[7] and $[H_3Mo_2O_7(OMe)_2]^-$: *m/z* 369[7]), tri- ($[nBu_4NMo_3O_{10}]^-$, $\mathbf{Mo_3}$: *m/z* 690), tetra- ($[nBu_4NMo_4O_{13}]^-$: *m/z* 834), penta- ($[nBu_4NMo_5O_{16}]^-$: *m/z* 973), and hexamolybdates ($[HMo_6O_{18}(OMe)_2]^-$: *m/z* 926[7]). Although all of these equilibrium species of **2** could participate in the formation of **3**, the trimolybdate species $\mathbf{Mo_3}$ could be selected preferentially as an essential building block because the $[Mo_3O_{10}]^{2-}$ unit in $\mathbf{Mo_3}$ is also found in **3** as a key $\{Mo(O)_2\}_3(\mu_3\text{-}O)(\mu_2\text{-}O)_3$ unit.[8]



Scheme 1. Proposed mechanism for the formation of **3** via the intermediate $\mathbf{3_{im}}$, generated from the reaction of **1** with two equivalents of **2** in MeOH at −78 °C. Methanolysis and equilibrium of **3** yields $\mathbf{3_{im}}$, $\mathbf{3_{OMe}}^{\ddagger}$, and other products.

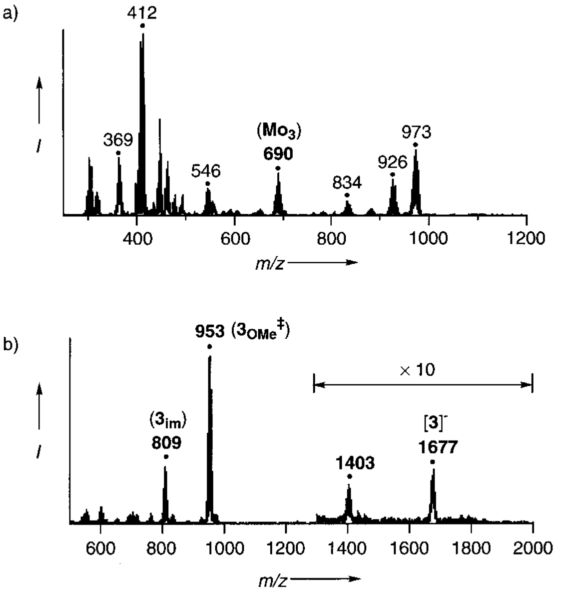


Figure 1. Negative-ion ESI mass spectra of cooled solutions (−78 °C) of **2** (a) and **3** (b) in MeOH. See text for details. *I* = relative intensity.

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The negative-ion ESI mass spectrum of a cooled solution (−78 °C) of **3** in MeOH in the range of *m/z* 2000 to 1300 shows two weak envelopes at *m/z* 1677 and 1403, which correspond to the molecular ion of **3** ($[\mathbf{3}]^-$: $[n\mathrm{Bu_4N(Cp^*Rh)_2Mo_6O_{20}(OMe)_2}]^-$) and a fragment ion of **3** ($[\mathbf{3}-n\mathrm{Bu_4N-OMe}]^-$: $[\mathrm{(Cp^*Rh)_2Mo_6O_{20}(OMe)}]^-$), respectively (Figure 1b). In the range of *m/z* 1300 to 100, the mass spectrum shows two prominent envelopes at *m/z* 953 (relative intensity $I = 100\,\%$) and 809 ($I = 34\,\%$). They correspond to the methanolysis species $[\mathrm{Cp^*RhMo_4O_{11}(OMe)_5}]^-$ ($\mathbf{3}_{\mathbf{OMe}}^{\mathbf{+}}$) and $[\mathrm{Cp^*RhMo_3O_8(OMe)_5}]^-$, respectively; the latter has the same molecular mass as $\mathbf{3}_{\mathbf{im}}$ [Scheme 1, Eqs. (1), (2)].[9] It is noteworthy that cluster **3** undergoes methanolysis to yield the same species as the intermediate $\mathbf{3}_{\mathbf{im}}$, which is produced from the reaction between **1** and **2** (see below). Measurements with the mass spectrometry/mass spectrometry (MS/MS) method have also been performed with $\mathbf{3}_{\mathbf{im}}$ and $\mathbf{3}_{\mathbf{OMe}}^{\mathbf{+}}$.[10]

$$\underset{\mathbf{3}}{[\mathrm{(Cp^*Rh)_2Mo_6O_{20}(OMe)_2}]^{2-}} + 8\,\mathrm{MeOH} \rightleftharpoons 2\,\underset{\mathbf{3}_{\mathbf{im}}}{[\mathrm{Cp^*RhMo_3O_8(OMe)_5}]^-} + 4\,\mathrm{H_2O} \quad (1)$$

