

# Interplay of Cubic Building Blocks in ( $\eta^6$ -arene)Ruthenium-Containing Tungsten and Molybdenum Oxides

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**Abstract:** A series of molybdenum and tungsten organometallic oxides containing  $\{\text{Ru}(\text{arene})\}^{2+}$  units (arene = *p*-cymene,  $\text{C}_6\text{Me}_6$ ) was obtained by condensation of  $[\{\text{Ru}(\text{arene})\text{Cl}_2\}_2]$  with oxomolybdates and oxotungstates in aqueous or nonaqueous solvents. The crystal structures of  $[\{\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)\}_4\text{W}_4\text{O}_{16}]$ ,  $[\{\text{Ru}(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})\}_4\text{W}_2\text{O}_{10}]$ ,  $[\{\{\text{Ru}(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})\}_2(\mu\text{-OH})_3\}_2][\{\text{Ru}(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})\}_2\text{W}_8\text{O}_{28}(\text{OH})_2\{\text{Ru}(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})(\text{H}_2\text{O})\}_2]$ , and  $[\{\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)\}_2\text{M}_5\text{O}_{18}\{\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\text{H}_2\text{O})\}]$  (M

= Mo, W) have been determined. While the windmill-type clusters  $[\{\text{Ru}(\eta^6\text{-arene})\}_4(\text{MO}_3)_4(\mu_3\text{-O})_4]$  (M = Mo, W; arene = *p*- $\text{MeC}_6\text{H}_4\text{iPr}$ ,  $\text{C}_6\text{Me}_6$ ), the face-sharing double cubane-type cluster  $[\{\text{Ru}(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})\}_4(\text{WO}_2)_2(\mu_3\text{-O})_4(\mu_4\text{-O})_2]$ , and the dimeric cluster  $[\{\text{Ru}(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})(\text{WO}_3)_3(\mu_3\text{-O})_3(\mu_3\text{-OH})\text{Ru}(\eta^6\text{-}p\text{-}$

$\text{MeC}_6\text{H}_4\text{iPr})(\text{H}_2\text{O})\}_2(\mu\text{-WO}_2)_2]^{2-}$  are based on cubane-like units,  $[\{\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)\}_2\text{M}_5\text{O}_{18}\{\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\text{H}_2\text{O})\}]$  (M = Mo, W) are more properly described as lacunary Lindqvist-type polyoxoanions supporting three ruthenium centers. Precubane clusters  $[\{\text{Ru}(\eta^6\text{-arene})\}(\text{MO}_3)_2(\mu\text{-O})_3(\mu_3\text{-O})]^{6-}$  are possible intermediates in the formation of these clusters. The cluster structures are retained in solution, except for  $[\{\text{Ru}(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})\}_4\text{Mo}_4\text{O}_{16}]$ , which isomerizes to the triple-cubane form.

**Keywords:** molybdenum • oxo ligands • polyoxometalates • ruthenium • tungsten

## Introduction

Organometallic oxides have been defined as compounds in which an oxometal core is surrounded by organometallic moieties.<sup>[1]</sup> However, this term is also commonly used for low-nuclearity compounds, for which organorhenium oxides are prototypical.<sup>[2]</sup> Organometallic derivatives of polyoxometalates form a specific class of organometallic oxides. This field, largely developed by the groups of Klemperer,<sup>[3]</sup> Finke,<sup>[4]</sup> and Isobe and Yagasaki,<sup>[5]</sup> was reviewed recently.<sup>[6]</sup> Organometallic derivatives of polyoxometalates are of interest owing to their ability to provide discrete analogues of solid-oxide-supported heterogeneous catalysts, to provide new insights into surface dynamics,<sup>[7, 8]</sup> to serve as precursors for transition metal nanoclusters,<sup>[9]</sup> and to display synergetic<sup>[10]</sup> or bifunctional<sup>[11]</sup> catalytic activity. They are divided into polyoxoanion-supported and polyoxoanion-incorporated compounds.<sup>[4a]</sup> The recognition of recurrent structural relationships between organometallic derivatives and parent polyoxometalates led us to recognize *fac*- $d^6\text{-}\{\text{M}'\text{L}_3\}$  units such as  $\{\text{M}'(\text{CO})_3\}^+$  (M' =

Mn, Re) as topological equivalents of *fac*- $d^0\text{-}\{\text{MO}_2\text{X}\}^+$  units (M = Mo; X = OR, Cl).<sup>[12]</sup> Furthermore, *fac*- $d^6\text{-}\{\text{M}'(\text{CO})_3\}^+$  fragments (M' = Mn, Re) are likely to be isolobal to *fac*- $d^0\text{-}\{\text{MO}_3\}$  fragments (M = Mo, W) according to Hartree–Fock calculations on  $\{\text{Re}(\text{CO})_3\}$  and  $\{\text{ReO}_3\}$ .<sup>[13]</sup> To check the validity of this analogy, we extended our initial studies to ( $\eta^6$ -arene)ruthenium(II) derivatives. Further interest in such derivatives comes from their potential as metathesis catalysts. Indeed, unsaturated ruthenium centers can be generated by arene photolysis, as it has already been exploited in ring-opening and ring-closing metathesis reactions.<sup>[14]</sup> Furthermore, arene photolysis of ( $\eta^6$ -arene)ruthenium-supported polyoxoanions could provide a new route to ruthenium-substituted polyoxometalates, which are of significant interest as oxidation catalysts.<sup>[15, 16]</sup> When we began this work, a few ruthenium complexes containing tri- or bidentate polyoxoanion ligands had been obtained from preformed polyoxoanions, for example,  $[\{(p\text{-cymene})\text{Ru}\}\text{Nb}_2\text{W}_4\text{O}_{19}]^{2-}$ ,<sup>[17]</sup>  $[\{(\text{C}_6\text{H}_6)\text{Ru}\}\text{W}_5\text{O}_{18}\text{TiCp}^*]$  (Cp\* =  $\eta^5\text{-C}_5\text{Me}_5$ ),<sup>[17]</sup>  $[\{(\text{C}_6\text{H}_6)\text{Ru}\}\text{P}_2\text{Nb}_3\text{W}_{15}\text{O}_{62}]^{7-}$ ,<sup>[18]</sup>  $[\{\text{RuCl}(\text{C}_8\text{H}_{12})(\text{MeCN})\}_5(\text{Nb}_2\text{W}_4\text{O}_{19})_2]^{3-}$ ,<sup>[19]</sup> and  $[\{\text{Ru}(\text{C}_8\text{H}_{12})(\text{MeCN})_2\}\text{HV}_4\text{O}_{12}]^-$ .<sup>[19]</sup> On the other hand, Süss-Fink et al. obtained the cluster  $[\{\text{Ru}(p\text{-cymene})\}_4\text{Mo}_4\text{O}_{16}]$ , which exhibits a unique windmill-like geometry, by condensation of sodium molybdate with  $[\{(p\text{-cymene})\text{RuCl}_2\}_2]$  in aqueous solution.<sup>[20a]</sup> They later reported the hexavanadate-supported complexes  $[\{\text{Ru}(\text{arene})\}_4\text{V}_6\text{O}_{19}]$  (arene = *p*-cymene,  $\text{C}_6\text{Me}_6$ ),<sup>[20b]</sup> the triple-cubane-type mixed clusters

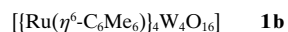
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$[\{\text{Ru}(p\text{-cymene})\}_4\text{-}_x(\text{Cp}^*\text{Rh})_x\text{Mo}_4\text{O}_{16}]$  ( $x = 1, 2$ ),<sup>[20b]</sup> and the rhombic tetranuclear cluster  $[\{\text{Ru}(p\text{-cymene})\}_2\text{Mo}_2\text{O}_4(\text{OMe})_4]$ .<sup>[20c]</sup> Here we report on the synthesis and structural characterization of further (arene)ruthenium-containing tungsten and molybdenum oxides based on cubic arrangements. A preliminary account of our work has appeared.<sup>[21]</sup>

## Results

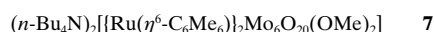
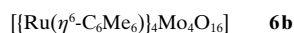
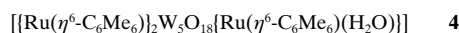
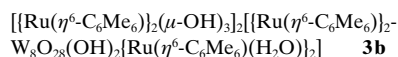
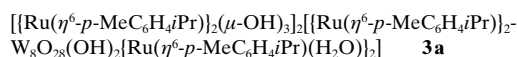
**Syntheses:** As previous work by Süss-Fink et al. dealt with condensation of sodium molybdate and sodium metavanadate with  $[\{(\text{arene})\text{RuCl}_2\}_2]$  in aqueous solution,<sup>[20a,b]</sup> our efforts were mainly directed towards the reactions of tungstates. In addition, these studies were extended to nonaqueous solvents, and this led us to investigate the condensation of molybdates under similar conditions.

Compound **1a** was obtained as a yellow precipitate by treating  $(n\text{Bu}_4\text{N})_2[\text{WO}_4]$  with  $[\{(\eta^6\text{-}p\text{-MeC}_6\text{H}_4i\text{Pr})\text{RuCl}_2\}_2]$  in acetonitrile at room temperature. Red crystals of  $2 \cdot 3\text{H}_2\text{O}$  later grew from the mother liquor. Compound **1b** was similarly obtained from  $[\{(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2\}_2]$ , but no by-product could be isolated in this case. Compounds **1a** and **1b** are insoluble in water and only slightly soluble in acetonitrile, but more soluble in dichloromethane, chloroform and methanol.



