A novel organometallic oxide cluster with multi-valley sites: synthesis and structure of [NBu$^n_4$]$_2$[{(η^5-C$_5$Me$_5$)Rh}$_2$Mo$_6$O$_{20}$(OMe)$_2$] and its framework transformations

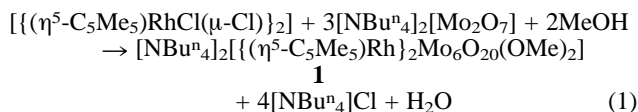Satoshi Takara, Takanori Nishioka, Isamu Kinoshita and Kiyoshi Isobe*

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A novel organometallic oxide cluster [NBu$^n_4$]$_2$[{(η^5-C$_5$Me$_5$)Rh}$_2$Mo$_6$O$_{20}$(OMe)$_2$] **1** with multi-valley sites is synthesized by the reaction of [NBu$^n_4$]$_2$[Mo$_2$O$_7$] and {(η^5-C$_5$Me$_5$)RhCl(μ-Cl)}$_2$] in a molar ratio of 4:1 in methanol, and displays unique framework transformations upon treatment with organometallic and oxometalate compounds.

Theoretical studies on catalytic hydrocarbon transformation on metal oxides showed that coordinatively unsaturated metal sites and valley sites in integrated cubic cluster models play an important role for activation of hydrocarbons.[1] Indeed, organometallic oxide clusters, such as the incomplete cubane-type cluster [{(η^5-C$_5$Me$_5$)Rh}$_2$Mo$_3$O$_9$(OMe)$_4$] **2**,[2a] the face-shared triply fused cubane-type cluster [{(η^5-C$_5$Me$_5$)Rh}$_4$Mo$_4$O$_{16}$] **3**,[2b] the valley-site structure [{(η^5-C$_5$Me$_5$)Rh}$_4$V$_6$O$_{19}$]^{2c,d} and the planar cluster [NBu$^n_4$]$_2$[{(η^3-C$_4$H$_7$)$_2$Rh}$_2$V$_4$O$_{12}$]^{2f} supported on silica, exhibit significant catalytic abilities and higher selectivities for oxidation and metathesis of propene.[3] Thus, our current efforts concentrate on the design and development of synthetic strategies for new organometallic oxide clusters with active sites owing to characteristic structures such as lacunary, incomplete cubic, or valley-site frameworks.[2a–e]

Here, we report on the structure and synthesis of the organometallic oxide cluster [NBu$^n_4$]$_2$[{(η-C$_5$Me$_5$)Rh}$_2$Mo$_6$O$_{20}$(OMe)$_2$] **1** with multi-valley sites and its framework transformations.

A mixture of [NBu$^n_4$]$_2$[Mo$_2$O$_7$][4] (2.55 g, 3.24 mmol) and [{(η^5-C$_5$Me$_5$)RhCl(μ-Cl)}$_2$][5] (0.50 g, 0.81 mmol) in 20 ml of methanol was allowed to stand for 4 h with stirring at room temp. and concentrated to 5 ml. Diethyl ether (80 ml) was then added slowly to give an orange precipitate of **1**. The crude product is recrystallized from methanol–diethyl ether (1.22 g, 79% yield based on Rh).† The formation of **1** may proceed according to eqn. (1).‡

$$[\{(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}(\mu\text{-Cl})\}_2] + 3[\text{NBu}^n_4]_2[\text{Mo}_2\text{O}_7] + 2\text{MeOH}$$
$$\rightarrow [\text{NBu}^n_4]_2[\{(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}\}_2\text{Mo}_6\text{O}_{20}(\text{OMe})_2]$$
$$\mathbf{1}$$
$$+ 4[\text{NBu}^n_4]\text{Cl} + \text{H}_2\text{O} \qquad (1)$$

An X-ray analysis of **1** reveals that the anion of **1** has C_i symmetry and is composed of four MoO$_6$ and two MoO$_5$(μ-OMe) octahedra interlinked along edges and two (η^5-C$_5$Me$_5$)Rh groups each sharing two edges with the octahedra (Fig. 1).§ The framework of **1** is in some respects similar to that of the γ-[Mo$_8$O$_{26}$]$^{4-}$ isomer found in [(Me$_3$N(CH$_2$)$_6$NMe$_3$]$_2$-[Mo$_8$O$_{26}$]·2H$_2$O, which also has C_i symmetry and is composed of six MoO$_6$ octahedra interlinked along edges and two MoO$_5$ trigonal bipyramids each sharing two edges with the octahedra.[6] The structure of **1** can be regarded as a framework which contains two (η^5-C$_5$Me$_5$)Rh(μ-OMe) groups rather than two MoO$_5$ trigonal bipyramids. It is noteworthy that (η^5-C$_5$Me$_5$)Rh moieties and methoxy groups in the framework of **1** form two unique large valley sites, constructed by Rh(1)Mo-(3*)Mo(1)Mo(2*) and Rh(1*)Mo(3)Mo(1*)Mo(2), while two small ones are constructed by Mo(1)Mo(2)Mo(3) and Mo-