$$2\,\underset{\mathbf{3}}{[\mathrm{(Cp^*Rh)_2Mo_6O_{20}(OMe)_2}]^{2-}} + 6\,\mathrm{MeOH} \rightleftharpoons 2\,\underset{\mathbf{3}_{\mathbf{OMe}}^{\mathbf{+}}}{[\mathrm{Cp^*RhMo_4O_{11}(OMe)_5}]^-} + [\mathrm{(Cp^*Rh)_2Mo_4O_{15}}]^{2-} + 3\,\mathrm{H_2O} \quad (2)$$

We have simultaneously monitored the intensity changes of three selected envelopes—namely, those at *m/z* 690 ($\mathbf{Mo_3}$), 809 ($\mathbf{3}_{\mathbf{im}}$), and 953 ($\mathbf{3}_{\mathbf{OMe}}^{\mathbf{+}}$)—during the reaction of **1** with two equivalents of **2** in MeOH (−78 °C) by rapid scanning[11] (Figure 2). After mixing of the reagents, the envelope at *m/z* 690 decreased immediately in intensity (Figure 2b, c, e), concomitant with the appearance and increase in intensities of the envelopes at *m/z* 809 and 953. Fortunately, we observed a time lag (ca. 2.4 s) in the appearance of the envelope at *m/z* 953 with respect to that at *m/z* 809 (compare Figure 2b with 2c). These results suggest that the intermediate $\mathbf{3}_{\mathbf{im}}$ was first generated by the reaction of **1** with **2** in MeOH, and then $\mathbf{3}_{\mathbf{im}}$ dimerized to **3**, which exists as equilibrium mixtures with $\mathbf{3}_{\mathbf{im}}$ and $\mathbf{3}_{\mathbf{OMe}}^{\mathbf{+}}$ [Eqs. (1), (2); Scheme 1].[9] The processes of forming **3** and the equilibrium will cause the time lag. After 7.8 s of mixing (Figure 2c–e), the intensity of the envelope at *m/z* 953 increased somewhat and remained constant, while the intensity of the envelope at *m/z* 809 dramatically decreased and then remained constant. The decrease in intensity of the envelope at *m/z* 809 is probably due to 1) the predominant consumption of the intermediate $\mathbf{3}_{\mathbf{im}}$ for the formation of **3** and 2) a low supply of $\mathbf{3}_{\mathbf{im}}$ resulting from the methanolysis of **3**.[12] Finally, after the disappearance of $\mathbf{Mo_3}$ (Figure 2d, e), the intensities of the envelopes at *m/z* 809 and 953 became constant.[13]

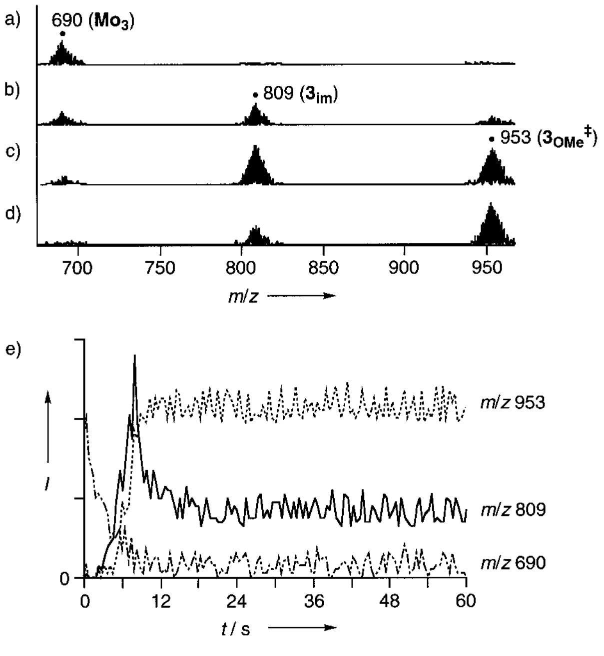

Figure 2. Time-dependent behavior of the three selected envelopes at *m/z* 690 ($\mathbf{Mo_3}$), 809 ($\mathbf{3}_{\mathbf{im}}$), and 953 ($\mathbf{3}_{\mathbf{OMe}}^{\mathbf{+}}$) during the reaction of **1** with two equivalents of **2** in cooled MeOH (−78 °C). The reaction was monitored by simultaneous and rapid scanning of ESI-MS (see ref. [11] and Experimental Section). a) Before mixing of **1** and **2**; b) 5.4 s after mixing; c) 7.8 s after mixing; d) 12.6 s after mixing; e) the changes in intensity of the three selected envelopes as a function of time.