In refluxing water,  $\text{Na}_2[\text{WO}_4] \cdot 2\text{H}_2\text{O}$  reacts with  $[\{(\eta^6\text{-}p\text{-MeC}_6\text{H}_4i\text{Pr})\text{RuCl}_2\}_2]$  to give a yellow microcrystalline product, which proved to be **3a**  $\cdot 6\text{H}_2\text{O}$ , which was recrystallized as **3a**  $\cdot 14\text{H}_2\text{O}$  from methanol/water. Crystals of **3a** can alternatively be obtained from a solution of **1a** in water. Compound **3a** is insoluble in water and is only slightly soluble in organic solvents, except for methanol. The reaction of  $[\{(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2\}_2]$  with  $\text{Na}_2[\text{WO}_4] \cdot 2\text{H}_2\text{O}$  in refluxing water gave a precipitate that mainly consisted of **4** with a small amount of **1b**, which was removed by washing with methanol. Later, a few crystals of a compound whose spectroscopic properties were quite similar to those of **3a**, and thus was designated as **3b**, deposited from the mother liquor. Compound **4** is insoluble in water, methanol, and acetonitrile, but soluble in chlorinated solvents, from which it can be recrystallized. Its molybdenum analogue **5** was similarly obtained, together with a substantial amount of **6b** and a third fraction **X**, which has not yet been identified. All components can easily be separated from the others owing to their different solubilities: **5** is soluble in  $\text{CH}_2\text{Cl}_2$  but insoluble in methanol, **6b** is soluble both in  $\text{CH}_2\text{Cl}_2$  and methanol, while **X** is only soluble in methanol, in which it transforms into **6b**. Alternatively, **5** can be obtained in almost quantitative yield by treating  $(n\text{Bu}_4\text{N})_2[\text{Mo}_2\text{O}_7]$  with  $[\{(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2\}_2]$  in refluxing methanol or acetonitrile. Crystals of **5** were obtained by recrystallization from acetonitrile. Compound **7** was obtained together with **5** when the reaction was carried in

methanol at room temperature. The structure of **7** is similar to that of  $(n\text{Bu}_4\text{N})_2[(\text{RhCp}^*)_2\text{Mo}_6\text{O}_{20}(\text{OMe})_2]$ .<sup>[22]</sup> Full details on the synthesis and characterization of **7** and other related compounds will be reported in a subsequent paper.



Although the course of a given reaction depends on the metal (Mo vs. W), the arene (*p*-cymene vs.  $\text{C}_6\text{Me}_6$ ) and the solvent (water vs. acetonitrile or methanol), and although mixtures of products are often obtained, some general trends emerge from our results. Reactions in aqueous solution were generally carried out in the presence of an excess of  $\text{Na}_2\text{MO}_4 \cdot 2\text{H}_2\text{O}$  ( $\text{M} = \text{Mo}, \text{W}$ ), with a typical M/Ru ratio of five. Only the distribution of products, not their nature, was possibly altered on decreasing this ratio. In contrast, the M/Ru ratio must be kept below two in nonaqueous solvents to avoid the formation of intractable oily materials from tetrabutylammonium oxometalates. Whereas the windmill-type molybdenum clusters  $[\{\text{Ru}(p\text{-cymene})\}_4\text{Mo}_4\text{O}_{16}]$ <sup>[20a]</sup> (**6a**) and **6b** are easily obtained in aqueous solution, the tungsten analogues **1** are preferably formed in acetonitrile. Condensation of  $(n\text{Bu}_4\text{N})_2[\text{WO}_4]$  with (arene)ruthenium dichloride dimers in refluxing water instead yields either **3a** or **4**. The effect of the arene ligand is also illustrated by the fact that the analogue of **4** with *p*-cymene could not be obtained to date, and that condensation of  $(n\text{Bu}_4\text{N})_2[\text{Mo}_2\text{O}_7]$  with  $[\{(\text{C}_6\text{H}_6)\text{RuCl}_2\}_2]$  or  $[\{(\eta^6\text{-}p\text{-MeC}_6\text{H}_4i\text{Pr})\text{RuCl}_2\}_2]$  in methanol yields the rhombic heterometallic clusters  $[\{\text{Ru}(\text{arene})\}_2\text{Mo}_2\text{O}_4(\text{OMe})_2]$ <sup>[20c]</sup> rather than  $[\{\text{Ru}(\text{arene})\}_2\text{Mo}_5\text{O}_{18}\{\text{Ru}(\eta^6\text{-arene})(\text{H}_2\text{O})\}]$  and  $(n\text{Bu}_4\text{N})_2[\{\text{Ru}(\text{arene})\}_2\text{Mo}_6\text{O}_{20}(\text{OMe})_2]$ , as were obtained with  $[\{(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2\}_2]$ .

**Reactivity in solution:** While compounds **1a**, **1b**, and **6b** retain the windmill-type geometry in chlorinated solvents, according to NMR spectroscopy (see below), **6a** undergoes isomerization to the triple-cubane geometry. The equilibrium was found to depend on the solvent: while the windmill and the triple-cubane forms are present in nearly equal concentrations in  $\text{CHCl}_3$  at room temperature, the triple-cubane form is largely predominant in  $\text{CH}_2\text{Cl}_2$ .<sup>[21]</sup> Although **1a** does not isomerize in solution, crystals of **2** slowly deposit from toluene-layered solutions of **1a** in acetonitrile or dichloromethane, and **3a** is readily obtained from an aqueous solution of **1a**. These observations are witness to the reactivity of **1a**, which warrants further study. On the other hand, the <sup>17</sup>O NMR spectrum of a solution of **2** in chloroform that was heated to reflux overnight in the presence of <sup>17</sup>O-enriched

water, shows, besides the signals of **2**, four weak signals attributed to **1a**.

**Spectroscopic characterization:** The clusters reported here can be divided into four structural types for which IR spectroscopy provides clear fingerprints between 1000 and 500  $\text{cm}^{-1}$ . The IR spectra of compounds with the windmill-like geometry (**1** and **6**) display four distinct absorption bands, one above 900  $\text{cm}^{-1}$ , two in the range 730–820  $\text{cm}^{-1}$  and one below 650  $\text{cm}^{-1}$ . The IR spectrum of **2**, like those of other multi-cubane-type clusters such as  $[(\text{Cp}^*\text{Rh})_4\text{Mo}_4\text{O}_{16}]$ ,<sup>[23a]</sup> and  $[(\text{Cp}^*\text{Rh})_4\text{Mo}_6\text{O}_{22}]$ ,<sup>[23b]</sup> shows two bands characteristic of *cis*- $\text{MO}_2$  fragments around 900  $\text{cm}^{-1}$ , while other bands associated with the oxometal core appear below 700  $\text{cm}^{-1}$ . Compounds **4** and **5** display similar IR spectra, with three bands in the range 880–950  $\text{cm}^{-1}$  and one below 730  $\text{cm}^{-1}$ . In contrast, **3a** and **3b** present a pattern of four bands between 950 and 730  $\text{cm}^{-1}$ .

The  $^1\text{H}$  NMR spectra indicate that all arene ligands are magnetically equivalent in **1a**, **1b**, **2**, and **6b**, which is consistent with the retention of the solid-state molecular structures on dissolution in chlorinated solvents. Three signals of equal intensity are observed for **4** and **5**, and three sets of signals with relative intensities of 2:1:1 for **3a**, which again is in agreement with the crystal structures. Two sets of signals whose relative intensities depend on the solvent are observed for the *p*-cymene ligands in **6a**, which suggests the presence of two distinct *p*-cymene-containing clusters, which were identified as the windmill and triple-cubane isomers by  $^{17}\text{O}$  NMR spectroscopy.<sup>[21]</sup> Free rotation of arene ligands around the ruthenium–arene bond axis was observed for all compounds except **1a**, the  $^1\text{H}$  NMR spectrum of which in  $\text{CDCl}_3$  displays four doublets for aromatic protons and two doublets for the methyl groups of the isopropyl substituent.

The  $^{17}\text{O}$  NMR spectra of enriched samples of **1a**, **1b**, and **6b** in chloroform display four signals with relative intensities 1:1:1:1. They are assigned to terminal ( $\text{O}_t$ ), two types of doubly bridging and quadruply bridging oxo ligands, in the order of increasing shielding, which is consistent with the windmill geometry. In contrast, the  $^{17}\text{O}$  NMR spectrum of **6a** in dichloromethane or chloroform consists of two sets of signals: one is assigned to the windmill isomer, and the other, which is composed of three signals of relative intensities 2:1:1, to the triple-cubane isomer by comparison with  $[(\text{Cp}^*\text{Rh})_4\text{Mo}_4\text{O}_{16}]$ .<sup>[23a]</sup>

$^{95}\text{Mo}$  or  $^{183}\text{W}$  spectra have been obtained only for a few compounds due to solubility problems. The  $^{183}\text{W}$  spectrum of **1a** in chloroform displays a single signal, while that of **3a** in methanol exhibits four signals; this is consistent in both cases with the retention of the solid-state structure upon dissolution. The  $^{95}\text{Mo}$  NMR spectrum of **5** in chloroform shows three signals of relative intensities 2:2:1, also in agreement with the crystal structure, and that of **6a** displays two signals whose relative intensities depend on the solvent, in accordance with the equilibrium between the windmill and the triple-cubane forms.

The UV/Vis spectra of **1–6** are reminiscent of those of the (arene)ruthenium dichloride dimer precursors, that is, they display two metal-to-ligand charge-transfer transitions be-

tween 300 and 450 nm. Ligand-to-metal charge-transfer transitions involving oxo ligands are observed at higher energy.

**Crystal structures:** Compounds **1b**·4 $\text{H}_2\text{O}$ · $\text{C}_6\text{H}_5\text{Me}$ , **2**·3 $\text{H}_2\text{O}$ ,<sup>[21]</sup> **3a**·14 $\text{H}_2\text{O}$ , **4**·3 $\text{H}_2\text{O}$ , and **5**·2 $\text{H}_2\text{O}$ · $\text{MeCN}$  were characterized by single-crystal X-ray diffraction.