(1*)Mo(2*)Mo(3*). For these two kinds of valley sites, a space-filling model¶ suggests that the small sites are much more open with exposed highly basic oxygens [O(2), O(4), O(8)], whereas the larger ones are rimmed with bulky pentamethyl-cyclopentadienyl, methoxy and Mo=O groups so as to form shallow cavities.

Bearing in mind that **1** might show high reactivity due to the presence of valley sites, we have been prompted to investigate the reactivity of **1** towards organometallic (electrophile) and oxometalate (nucleophile) compounds. Consequently, cluster framework transformations of **1** occur in both, for example, by treatments with {(η^5-C$_5$Me$_5$)Rh}$^{2+}$ and with [Mo$_2$O$_7$]$^{2-}$ in methanol to produce the incomplete double cubane-type cluster of **2** and the triply fused cubane-type cluster of **3**, respectively (Scheme 1).‖ The basic bridging oxygens [O(2), O(4), O(8)] in the small valley sites can interact freely with metal cations, hence in the formation of **2**, landing of the added {(η^5-C$_5$Me$_5$)Rh}$^{2+}$ cations on the small valley sites probably triggers an initial step of the transformation. On the other hand for the formation of **3**, the added [Mo$_2$O$_7$]$^{2-}$ anions will approach the rhodium(**iii**) centres in the shallow cavities by electrostatic force of attraction: the parts of Rh^{III} centres in the shallow cavities are most exposed to attack by nucleophiles. By the action of an excess of [Mo$_2$O$_7$]$^{2-}$ some of the weak Rh–O
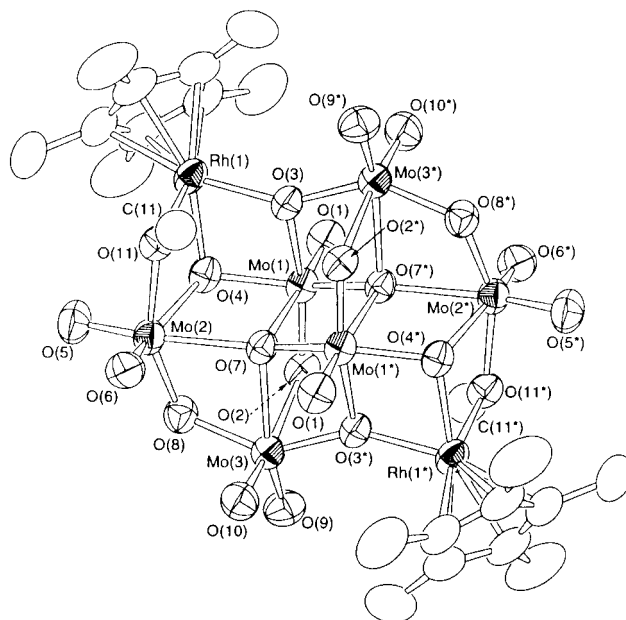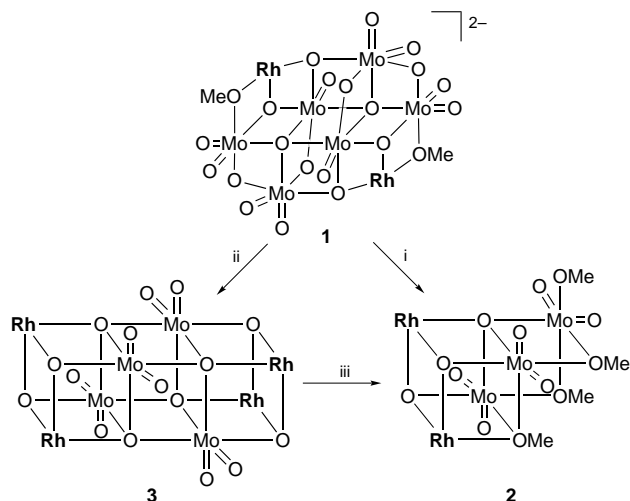