To confirm the existence of the methoxo ligands in $\mathbf{3}_{\mathbf{im}}$, the reaction of **1** with **2** has been carried out in $\mathrm{CD_3OD}$ at −78 °C. The ESI-MS results show that the envelope at *m/z* 809 ($[\mathrm{Cp^*RhMo_3O_8(OCH_3)_5}]^-$) shifts to *m/z* 824 ($[\mathrm{Cp^*RhMo_3O_8(OCD_3)_5}]^-$); that is, the labeled methoxo ligands ($\mathrm{OCD_3}$) are incorporated into $\mathbf{3}_{\mathbf{im}}$. Although many geometrical isomers are assumed for $\mathbf{3}_{\mathbf{im}}$, we propose the isomer depicted in Scheme 1, where two $\mathbf{3}_{\mathbf{im}}$ units are spontaneously assembled into **3** with release of methoxo ligands. Such spontaneous self-assembly by utilizing methoxo ligands as leaving groups was similarly demonstrated in $[\mathrm{(Cp^*Rh)_4Mo_6O_{22}}]$.[3b] The MS/MS fragmentation pattern of $\mathbf{3}_{\mathbf{im}}$ indicates that the proposed structure is appropriate.[10]

The employment of MeCN as the solvent for the reaction of **1** with **2**[6] leads to the selective formation of the triple-cubane-type oxide cluster $[\mathrm{(Cp^*Rh)_4Mo_4O_{16}}]$,[2, 3a] but no **3**. These results clearly show that the use of MeOH as the solvent is essential for the formation of **3** with two methoxo ligands via the intermediate $\mathbf{3}_{\mathbf{im}}$ with five methoxo ligands.

Experimental Section

It was confirmed that the observed distribution of isotopomers of all ions discussed in this study matches well with the calculated values.

Procedure: Before each measurement, the flow pass (fused silica capillary, ca. 400 mm long, 0.075 mm inner diameter) in the system was precooled by flushing with MeOH cooled to −78°C in a acetone/dry ice bath. The temperature of the sprayer of the API 300 triple quadrupole mass spectrometer (PE-Sciex), measured by a thermocouple (Anritu, HFT-50), was approximately 25 °C. A solution of **1** (0.25 mM) in MeOH (2 mL) was added rapidly to a solution of **2** (0.50 mM) in MeOH (2 mL) at −78 °C by standard Schlenk technique. The resulting solution was then delivered immediately (within 1 s after mixing) to the sprayer through the fused silica capillary under a constant Ar pressure (0.1 MPa). The sprayer was held at a potential of −4.5 kV, and compressed $\mathrm{N_2}$ was employed to assist liquid nebulization. The orifice potential was maintained at −25 V. The negative-ion ESI mass spectra were measured in the range of *m/z* 100 to 2000. The MS/MS measurements were carried out at room temperature.

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[6] The form of **2** in solution is dependent on the solvent. In contrast to the case of MeOH, **2** exists intact in MeCN. This was confirmed by ESI-MS and ^{17}O NMR spectroscopy: a) The negative-ion ESI mass spectrum of a solution of **2** in MeCN in the range of *m/z* 100 to 1000 showed only two envelopes at *m/z* 303 ($[HMo_2O_7]^-$) and 546 ($[nBu_4NMo_2O_7]^-$); b) ^{17}O NMR spectroscopy: V. W. Day, M. F. Fredrich, W. G. Klemperer, *J. Am. Chem. Soc.* **1977**, *99*, 6146–6148.

[7] The existence of the methoxo ligands in these species was confirmed by isotopic labeling experiments using CD_3OD as solvent.

[8] The MS/MS spectra of $\mathbf{Mo_3}$ (*m/z* 690) exhibit peaks at *m/z* 448 and 432, which correspond to the negative ions of $[Mo_3O_{10}]$ and $[Mo_3O_9]$, respectively, suggesting that the proposed structure of $\mathbf{Mo_3}$, $[\{Mo(O)_2\}_3(\mu_3\text{-}O)(\mu_2\text{-}O)_3]^{2-}$, is appropriate.