The molecular structure of **1b** in **1b**·4 $\text{H}_2\text{O}$ · $\text{C}_6\text{H}_5\text{Me}$  is displayed in Figure 1. The cluster has a windmill-like geometry quite similar to that of  $[(\text{Ru}(p\text{-cymene}))_4\text{Mo}_4\text{O}_{16}]$  (**6a**) in **6a**·2 $\text{C}_6\text{H}_5\text{Me}$ .<sup>[20a]</sup> In the course of our studies, we obtained additional X-ray diffraction data for **6a** and **6a**· $\text{C}_6\text{H}_5\text{Me}$ . The molecular structure of **6a** in these crystals is the same as in **6a**·2 $\text{C}_6\text{H}_5\text{Me}$ .<sup>[20a]</sup> X-ray diffraction data were also obtained for **1a**· $\text{C}_6\text{H}_5\text{Me}$ : despite the poor quality of the data due to

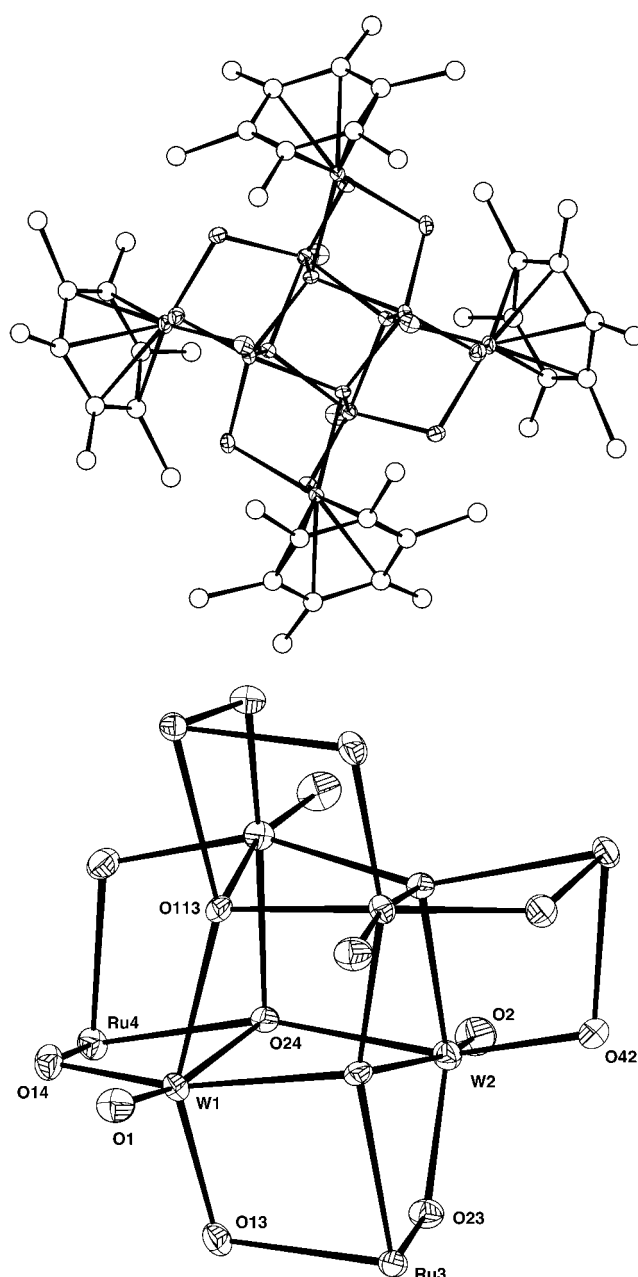


Figure 1. Structure of **1b** (top) and of its oxometallic core (bottom; 20% probability thermal ellipsoids in both).<sup>[46]</sup>

decay during data collection, the molecular structure of **1a** emerged clearly from the crystal structure determination and again is similar to those of **1b** and **6a**. There is also no doubt that **6b**, whose IR spectrum is similar to those of **1a**, **1b** and **6a** (see above), also displays the same geometry. Thus the four isostructural clusters **1a**, **1b**, **6a**, and **6b** contain a  $[\text{M}_4\text{O}_{16}]^{8-}$  polyoxoanion ( $\text{M} = \text{Mo}$ ,  $\text{W}$ ) that supports four  $\{(\eta^6\text{-arene})\text{Ru}\}^{2+}$  fragments. They can alternatively be viewed as being composed of four edge-sharing incomplete cubane-type units  $[\{\text{Ru}(\eta^6\text{-arene})\}(\text{WO}_3)_2(\mu\text{-O})_3(\mu_3\text{-O})]^{6-}$ .

While the centrosymmetric cluster **2** (Figure 2) has a face-sharing double-cubane framework consisting of two fused  $[\{\text{Ru}(\eta^6\text{-arene})\}_2(\text{WO}_3)_2(\mu_3\text{-O})_4]^{4-}$  cubes,<sup>[21]</sup> the centrosymmetric anion of **3a** is made up of two crystallographically equivalent cuboidal  $[\{\text{Ru}(\text{arene})\}(\text{WO}_3)_3(\mu_3\text{-O})_3(\mu_3\text{-OH})]^{5-}$  clusters linked together by two equivalent *cis*- $\{\text{WO}_2\}^{2+}$  groups, each of which supports a  $\{\text{Ru}(\text{arene})(\text{H}_2\text{O})\}^{2+}$  unit (Figure 3). The tungsten atoms of the cubane-like unit are connected to the linking  $\{\text{WO}_2\}^{2+}$  groups in different ways: while W1 and W2, which support the Ru6 center, are each connected to a single  $\{\text{WO}_2\}^{2+}$  group, W4 is connected to both W3 and W3'. The linking groups exhibit  $\text{WO}_6$  coordination to two terminal oxo ligands and four doubly-bridging oxo ligands, with a typical two short/two intermediate/two long bonding pattern. The W-O-W bridges are unsymmetrical: the W-O bond to the cubane-like unit is consistently shorter than the other. Consideration of bond valence sums for the oxygen atoms revealed that O600 is in a terminal  $\text{H}_2\text{O}$  ligand, while O124 belongs to a  $\mu_3$ -hydroxo ligand. The structure of  $[\{\text{Ru}(\eta^6\text{-}i\text{-}p\text{-}\text{MeC}_6\text{H}_4\text{iPr})\}_2(\mu\text{-OH})_3]^{+}$ , the cation of **3a** (Figure 4), was previously reported.<sup>[24]</sup>

Clusters **4** (Figure 5) and **5** (Figure 6) can be described on the basis of two edge-sharing  $[\{\text{Ru}(\text{arene})\}(\text{MO}_3)_3(\mu_3\text{-O})_4]^{6-}$  cubes linked by two oxo ligands, whereby one cube supports a  $\{\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\text{H}_2\text{O})\}^{2+}$  fragment. The cubic arrangement in compound **4** is very similar to that reported for  $[\text{TeMo}_8\text{O}_{29}(\text{OH}_2)]^{2-}$ <sup>[25]</sup> Alternatively, **4** and **5** can be viewed as lacunary Lindqvist-type polyanions  $[\text{M}_5\text{O}_{18}]^{6-}$  supporting one  $\{\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\text{H}_2\text{O})\}^{2+}$  and two  $\{\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)\}^{2+}$  fragments. Each  $\{\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)\}^{2+}$  fragment is attached to a triangle of bridging oxygen atoms, as is observed in a number of polyoxoanion  $\kappa^3\text{O}$ -supported organometallic compounds,<sup>[6]</sup> while the  $\{\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\text{H}_2\text{O})\}^{2+}$  fragment is bound to two adjacent oxygen atoms of the four that delineate the vacancy

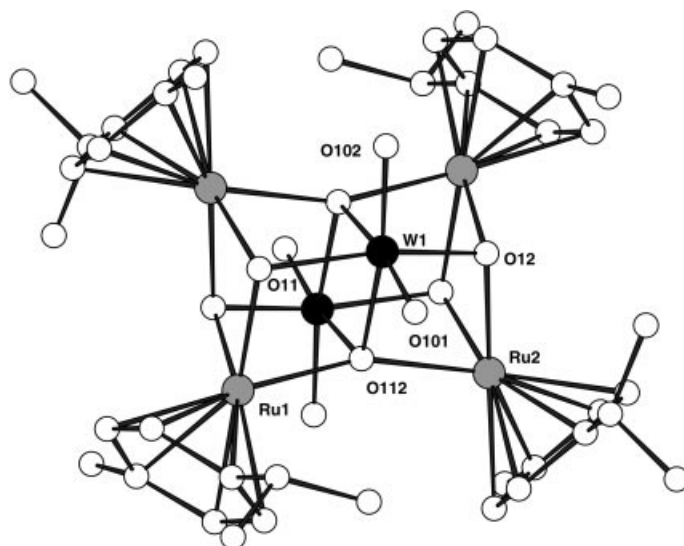


Figure 2. Structure of **2**.

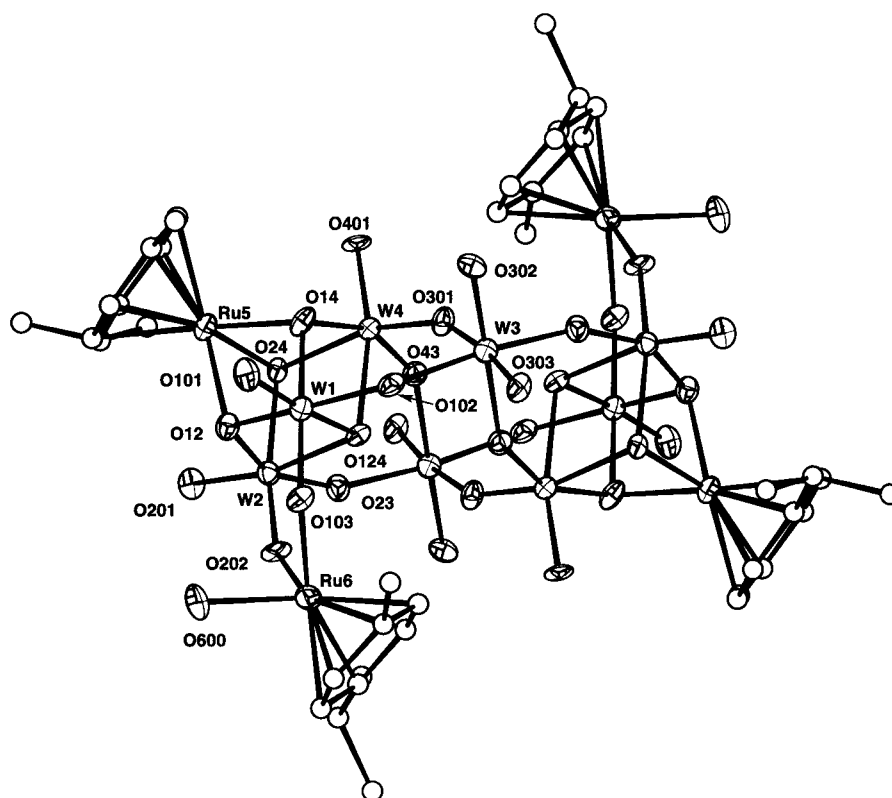


Figure 3. Structure of the anion in **3a** (20% probability thermal ellipsoids).<sup>[46]</sup>

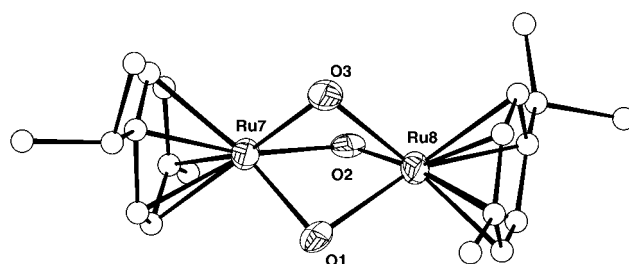


Figure 4. Structure of the cation in **3a** (20% probability thermal ellipsoids).<sup>[46]</sup>