Fig. 1 Structure of the anion in **1**. Selected bond lengths (Å): Mo(1)–O(1) 1.696(3), Mo(1)–O(2) 1.744(3), Mo(1)–O(3) 2.152(3), Mo(1)–O(4) 1.928(3), Mo(1)–O(7) 1.916(3), Mo(2)–O(4) 2.178(3), Mo(2)–O(5) 1.695(4), Mo(2)–O(6) 1.708(3), Mo(2)–O(7) 2.299(3), Mo(2)–O(8) 1.892(3), Mo(2)–O(11) 1.411(6), Mo(3)–O(2) 2.363(3), Mo(3)–O(3) 1.908(3), Mo(3)–O(7) 2.277(3), Mo(3)–O(8) 1.946(3), Mo(3)–O(9) 1.703(4), Mo(3)–O(10) 1.704(4), Rh(1)–O(3) 2.068(3), Rh(1)–O(4) 2.100(3), Rh(1)–O(11) 2.109(3).

Scheme 1 Rh = Rh(η^5-C$_5$Me$_5$). *Reagents and conditions:* i, [{(η^5-C$_5$Me$_5$)RhCl(μ-Cl)}$_2$] 1 equiv., MeOH, 27 °C; ii, [NBu$^n_4$]$_2$[Mo$_2$O$_7$] 4 equiv., MeOH, 27 °C; iii, *p*-hydroquinone, MeOH, reflux; see ref. 2(*a*).

[*e.g.* Rh(1)–O(11) and Rh(1)–O(3)] bonds in the large valley sites may be cleaved to cause a new condensation of oxomolybdates on the vacant sites of the (η-C$_5$Me$_5$)Rh centres to afford the most stable species, the triply fused cubane-type cluster [{(η^5-C$_5$Me$_5$)Rh}$_4$Mo$_4$O$_{16}$] **3**. Although the transformations mentioned above to form **2** and **3** might contain complicated steps to be elucidated, the unique valley sites of **1** can fulfil its function to initiate the framework transformations and cluster **1** may act as a convenient molecular platform towards other cationic and anionic transition-metal fragments. The transformations are also particularly important for constructing new oxide cluster architecture; the multi-valley sites cluster **1** is a prominent building block for preparation of larger clusters.

Footnotes

† The cluster was analysed satisfactorily (C, H, N) for **1**. Selected IR data (**1**, Nujol) ν/cm^{-1} 440w, 487w, 522m, 638m, 680s, 742m, 858s, 900s, 1040m, 1063m, 1162w, 1663m, 3500m (br).

‡ Excess dimolybdate acts as a base for deprotonation of methanol molecules coordinated to molybdenum atoms. 1 Equiv. of dimolybdate is insufficient to produce **3**, formation of **3** needing 4 equiv. of [Mo$_2$O$_7$]$^{2-}$ relative to **1**, as described in Scheme 1.

§ *Crystal data* for C$_{54}$H$_{108}$Mo$_6$N$_2$O$_{22}$Rh$_2$, **1**: single crystals of **1** suitable for X-ray crystallography were grown by slow diffusion of diethyl ether into a methanol solution. An orange crystal of dimensions 0.4 × 0.2 × 0.2 mm was mounted on a glass fibre. Cluster **1** crystallizes in the trigonal space group $R\bar{3}$ (no. 148) with a = 41.954(3), c = 12.925(3) Å, U = 19701(4) Å^3, Z = 9, and D_c = 1.455 g cm^{-3}. A total of 10 722 reflections were collected on a Rigaku AFC-7 diffractometer with graphite-monochromated Mo-Kα radiation *via* a ω-scan technique in the limit of 2θ ⩽ 55.0° at 296 K. The reflections with $I > 3\sigma(I)$ were corrected for Lorentz-polarization factors but not for extinction. An absorption correction was applied using an empirical ψ-scan method. All crystallographic calculations were carried out using teXsan programs. The positions of the rhodium and molybdenum atoms were obtained by SHELXS86 direct methods. The remaining atoms were located on difference Fourier maps. Hydrogen atoms were fixed at calculated positions and used for structure-factor calculations. 388 variables were refined by full-matrix least-squares techniques using 5960 independent reflections and converged to R = 0.035, R_w = 0.041 and GOF = 1.21. A final difference Fourier map yielded $\Delta\rho_{max}$ = +0.40 e Å^{-3}, $\Delta\rho_{min}$ = −0.38 e Å^{-3}. Atomic coordinates, bond lengths, angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/428.

¶ Available as supplementary data.

‖ Complexes **2** and **3** were identified by spectroscopic data; see ref. 2(*a*) and 2(*b*).

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