[9] ^{95}Mo NMR experiments of **3** have been performed both in CD_3OD and CD_2Cl_2 at room temperature. Although the spectrum in CD_2Cl_2 shows three signals with nearly equal intensity at $\delta = 30.0$ ($I = 78\%$), 86.6 ($I = 100\%$), and 167.2 ($I = 89\%$)—supporting preservation of the solid-state structure—the spectrum in CD_3OD is much more complicated and gives five broad signals with different intensities at $\delta = -9.0$ ($I = 53\%$), 50.8 ($I = 100\%$), 95.5 ($I = 56\%$), 113.5 ($I = 51\%$), and 155.3 ($I = 43\%$). The results of ^{95}Mo NMR and ESI-MS experiments (the observation of the envelopes for $\mathbf{3_{im}}$ (*m/z* 809) and $\mathbf{3_{OMe}}^+$ (*m/z* 953)) suggest that in MeOH, cluster **3** exists as equilibrium mixtures [Eqs. (1), (2)]. These equilibria, which lie far to the right, may be reached very quickly. The species $[(Cp^*Rh)_2Mo_4O_{15}]^{2-}$ in Equation (2), which was not detected by ESI-MS, may react with further MeOH to establish a new equilibrium.

[10] The MS/MS spectra of $\mathbf{3_{im}}$ (*m/z* 809) exhibit peaks at *m/z* 778, 685, 587, 399, and 368, which correspond to the negative ions of $[Cp^*RhMo_3O_8(OMe)_4]$, $[Cp^*RhMo_3O_8(OMe)]$, $[Cp^*RhMo_2O_4(OMe)_3]$, $[Cp^*RhMoO_2(OMe)]$, and $[Cp^*RhMoO_2]$, respectively. The MS/MS spectra of $\mathbf{3_{OMe}}^+$ (*m/z* 953) exhibit peaks at *m/z* 763, 732, 588, 541, and 540, which correspond to the negative ions of $[Cp^*RhMo_3O_9(OMe)_3]$, $[Cp^*RhMo_3O_9(OMe)_2]$, $[Cp^*RhMo_2O_6(OMe)_2]$, $[Cp^*RhMo_2O_5(OMe)]$, and $[Cp^*RhMo_2O_3(OMe)_2]$, respectively. These results indicate that the proposed structures of $\mathbf{3_{im}}$ and $\mathbf{3_{OMe}}^+$ shown in Scheme 1 are appropriate.

[11] Scan range: 674.9–705.1, 794.9–825.1, and 936.9–967.1 amu (atomic mass unit); step size: 0.2 amu; dwell time per step: 0.001 s; scan time: 0.47 s. The envelope of the molecular ion of **3** at *m/z* 1677 was not selected in the rapid scanning experiments because the intensity was too weak.

[12] We have conducted a reaction of **2** with **3** in MeOH at room temperature in order to check whether there are routes for the formation of $\mathbf{3_{OMe}}^+$ through $\mathbf{3_{im}}$, which would account for the reduction in intensity of $\mathbf{3_{im}}$ between ca. 8–14 s (Figure 2e). However, $\mathbf{3_{im}}$ does not react with the dimolybdate or any heavier species produced from **2** in MeOH; intensity changes in the envelopes at *m/z* 809 and 953 are not observed during the reaction of **2** with one equivalent of **3**. Furthermore, the fragmentation patterns of $\mathbf{3_{im}}$ are different from that of $\mathbf{3_{OMe}}^+$,[10] suggesting that there is no relationship between $\mathbf{3_{im}}$ and $\mathbf{3_{OMe}}^+$. Therefore, we believe that the existence of the intermediate $\mathbf{3_{im}}$ is essential.

[13] The spectrum after 18 s of reaction is essentially identical to that of **3** (Figure 1b).

The First Bismuth Phosphide Complex: $[Li(thf)_4]^+[\{(tBuP)_3\}_2Bi]^-$**

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Although amide[1] and imido[2] complexes of the heavier Group 15 elements (Sb and Bi) have been reported in recent years, for the related phosphorus compounds (containing R_2P^- or RP^{2-} groups) only those of Sb have appeared in the literature.[3] Moreover, the only examples of complexes containing Bi–P bonds to be structurally characterized are Bi^{III} halides in which neutral phosphane ligands coordinate the metal centers.[4] In recent studies of the reactions of $[E(NMe_2)_3]$ (E = As, Sb) with primary phosphido alkali metal complexes ([RPHM]; M = Li, Na), we showed that heterocyclic anions of the type $[(RP)_nE]^-$ are generated[5] prior to the ultimate formation of Zintl compounds containing E_7^{3-} ions.[6] Prompted by the absence of structurally characterized Bi phosphides, which would have the potential for the formation of elusive polyatomic Bi_5^{3-} and Bi_3^{3-} ions by this low-temperature route,[7] we decided to investigate the

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