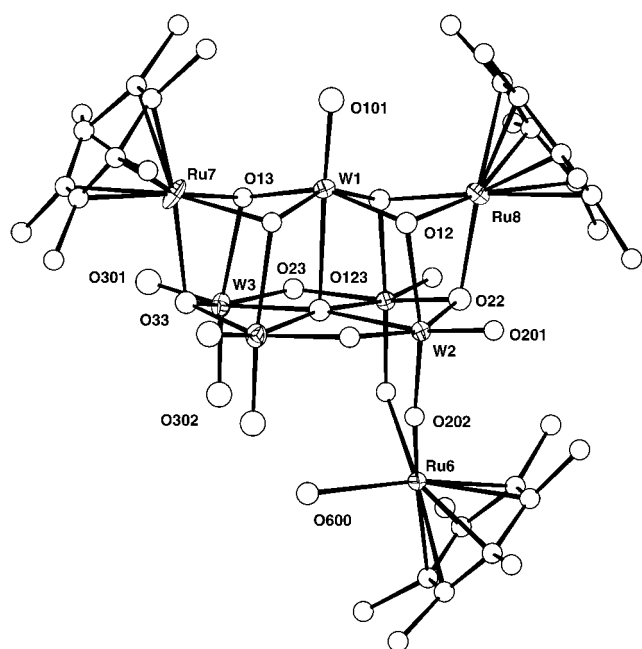


Figure 5. Structure of **4** (20% probability thermal ellipsoids).<sup>[46]</sup>

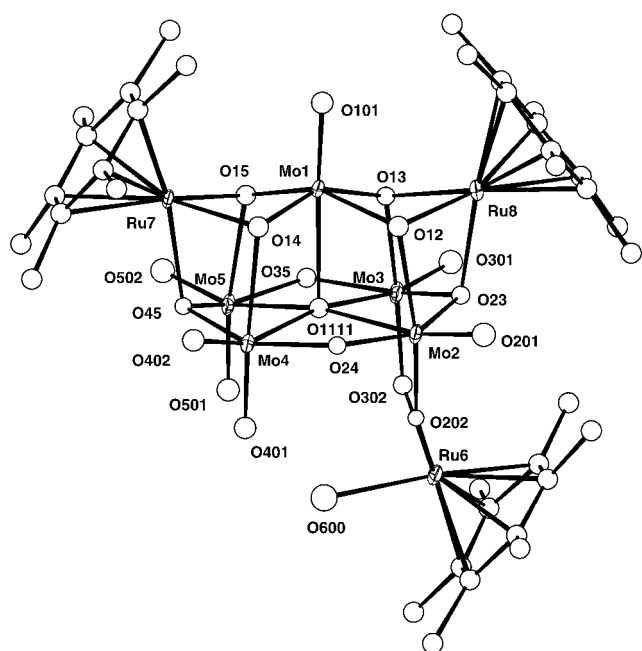


Figure 6. Structure of **5** (20% probability thermal ellipsoids).<sup>[46]</sup>

in the polyanion, in a similar way to the  $\{\text{Cp}^*\text{Rh}(\text{H}_2\text{O})\}^{2+}$  fragment in  $[\{\text{Cp}^*\text{Rh}(\text{H}_2\text{O})\}\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})]^{12-}$ .<sup>[26]</sup>

All the  $\text{M}_4\text{O}_4$  cores identified in **1–6** are highly distorted. The edge lengths of the central  $\text{W}_4\text{O}_4$  unit in **1b** range from 2.054(5) to 2.495(6) Å. They reflect the various influences of *trans* ligands: the  $\text{W1–O24}$  and  $\text{W2–O113'}$  bonds *trans* to terminal oxo ligands are about 0.4 Å longer than the  $\text{W1–O113}$ ,  $\text{W1–O113'}$ ,  $\text{W2–O24}$  and  $\text{W2–O24'}$  bonds, which are *trans* to  $\mu$ -oxo ligands. Similar effects are observed in **6a**.<sup>[20a]</sup> In **2**, the edges of the face shared by the two fused cubes are lengthened owing to the *trans* influence of terminal oxo ligands. In **3a**, the mean length of the edges involving O124,

which is *trans* to the terminal oxo ligands at W1, W2, and W4 and is also protonated, is about 0.18 Å longer than the mean length of those involving O12, O14, and O24. Although **4** and **5** are quite similar, a close examination reveals some small but systematic differences. Indeed, the effect of the  $\{\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\text{H}_2\text{O})\}^{2+}$  fragment on the geometry of the supporting cube is more apparent in **5** than in **4**. The M–O bonds which support the Ru6 center are slightly longer in **5** than in **4**, and the short/long alternation of *trans* bonds is more pronounced along the  $\text{O202–Mo2–O12–Mo1–O15–Mo5–O501}$  and  $\text{O302–Mo3–O13–Mo1–O14–Mo4–O401}$  sequences in **5** than along the corresponding  $\text{O202–W2–O12–W1–O13–W3–O302}$  sequence in **4**. It follows that the cube supporting the Ru6 fragment is less distorted than the other one in **5**. This might be connected with the observation that the displacements of the metal atoms in iso-<sup>[27a]</sup> and heteropolyanions,<sup>[27b]</sup> which render some anions chiral,<sup>[28]</sup> are usually much less pronounced in tungstates than in molybdates.

All the ruthenium centers are formally six-coordinate and achieve a 18-electron configuration by coordination to three bridging oxo ligands, two bridging oxo ligands and one molecule of water, or three bridging hydroxo ligands in the cation of **3a**. For any  $\text{Ru}(\eta^6\text{-arene})$  fragment, the Ru–O bond lengths are quite similar when the ruthenium atom is attached to a triangle of chemically equivalent oxo ligands, as is the case in **3a**, **4**, and **5**. In contrast, the  $\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)$  fragments are unsymmetrically bonded to the polyoxoanion core in **1b**, and the Ru–( $\mu_4$ -O) bonds are significantly longer than the Ru–( $\mu$ -O) bonds. However, no significant difference is observed between the Ru–( $\mu$ -O) and Ru–( $\mu_4$ -O) bond lengths in **6a**,<sup>[20a]</sup> nor between Ru–( $\mu_3$ -O) and Ru–( $\mu_4$ -O) bond lengths in **2**. Hence, the asymmetry observed in **1b** possibly reflects steric effects and is reflected in the <sup>1</sup>H NMR spectroscopic properties of this compound.

## Discussion

There are two interdependent issues regarding the syntheses and structures of **1–6**: 1) Does the distinction established by Finke et al.<sup>[4a]</sup> between incorporated and supported organometallic fragments still apply to such compounds? 2) Do the results provide some insight in the formation pathways of these compounds?

The distinction between polyoxometalate-supported and polyoxometalate-incorporated (or -integrated) organometallic species is somewhat arbitrary, because it primarily relies on the recognition of a central oxometal core which can exist in the free form or, at least, which can be recognized as a common structural type in polyoxometalate chemistry. In the above description of the structure of **4**, two  $\{\text{Ru}(\text{arene})\}^{2+}$  moieties were viewed as being integrated in cubic cores, while the third was considered to be supported on a cubane surface. Alternatively, the structure of **4** could be viewed as a central lacunary Lindqvist-type  $\{\text{W}_5\text{O}_{18}\}^{6-}$  polyoxotungstate core that supports three  $\{\text{Ru}(\text{arene})\}^{2+}$  moieties. Similarly, the vanadium compounds  $[\{\text{Ru}(\eta^6\text{-}i\text{-PrC}_6\text{H}_4\text{Pr})\}_4\text{V}_6\text{O}_{19}]^{20b}$  and  $[(\text{RhCp}^*)_4\text{V}_6\text{O}_{19}]$  can be viewed as Lindqvist-type anions  $[\text{V}_6\text{O}_{19}]^{8-}$  supporting four organometallic fragments, or alter-

natively as four edge-sharing  $[M(\text{VO})_3\text{L}_3(\mu_3\text{-O})_3]$  cubes ( $M = \text{Ru}, \text{Rh}$ ;  $\text{L}_3 = \text{arene}, \text{Cp}^*$ ).<sup>[29]</sup> Beyond apparent structural relationships, a detailed analysis of the geometry could provide a clue to distinguishing between supported and integrated complexes. Indeed, structural changes in the oxometal core upon the attachment of organometallic units are expected to be larger in integrated than in supported compounds. Among the derivatives of the lacunary Lindqvist-type  $[\text{M}_5\text{O}_{18}]^{6-}$  ions ( $M = \text{W}, \text{Mo}$ ), the  $[\text{Cp}^*\text{TiM}_5\text{O}_{18}]^{3-}$  complexes ( $\text{Cp}^* = \text{C}_5\text{H}_5, \text{C}_5\text{Me}_5$ ;  $M = \text{Mo}, \text{W}$ )<sup>[30]</sup> are usually considered to be integrated derivatives, while the lanthanide complexes  $[\text{Ln}(\text{W}_5\text{O}_{18})_2]^{n-}$ <sup>[31]</sup> appear to be best described as supported derivatives. Indeed, although the free ligands are unknown, the structural changes upon coordination of the titanium center are larger than with lanthanides. Let us use the subscripts *ax* and *eq* to distinguish the two kinds of terminal oxo ligands linked to the four metal atoms that delimit the lacuna in the  $[\text{M}_5\text{O}_{18}]^{6-}$  ions. The  $M\text{-O}_{\text{eq}}$  and  $M\text{-O}_{\text{ax}}$  bond lengths are likely to be roughly equal in the free ligands. The difference is only 0.05 Å in  $[\text{Ln}(\text{W}_5\text{O}_{18})_2]^{n-}$  (average for complexes in ref. [31]), while it increases to 0.15 Å in  $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)]\text{W}_5\text{O}_{18}]^{3-}$ .<sup>[30c]</sup> Similarly, it appears that the  $M\text{-O}$  bonds involved in the binding of the  $\{\text{Ru}(\eta^6\text{-arene})(\text{H}_2\text{O})\}^{2+}$  fragment in clusters **3a**, **4**, and **5** retain appreciable multiple bond character, so that these fragments are best described as supported, as is also the case for the  $\{\text{Cp}^*\text{Rh}(\text{H}_2\text{O})\}^{2+}$  fragment in  $[\{\text{Cp}^*\text{Rh}(\text{H}_2\text{O})\}\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}]^-$ .<sup>[26]</sup>

The other two Ru-containing units in **4** are of a different type. Since the bond length range involving doubly and triply bridging oxygen atoms may overlap, the conclusion about the nature, supported or integrated, of the organometallic fragments is not straightforward in this case. Tentatively, we can compare the  $\text{W}\text{-O}$  bond lengths within  $\text{OW}_2\text{Ru}$  groups with those of  $\text{OW}_2$  groups in the same compound, like comparing  $\text{W}\text{-O}$  distances in  $\text{OWRu}$  with  $\text{W}\text{-O}$  distances involving terminal oxygen atoms in the previous examples. More generally, this comes down to comparing, within the same species,  $\text{W}\text{-O}$  distances in  $\text{OW}_x\text{Ru}$  and  $\text{OW}_x$  groups that are chemically as close as possible ( $x = 1$  for Ru6 and  $x = 2$  for Ru7 and Ru8 in **4**). This defines what we will subsequently refer to as an internal criterion, with no need to refer to the external criterion of a related free polyoxometalate ligand. In **4**, the  $\text{W1}\text{-O12}$  and  $\text{W1}\text{-O13}$  bond lengths (av 1.92 Å) are similar to those of  $\text{W2}\text{-O23}$  and  $\text{W3}\text{-O23}$  (av 1.90 Å), while those of  $\text{W2}\text{-O22}$  and  $\text{W3}\text{-O33}$  (av 2.01 Å) are 0.1 Å longer. However, the deviation due to the attachment of Ru7 and Ru8 centers remains small, and we therefore consider them to be supported. Furthermore, related bond lengths in the lanthanide derivatives  $[\text{Ln}(\text{W}_5\text{O}_{18})_2]^{n-}$  fall in the range of 1.86–2.02 Å.<sup>[31]</sup>

In **1**, the average  $\text{W}\text{-O}_{\text{terminal}}$  distance is 1.708 Å, as opposed to an average of 1.805 Å for the  $\text{W1}\text{-O13}$ ,  $\text{W1}\text{-O14}$ ,  $\text{W2}\text{-O23}$ , and  $\text{W2}\text{-O42}$  bond lengths, that is, only 0.1 Å longer. The latter value compares well with the mean value of 1.803 Å for similar  $\text{W}\text{-O}$  bonds in the  $\text{WOIr}$  groups of  $[\{\text{Ir}(\text{cod})\}_6\text{W}_4\text{O}_{16}]^{2-}$  ( $\text{cod} = 1,5\text{-cyclooctadiene}$ ).<sup>[32]</sup> Discrete cubic  $[\text{W}_4\text{O}_{16}]^{8-}$  with a lithium cation at its center is found in  $\text{Li}_7[\text{LiW}_4\text{O}_{16}]$ .<sup>[33]</sup> The  $\text{W}\text{-O}$  distances involving terminal and triply bridging oxygen

atoms were reported to be 1.87 and 2.21 Å, respectively. Although no standard deviations were given, these seem to be overestimates, since the corresponding  $\text{W}\text{-}(\mu_3\text{-O})$  bond lengths in  $[\{\text{Ir}(\text{cod})\}_6\text{W}_4\text{O}_{16}]^{2-}$  averaged to only 2.104 Å.<sup>[32]</sup> So, coming back to compound **1**, both internal and external criteria support the description of the arene–ruthenium moieties as supported.

Since no recognized isopolymetalate structure can be related to that of **3**, only the internal criterion can be applied. The difference between the average of  $\text{W1}\text{-O12}$ ,  $\text{W1}\text{-O14}$ ,  $\text{W2}\text{-O12}$ ,  $\text{W2}\text{-O24}$ ,  $\text{W4}\text{-O14}$ , and  $\text{W4}\text{-O24}$  distances (2.04 Å) in  $\text{OW}_2\text{Ru}$  groups and that of the  $\text{W1}\text{-O102}$ ,  $\text{W2}\text{-O23}$ ,  $\text{W4}\text{-O43}$ , and  $\text{W4}\text{-O301}$  distances in  $\text{OW}_2$  groups (1.86 Å) is 0.18 Å larger. This favors the description of the ruthenium–arene fragments as integrated.

Although alternative descriptions could be offered, cubane-type  $\{\text{M}_4(\mu_3\text{-O})_4\}$  ( $M = \text{Ru}$  and/or  $\text{Mo}, \text{W}$ ) units can be recognized in **1–6**. Thus, compound **2** can be derived from  $[\{\text{Ru}(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})\}_2(\text{WO}_3)_2(\mu_3\text{-O})_4]^{4-}$ , while compounds **3–5** can be viewed as based on  $[\{\text{Ru}(\eta^6\text{-arene})\}(\text{MO}_3)_3(\mu_3\text{-O})_4]^{6-}$  units (**3**, **4**:  $M = \text{W}$ ; **5**:  $M = \text{Mo}$ ). These  $\{\text{RuM}_3(\mu_3\text{-O})_4\}$  and  $\{\text{Ru}_2\text{M}_2(\mu_3\text{-O})_4\}$  cubane-like species are intermediates between the homometallic  $\{\text{Ru}_4(\mu_3\text{-O})_4\}$  and  $\{\text{M}_4(\mu_3\text{-O})_4\}$  cores. The  $\{\text{Ru}_3\text{M}(\mu_3\text{-O})_4\}$  unit, which would complete the series, has not been observed so far. The  $\{\text{Ru}_4(\mu_3\text{-O})_4\}$  core is known in  $[\{\text{Ru}(\eta^6\text{-C}_6\text{H}_6)_4(\mu_3\text{-OH})_4\}]^{4+}$ .<sup>[34]</sup> The  $\{\text{M}_4(\mu_3\text{-O})_4\}$  core is quite common in cyclopentadienyl oxide clusters of Groups 5 and 6,<sup>[1]</sup> and  $\{\text{Mo}_4(\mu\text{-O})_4\}^{n+}$  cores are found in multiple cubane-type organometallic oxide clusters<sup>[23]</sup> and in extended solids.<sup>[35]</sup> However, discrete  $[(\text{MO}_3)_4(\mu_3\text{-O})_4]^{8-}$  clusters ( $M = \text{Mo}, \text{W}$ ) are represented solely by  $[\text{LiW}_4\text{O}_{16}]^{7-}$ .<sup>[33]</sup> Presumably in part because of the high charge density in such species, and also because the environment of the metal atoms violates Lipscomb's rule.<sup>[36]</sup> Similarly, the species  $[\{\text{Ru}(\eta^6\text{-arene})\}_x(\text{MO}_3)_{4-x}(\mu_3\text{-O})_4]^{(8-2x)-}$  ( $x = 1\text{--}3$ ) should be quite reactive. Their stabilization could be achieved in several ways: 1) Alkylation, that is, replacement of some terminal oxo ligands by alkoxo groups. For example, the cubane-type clusters  $[\{\text{M}(\text{CO})_3\}_2(\text{MoO}_3)_2(\mu_3\text{-O})_4]^{6-}$  ( $M = \text{Mn}, \text{Re}$ ) are not expected to be stable, but they have been isolated as the methoxo derivatives  $[\{\text{M}(\text{CO})_3\}_2\text{Mo}_2\text{O}_5(\text{OMe})_5]^-$ .<sup>[12]</sup> 2) Capping by organometallic groups. For example  $[(\text{WO}_3)_4(\mu_3\text{-O})_4]^{8-}$  is stabilized when capped by six  $\{\text{Ir}(1,5\text{-cod})\}^+$  groups.<sup>[32]</sup> 3) Oligomerization by formation of  $\text{M}\text{-O}\text{-M}$  bridges. For instance,  $[\{\text{M}(\text{CO})_3\}_2\text{Mo}_6\text{O}_{16}(\text{OMe})_2\{\text{MeC}(\text{CH}_2\text{O})_3\}_2]^{2-}$  can be viewed as resulting from the condensation of two  $[\{\text{M}(\text{CO})_3\}\text{Mo}_3\text{O}_9(\text{OMe})\{\text{MeC}(\text{CH}_2\text{O})_3\}]^{3-}$  anions by sharing of two oxo ligands. In this case, however, the tetranuclear unit does not display the cubane-type geometry but the alternative rhomblike geometry.<sup>[12]</sup>

Let us discuss the molecular structures of **1–6** according to the above considerations. As far as Lipscomb's rule is concerned, stabilization of the  $[\{\text{Ru}(\eta^6\text{-arene})\}_2(\text{MO}_3)_2(\mu_3\text{-O})_4]^{4-}$  only requires the coordination of one further  $\{\text{Ru}(\eta^6\text{-arene})\}^{2+}$  group. This would lead to the incomplete double cubane-type clusters  $[\{\text{Ru}(\eta^6\text{-arene})\}_3(\text{MO}_3)_2(\mu\text{-O})_2(\mu_3\text{-O})_3(\mu_4\text{-O})]^{2-}$ , which were not observed in the course of this work. However,  $[\{\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)\}_2(\text{MoO}_2)_3(\text{OMe})(\mu\text{-OMe})_2(\mu_3\text{-OMe})(\mu_3\text{-O})_2(\mu_4\text{-O})]$  provides an example for the incomplete

double-cubane geometry. In this case, stabilization of the parent  $[\{\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{MoO}_3)_2(\mu_3\text{-O})_4\}]^{4-}$  core arises from the coordination of one *fac*- $\{\text{MoO}_2(\text{OMe})\}^+$  unit and the replacement of three oxo ligands by methoxo groups.<sup>[23b]</sup> Attachment of another  $\{\text{Ru}(\eta^6\text{-arene})\}^{2+}$  group to the species  $[\{\text{Ru}(\eta^6\text{-arene})\}_3(\text{MO}_2)_2(\mu\text{-O})_2(\mu_3\text{-O})_3(\mu_4\text{-O})]^{2-}$  would lead to double-cubane cluster  $[\{\text{Ru}(\eta^6\text{-arene})\}_4(\text{MO}_2)_2(\mu_3\text{-O})_4(\mu_4\text{-O})_2]$ . This is actually the structure displayed by **2** (arene = *p*-MeC<sub>6</sub>H<sub>4</sub>iPr; M = W). Compounds **3a** and **3b** provide even more conclusive evidence for the intermediate formation of mono-cubane cores, in this case  $[\{\text{Ru}(\eta^6\text{-arene})\}(\text{WO}_3)_3(\mu_3\text{-O})_4]^{6-}$ , or more exactly  $[\{\text{Ru}(\eta^6\text{-arene})\}(\text{WO}_3)_3(\mu_3\text{-O})_3(\mu_3\text{-OH})]^{5-}$ . Coordination of one  $\{\text{Ru}(\eta^6\text{-arene})(\text{H}_2\text{O})\}^{2+}$  group and one *cis*- $\{\text{WO}_2\}^{2+}$  unit prevents violation of Lipscomb's rule. Dimerization occurs to fulfil the coordination preference of the additional tungsten center. Although **4** and **5** could formally be described as two  $[\{\text{Ru}(\eta^6\text{-arene})\}(\text{MO}_3)_3(\mu_3\text{-O})_4]^{6-}$  (M = W, Mo) cubic units fused by sharing one M–( $\mu_3\text{-O}$ ) edge, and further linked by two oxo ligands, the formation pathway of these clusters more likely involves the incomplete cubane-type species  $[\{\text{Ru}(\eta^6\text{-arene})\}(\text{MO}_3)_2(\mu\text{-O})_3(\mu_3\text{-O})]^{6-}$ . Such precubane-type clusters could also be recognized in **1** and **6**, although these compounds are more properly described as  $[(\text{MO}_3)_4(\mu_3\text{-O})_4]^{8-}$  cores capped by four  $\{\text{Ru}(\eta^6\text{-arene})\}^{2+}$  groups. Note that the trinuclear clusters  $\{(\text{MO}_3)_3(\mu\text{-O})_3(\mu_3\text{-O})\}$  (M = V, Nb, Mo, W), which are recurrent units in polyoxometalate structures, are nothing more than precubane clusters. Although such clusters are unknown as discrete species, stable analogues such as  $[\{\text{Mo}(\text{H}_2\text{O})_3(\mu\text{-O})_3(\mu_3\text{-O})\}]^{4-}$ ,<sup>[37]</sup>  $[(\text{TiCp}^*)_3(\mu\text{-O})_3(\mu_3\text{-CR})]^{38a}$  and  $[(\text{TiCp}^*)_3(\mu\text{-NH})_3(\mu_3\text{-N})]^{38b}$  have been characterized, while others such as  $[\{\text{Mo}_3(\mu\text{-O})_3(\mu_3\text{-O})(\text{H}_2\text{O})_5(\mu\text{-OH})_2\}]^{8+}$  can be recognized in oligomers.<sup>[39]</sup> Therefore, precubane clusters  $[\{\text{Ru}(\eta^6\text{-arene})\}(\text{MO}_3)_2(\mu\text{-O})_3(\mu_3\text{-O})]^{6-}$  could be key intermediates in the formation of **1–6**.

## Conclusion

Several polyoxometalates incorporating  $\{\text{Ru}(\eta^6\text{-arene})\}^{2+}$  units have been characterized. While  $[\{\text{Ru}(\eta^6\text{-arene})\}_4(\text{MO}_3)_4(\mu_3\text{-O})_4]$  (**1** and **6**),  $[\{\text{Ru}(\eta^6\text{-arene})\}_4(\text{WO}_2)_2(\mu_3\text{-O})_4(\mu_4\text{-O})_2]$  (**2**), and  $[\{\text{Ru}(\eta^6\text{-arene})\}(\text{WO}_3)_3(\mu_3\text{-O})_3(\mu_3\text{-OH})\text{Ru}(\eta^6\text{-arene})(\text{H}_2\text{O})_2(\mu\text{-WO}_2)_2]^{2-}$  (**3**) are based on cubane-type units,  $[\{\text{Ru}(\eta^6\text{-arene})\}_2\text{M}_5\text{O}_{18}\{\text{Ru}(\eta^6\text{-arene})(\text{H}_2\text{O})\}]$  (**4** and **5**) are more properly described as a Lindqvist-type lacunary pentametalate polyanion supporting three ruthenium centers. We are now investigating the influence of the arene and that of the metal (Mo vs W) on the course of the synthetic pathways and we are exploring the reactivity of the products.

## Experimental Section

**Materials:** (*n*Bu<sub>4</sub>N)<sub>2</sub>[Mo<sub>2</sub>O<sub>7</sub>],<sup>[40]</sup> (*n*Bu<sub>4</sub>N)<sub>2</sub>[WO<sub>4</sub>],<sup>[41]</sup>  $[\{\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr}\}\text{RuCl}_2]_2$ ,<sup>[42]</sup> and  $[\{\eta^6\text{-}C_6\text{Me}_6\}\text{RuCl}_2]_2$ <sup>[42]</sup> were prepared as described in the literature. Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O and Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O were obtained from commercial sources and used as received. Organic solvents were of reagent grade.

**Methods:** IR spectra were recorded on KBr pellets on a Bio-Rad FT 165 spectrometer. The <sup>1</sup>H, <sup>17</sup>O and <sup>183</sup>W NMR spectra were obtained on a Bruker AC 300 spectrometer (11.8 T). <sup>95</sup>Mo spectra were obtained on a Bruker AC 500 spectrometer. Electronic absorption spectra were recorded with a Shimadzu UV-2101PC spectrometer. Elemental analyses were performed by the Service Central d'Analyse of the CNRS (Vernaison, France). <sup>17</sup>O-enriched samples (unless otherwise stated) were obtained by heating CHCl<sub>3</sub> solutions containing 10% <sup>17</sup>O-enriched water at 60 °C for 2 h.

**Preparation of  $[\{\text{Ru}(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})_4\text{W}_4\text{O}_{16}\}]$  (**1a**) and  $[\{\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr}\}\text{RuCl}_2]_2$  (**2**):** (*n*Bu<sub>4</sub>N)<sub>4</sub>[WO<sub>4</sub>] (0.733 g, 1 mmol) and  $[\{\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr}\}\text{RuCl}_2]_2$  (0.306 g, 0.5 mmol) were dissolved in CH<sub>3</sub>CN (15 mL). The mixture was stirred for 5 h at room temperature. The yellow precipitate of **1a** was washed with CH<sub>3</sub>CN (3 mL). Slow evaporation of the filtrate at 25–30 °C afforded sticky, red crystals of **2**·3H<sub>2</sub>O. **1a**: yield: 0.215 g (51%); IR (KBr):  $\tilde{\nu}$  = 935 (s), 878 (w), 803 (s), 750 (s), 608 (m) (WO) cm<sup>-1</sup>; <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>, 22 °C, TMS):  $\delta$  = 1.345 (d, <sup>3</sup>J(H,H) = 6.9 Hz, 3H; ArCH(CH<sub>3</sub>)<sub>2</sub>), 1.34 (d, <sup>3</sup>J(H,H) = 6.9 Hz, 3H; ArCH(CH<sub>3</sub>)<sub>2</sub>), 2.41 (s, 3H; ArCH<sub>3</sub>), 3.05 (hept, 1H; <sup>3</sup>J(H,H) = 6.9 Hz, ArCH(CH<sub>3</sub>)<sub>2</sub>), 5.34 (d, 1H; <sup>3</sup>J(H,H) = 5.7 Hz, ArH), 5.56 (d, 1H; <sup>3</sup>J(H,H) = 5.8 Hz, ArH), 5.64 (d, 1H; <sup>3</sup>J(H,H) = 5.7 Hz, ArH), 5.75 (d, 1H; <sup>3</sup>J(H,H) = 5.8 Hz, ArH); <sup>17</sup>O NMR (40.7 MHz, CDCl<sub>3</sub>, 50 °C, bulk water):  $\delta$  = 676 (s, 4 O, O<sub>i</sub>), 399 (s, 4 O,  $\mu_2\text{-O}$ ), 329 (s, 4 O,  $\mu_2\text{-O}$ ), 27 (s, 4 O,  $\mu_4\text{-O}$ ); <sup>183</sup>W NMR (20.8 MHz, CDCl<sub>3</sub>, 22 °C, 2 mol L<sup>-1</sup> Na<sub>2</sub>WO<sub>4</sub> in alkaline D<sub>2</sub>O):  $\delta$  = 351; UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 390 (3100), 330 nm (sh, 8500 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); elemental analysis (%) calcd for C<sub>40</sub>H<sub>50</sub>O<sub>16</sub>Ru<sub>4</sub>W<sub>4</sub>: C 24.86, H 2.92, Ru 20.92, W 38.05; found: C 24.29, H 2.91, Ru 19.23, W 37.35. **2**·3H<sub>2</sub>O: yield: 0.04 g (10%); IR (KBr):  $\tilde{\nu}$  = 916 (s), 897 (w; W=O<sub>i</sub>), 652 (m), 624 (sh), 607 (s), 574 (m), 512 (m; W–O<sub>i</sub>) cm<sup>-1</sup>; <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>, 22 °C, TMS):  $\delta$  = 1.395 (d, <sup>3</sup>J(H,H) = 6.8 Hz, 6H; ArCH(CH<sub>3</sub>)<sub>2</sub>), 2.29 (s, 3H; ArCH<sub>3</sub>), 3.07 (h, 1H; <sup>3</sup>J(H,H) = 6.8 Hz, ArCH(CH<sub>3</sub>)<sub>2</sub>), 5.29 (d, 2H; <sup>3</sup>J(H,H) = 5.9 Hz, ArH), 5.34 (d, 2H; <sup>3</sup>J(H,H) = 5.9 Hz, ArH); natural-abundance <sup>17</sup>O NMR (40.7 MHz, CDCl<sub>3</sub>, 50 °C, bulk water):  $\delta$  = 665 (s, O<sub>i</sub>), –12 (s,  $\mu_3\text{-O}$ ), –25 (s,  $\mu_4\text{-O}$ ); UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 400 (sh, 2300), 355 (4000), 292 nm (sh, 8000 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); elemental analysis (%) calcd for C<sub>40</sub>H<sub>62</sub>O<sub>13</sub>Ru<sub>4</sub>W<sub>2</sub>: C 31.55, H 4.07, Ru 26.55, W 24.14; found: C 31.59, H 4.19, Ru 25.13, W 23.79.

**Preparation of  $[\{\text{Ru}(\eta^6\text{-}C_6\text{Me}_6)\}_4\text{W}_4\text{O}_{16}]$  (**1b**):** (*n*Bu<sub>4</sub>N)<sub>4</sub>[WO<sub>4</sub>] (0.733 g, 1 mmol) and  $[\{\eta^6\text{-}C_6\text{Me}_6\}\text{RuCl}_2]_2$  (0.334 g, 0.5 mmol) were dissolved in CH<sub>3</sub>CN (15 mL). The mixture was stirred for 5 h at room temperature. The yellow precipitate was washed with CH<sub>3</sub>CN (3 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub>. After concentration to about 5 mL, the extract was layered with toluene. A batch of crystals with composition **1b**·2C<sub>7</sub>H<sub>8</sub> was obtained after two days. However, the single crystal selected for the X-ray structure determination had the composition **1b**·C<sub>7</sub>H<sub>8</sub>·4H<sub>2</sub>O. **1b**·2C<sub>7</sub>H<sub>8</sub>: yield: 0.3 g (56%); IR (KBr):  $\tilde{\nu}$  = 931 (m), 818 (s), 757 (s), 591 (m), 497 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>, 22 °C, TMS):  $\delta$  = 2.20 (s, C<sub>6</sub>(CH<sub>3</sub>)<sub>6</sub>), 2.37 (s, toluene), 7.14–7.29 (m, toluene); <sup>17</sup>O NMR (40.7 MHz, CDCl<sub>3</sub>, 25 °C, bulk water):  $\delta$  = 651 (s, 4 O, O<sub>i</sub>), 409 (s, 4 O,  $\mu\text{-O}$ ), 338 (s, 4 O,  $\mu\text{-O}$ ), 33 (s, 4 O,  $\mu_4\text{-O}$ ); UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 404 (3300), 330 (sh, 9200), 285 nm (sh, 13000 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); elemental analysis (%) calcd for C<sub>62</sub>H<sub>88</sub>O<sub>16</sub>Ru<sub>4</sub>W<sub>4</sub>: C 33.41, H 3.98, Ru 18.14, W 32.99; found: C 33.75, H 3.93, Ru 17.58, W 31.01.

**Preparation of  $[\{\text{Ru}(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})_2(\mu\text{-OH})_2\}[\{\text{Ru}(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})_2\text{W}_8\text{O}_{28}(\text{OH})_2\}\{\text{Ru}(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})_2(\text{H}_2\text{O})_2\}]]$  (**3a**):** A mixture of Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (0.656 g, 2 mmol) and  $[\{\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr}\}\text{RuCl}_2]_2$  (0.612 g, 1 mmol) in distilled water (30 mL) was refluxed overnight. The resulting yellow precipitate was washed with water until the filtrate was colourless, leaving analytically pure **3a**·6H<sub>2</sub>O. Crystals of **3a**·14H<sub>2</sub>O were grown from a solution of **3a**·6H<sub>2</sub>O in MeOH/H<sub>2</sub>O (1/1). **3a**·6H<sub>2</sub>O: yield: 0.82 g (83%); IR (KBr):  $\tilde{\nu}$  = 926 (m), 875 (s), 817 (s), 736 (s; M–O) cm<sup>-1</sup>; <sup>1</sup>H NMR (300.13 MHz, CD<sub>3</sub>OD, 22 °C, TMS):  $\delta$  = 1.28 (d, <sup>3</sup>J(H,H) = 6.9 Hz, 6H; ArCH(CH<sub>3</sub>)<sub>2</sub>), 1.31 (d, <sup>3</sup>J(H,H) = 6.9 Hz, 12H; ArCH(CH<sub>3</sub>)<sub>2</sub>), 1.43 (d, <sup>3</sup>J(H,H) = 6.9 Hz, 6H; ArCH(CH<sub>3</sub>)<sub>2</sub>), 2.20 (s, 6H; ArCH<sub>3</sub>), 2.23 (s, 3H; ArCH<sub>3</sub>), 2.24 (s, 3H; ArCH<sub>3</sub>), 2.80 (h, 2H; <sup>3</sup>J(H,H) = 6.9 Hz, ArCH(CH<sub>3</sub>)<sub>2</sub>), 2.9–3.0 (m, 2H), 5.2–6.1 (m, 16H; ArH); UV/Vis (MeOH):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 400 (sh, 2700), 310 (sh, 9900), 260 nm (sh, 59000 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); elemental analysis (%) calcd for C<sub>80</sub>H<sub>136</sub>O<sub>44</sub>Ru<sub>8</sub>W<sub>8</sub>: C 23.54, H 3.36, Ru 19.81, W 36.04; found: C 23.37, H 3.37, Ru 19.17, W 35.48.

**Preparation of  $[(\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)_2\text{W}_5\text{O}_{18}[\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\text{H}_2\text{O})])]$  (**4**):** A mixture of  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (0.820 g, 2.5 mmol) and  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]$  (0.167 g, 0.25 mmol) in distilled water (10 mL) was refluxed overnight. The yellow precipitate was filtered and washed first with water and then with MeOH until the filtrates were colorless. The solid was then extracted with  $\text{CH}_2\text{Cl}_2$ . Removal of the solvent from the extract afforded pure  $4 \cdot 3\text{H}_2\text{O}$ . Crystals of composition  $4 \cdot 7\text{H}_2\text{O}$  were obtained after two days from a concentrated solution of  $4 \cdot 3\text{H}_2\text{O}$  in  $\text{CH}_2\text{Cl}_2$  layered with toluene. **4**· $3\text{H}_2\text{O}$ : yield: 0.12 g (71 %); IR (KBr):  $\tilde{\nu} = 944$  (s), 907 (s), 886 (s), 803 (w, br), 727 (s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300.13 MHz,  $\text{CDCl}_3$ , 22 °C, TMS):  $\delta = 2.20$  (s, 18H), 2.27 (s, 18H), 2.34 (s, 18H); UV/Vis ( $\text{CHCl}_3$ )  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 390 (sh, 5400), 339 nm ( $8200 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ); elemental analysis (%) calcd for  $\text{C}_{36}\text{H}_{62}\text{O}_{22}\text{Ru}_3\text{W}_5$ : C 20.90, H 3.02, Ru 14.65, W 44.42; found: C 20.84, H 3.01, Ru 14.62, W 41.69.

**Preparation of  $[(\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)_2\text{Mo}_5\text{O}_{18}[\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\text{H}_2\text{O})])]$  (**5**) and  $[(\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)_4\text{Mo}_4\text{O}_{16})]$  (**6b**):** A mixture of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  (0.605 g, 2.5 mmol) and  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]$  (0.167 g, 0.25 mmol) in distilled water (10 mL) was stirred at room temperature for two days. The red precipitate was collected by filtration and washed with water until the filtrate was colorless. The solid was first extracted with MeOH and then with  $\text{CH}_2\text{Cl}_2$ . Evaporation of the  $\text{CH}_2\text{Cl}_2$  extract afforded pure  $5 \cdot 2\text{H}_2\text{O}$ . Slow evaporation of the MeOH extract afforded a yellow crystals of **6**, which could alternatively be obtained by evaporation to dryness followed by extraction with  $\text{CH}_2\text{Cl}_2$ . Crystals of composition  $5 \cdot \text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$  suitable for X-ray analysis were obtained from a solution of  $5 \cdot 2\text{H}_2\text{O}$  in acetonitrile. **5**· $2\text{H}_2\text{O}$ : yield: 0.063 g (24 %); IR (KBr):  $\tilde{\nu} = 923$  (s), 895 (m), 853 (s), 706 (m)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300.13 MHz,  $\text{CDCl}_3$ , 22 °C, TMS):  $\delta = 2.22$  (s, 18H), 2.23 (s, 18H), 2.30 (s, 18H);  $^{95}\text{Mo}$  NMR (500 MHz,  $\text{CDCl}_3$ , 22 °C, external aqueous alkaline  $\text{Na}_2\text{MoO}_4$ ):  $\delta = 150$  (s, 2Mo), 95 (s, 2Mo), 55 (s, 1Mo); UV/Vis ( $\text{CHCl}_3$ )  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 470 (sh, 5200), 340 nm (sh,  $8900 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ); elemental analysis (%) calcd for  $\text{C}_{36}\text{H}_{60}\text{Mo}_5\text{O}_{21}\text{Ru}_3$ : C 26.83, H 3.75, Mo 29.76, Ru 18.81; found: C 27.85, H 3.50, Mo 28.60, Ru 18.25. **6b**: yield: 0.066 g (33 %); IR (KBr):  $\tilde{\nu} = 917$  (s), 792 (s), 744 (s), 584 (m), 496 (m)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300.13 MHz,  $\text{CDCl}_3$ , 22 °C, TMS):  $\delta = 2.20$  (s,  $\text{C}_6(\text{CH}_3)_6$ );  $^{17}\text{O}$  NMR (40.7 MHz,  $\text{CDCl}_3$ , 22 °C, bulk water):  $\delta = 800$  (s,

4O; O<sub>1</sub>), 542 (s, 4O;  $\mu$ -O), 452 (s, 4O;  $\mu$ -O), 69 (s, 4O;  $\mu_4$ -O); UV/Vis ( $\text{CHCl}_3$ )  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 410 (sh, 7200), 330 nm ( $13400 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ); elemental analysis (%) calcd for  $\text{C}_{49}\text{H}_{72}\text{O}_{16}\text{Mo}_4\text{Ru}_4$ : C 34.05, H 4.29, Mo 22.67, Ru 23.88; found: C 34.12, H 4.35, Mo 21.66, Ru 23.29.

**Alternative preparation of **5**:** A solution of  $(n\text{-Bu}_4\text{N})[\text{Mo}_2\text{O}_7]$  (0.394 g, 0.5 mmol) and  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]$  (0.167 g, 0.25 mmol) in MeOH (10 mL) was refluxed for 4 h. The red precipitate was filtered off and washed with MeOH until the filtrates were colorless. The solid was then extracted with  $\text{CH}_2\text{Cl}_2$ , and evaporation of the solvent afforded  $5 \cdot 2\text{H}_2\text{O}$ , which was identified spectroscopically; yield: 0.24 g (91 %).

**Crystal structure analyses:** Crystal structure data are summarized in Table 1. Data were recorded at room temperature on an Enraf-Nonius CAD4 diffractometer or an Enraf-Nonius MACH3 with graphite-monochromated  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). Crystals were put in glass capillaries filled with the mother liquor. Lattice parameters and the orientation matrix were obtained from a least-squares fit of 25 automatically centered reflections in the range  $14\text{--}14.2^\circ$  for **1b**, **3a** and **5**, and  $10\text{--}10.2^\circ$  for **4**. References were periodically monitored for intensity and orientation control. Intensities were corrected for Lorentzian and polarization effects and for absorption (empirical). Only those with  $I > 3\sigma(I)$  were retained for calculations. Data processing was performed with the program CRYSTALS.<sup>[43]</sup> The structures were solved by direct methods<sup>[44]</sup> and subsequent electron density maps. Clusters **1b** and **3** were refined anisotropically except for carbon atoms, while **4** and **5** were refined isotropically except for metal atoms. In all cases solvent molecules were refined isotropically. Hydrogen atoms were not included in the refinements, except for **5**, for which they were introduced in calculated positions and refined with a unique isotropic thermal parameter. Neutral-atom scattering factors were used, and anomalous dispersion correction was applied.<sup>[45]</sup> Final residuals are listed in Table 2. Molecular structures were drawn with the program CAMERON.<sup>[46]</sup> The crystal structure of  $2 \cdot 3\text{H}_2\text{O}$  was previously reported.<sup>[21]</sup> The anions in **3a**· $14\text{H}_2\text{O}$  are located at crystallographic inversion centers, and the asymmetric unit contains one “[ $\text{Ru}(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})\text{W}_4\text{O}_{14}(\text{OH})[\text{Ru}(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})]$ ” half-anion in addition to

Table 1. Crystal structure data for **1b**, **3a**, **4**, and **5**.

	<b>3a</b> · $14\text{H}_2\text{O}$	<b>1b</b> · $4\text{H}_2\text{O} \cdot \text{C}_7\text{H}_8$	<b>4</b> · $7\text{H}_2\text{O}$	<b>5</b> · $\text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$
formula	$\text{C}_{80}\text{H}_{152}\text{O}_{52}\text{Ru}_8\text{W}_8$	$\text{C}_{55}\text{H}_{88}\text{O}_{20}\text{Ru}_4\text{W}_4$	$\text{C}_{36}\text{H}_{70}\text{O}_{26}\text{Ru}_3\text{W}_5$	$\text{C}_{38}\text{H}_{63}\text{Mo}_5\text{NO}_{21}\text{Ru}_3$
$M_r$ [ $\text{g mol}^{-1}$ ]	4225.43	2208.97	2141.39	1652.82
color	dark yellow	orange	yellow	red
crystal system	monoclinic	monoclinic	orthorhombic	triclinic
space group	$P2_1/n$	$C2/c$	$Pm\bar{c}n$	$P\bar{1}$
$T$	ambient	ambient	ambient	ambient
$a$ [ $\text{\AA}$ ]	14.125(3)	19.651(4)	14.791(2)	11.488(4)
$b$ [ $\text{\AA}$ ]	28.027(4)	15.844(4)	21.796(7)	14.236(2)
$c$ [ $\text{\AA}$ ]	17.062(9)	24.076(1)	37.913(7)	17.546(5)
$\alpha$ [ $^\circ$ ]	90	90	90	78.96(2)
$\beta$ [ $^\circ$ ]	99.33(3)	106.92(3)	90	82.96(3)
$\gamma$ [ $^\circ$ ]	90	90(1)	90	73.97(2)
$V$ [ $\text{\AA}^3$ ]	6665(4)	7171(4)	12222(5)	2700(2)
$Z$	2	4	8	2
$\rho_{\text{calcd}}$ [ $\text{g cm}^{-3}$ ]	2.10	2.05	2.33	2.03
$\mu$ [ $\text{cm}^{-1}$ ]	79.5	73.92	103.53	19.66
$2\theta_{\text{max}}$ [ $^\circ$ ]	50	56	50	50
decay of standard reflections [%]	55.7	4.22	5.87	18.7
reflections measured	12490	9201	11693	10018
unique reflections ( $R_{\text{int}}$ )	11709 (0.053)	8636 (0.027)	11184	9451 (0.053)
observed reflections [ $I > 3\sigma(I)$ ]	4711	6042	2910	2719
absorption correction	$\psi$ scan [min = 1.78, max = 1.80]	$\psi$ scan [min = 1.00, max = 1.97]	$\psi$ scan [min = 0.70, max = 1.00]	$\psi$ scan [min = 1.00, max = 1.27]
refined parameters	432	397	343	322
$R^{\text{[a]}}$	0.058	0.048	0.056	0.067
$R_w^{\text{[b]}}$	0.070	0.053	0.065	0.075
weighting coefficients	9.61, −1.99, 7.60	11.3, −4.52, 8.24	4.71, −0.97, 3.74	3.80, −0.675, 2.86
goodness of fit $S$	1.17	0.99	1.10	1.15
$\Delta\rho$ (max/min) [ $\text{e \AA}^{-3}$ ]	−1.11/1.35	−2.21/1.77	−1.41/1.83	−1.58/1.46

[a]  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ , [b]  $R_w = [\sum w|F_o| - |F_c|]^2 / \sum wF_o^2$  ( $w = w'[1 - \{(|F_o| - |F_c|) / (6\sigma(F_o))\}^2]$ , where  $w' = 1/\sum_i A_i T_i(X)$  and  $X$  is  $F_o/F_c$  (max) with three coefficients for a Chebyshev Series).



Table 2. Selected bond lengths [Å] in **1b**, **3a**, **4**, and **5**.

<b>1b</b>							
W1–O1	1.711(6)	W1–O13	1.825(6)	W1–O14	1.780(6)	W1–O113	2.054(5)
W1–O24	2.465(5)	W1–O113'	2.059(5)	W2–O2	1.705(7)	W2–O23	1.795(6)
W2–O24	2.077(5)	W2–O24'	2.056(5)	W2–O42	1.819(6)	W2–O113	2.495(6)
Ru3–O13	2.075(6)	Ru3–O23	2.071(6)	Ru3–O113'	2.161(5)	Ru4–O14	2.085(6)
Ru4–O24	2.155(5)	Ru4–O42'	2.081(6)				
<b>3a</b>							
W1–O12	2.02(2)	W1–O14	2.04(2)	W1–O101	1.73(2)	W1–O102	1.89(2)
W1–O103	1.77(2)	W1–O124	2.22(1)	W2–O12	2.06(2)	W2–O23	1.86(2)
W2–O24	2.02(2)	W2–O124	2.24(1)	W2–O201	1.72(1)	W2–O202	1.78(1)
W3–O23'	1.96(2)	W3–O43'	2.07(2)	W3–O102	1.95(2)	W3–O301	2.16(2)
W3–O302	1.74(2)	W3–O303	1.71(2)	W4–O14	2.04(1)	W4–O24	2.05(1)
W4–O43	1.86(2)	W4–O124	2.24(1)	W4–O301	1.81(2)	W4–O401	1.77(1)
Ru5–O12	2.08(2)	Ru5–O14	2.08(2)	Ru5–O24	2.09(1)	Ru6–O103	2.06(2)
Ru6–O202	2.05(2)	Ru6–O600	2.15(2)	Ru7–O1	2.08(2)	Ru7–O2	2.07(2)
Ru7–O3	2.14(2)	Ru8–O1	2.08(2)	Ru8–O2	2.08(2)	Ru8–O3	2.09(2)
<b>4</b>							
W1–O12	1.92(3)	W1–O13	1.93(3)	W1–O101	1.74(4)	W1–O123	2.38(4)
W2–O12	2.10(2)	W2–O22	2.02(2)	W2–O23	1.89(3)	W2–O123	2.35(3)
W2–O201	1.72(3)	W2–O202	1.76(2)	W3–O13	2.20(2)	W3–O23	1.91(3)
W3–O33	1.99(2)	W3–O123	2.31(3)	W3–O301	1.71(3)	W3–O302	1.74(3)
Ru6–O600	2.16(4)	Ru6–O202	2.06(2)	Ru7–O13	2.16(3)	Ru7–O33	2.14(4)
Ru8–O12	2.11(3)	Ru8–O22	2.08(4)				
<b>5</b>							
Mo1–O12	1.96(2)	Mo1–O13	1.97(2)	Mo1–O14	1.91(2)	Mo1–O15	1.87(2)
Mo1–O101	1.69(2)	Mo1–O1111	2.33(2)	Mo2–O12	2.08(2)	Mo2–O23	2.00(2)
Mo2–O24	1.90(2)	Mo2–O201	1.71(2)	Mo2–O202	1.77(2)	Mo2–O1111	2.35(2)
Mo3–O13	2.05(2)	Mo3–O23	1.98(2)	Mo3–O35	1.90(2)	Mo3–O301	1.69(2)
Mo3–O302	1.77(2)	Mo3–O1111	2.39(2)	Mo4–O14	2.25(2)	Mo4–O24	1.91(2)
Mo4–O45	1.98(2)	Mo4–O401	1.68(2)	Mo4–O402	1.70(2)	Mo4–O1111	2.24(2)
Mo5–O15	2.25(2)	Mo5–O35	1.92(2)	Mo5–O45	1.97(2)	Mo5–O501	1.66(2)
Mo5–O502	1.68(2)	Mo5–O1111	2.30(2)	Ru6–O202	2.04(2)	Ru6–O302	2.02(2)
Ru6–O600	2.17(2)	Ru7–O14	2.11(2)	Ru7–O15	2.12(2)	Ru7–O45	2.13(2)
Ru8–O12	2.10(2)	Ru8–O13	2.10(2)	Ru8–O23	2.09(2)		

a  $[\{\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)_2(\mu\text{-OH})_3\}]^+$  cation and seven molecules of water. The clusters and the molecules of toluene in **1b**  $\cdot$  C<sub>7</sub>H<sub>8</sub>  $\cdot$  4H<sub>2</sub>O possess crystallographic C<sub>2</sub> symmetry, and the asymmetric unit contains one “[Ru(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)<sub>2</sub>W<sub>2</sub>O<sub>8</sub>]” half-cluster, one half-molecule of toluene and two water molecules, each of which is disordered over two general positions with equal occupancies. One C<sub>6</sub>Me<sub>6</sub> ligand was also found to be disordered over two positions with equal occupancies and related through a 30° rotation around the ruthenium–arene bond axis. The clusters in **4**  $\cdot$  7H<sub>2</sub>O have crystallographic C<sub>s</sub>-m symmetry and the unit cell contains two clusters and water molecules. In **5**  $\cdot$  2H<sub>2</sub>O  $\cdot$  MeCN, the clusters and the solvent molecules occupy general positions. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-160122 (**1b**), CCDC-160123 (**3a**), CCDC-160124 (**4**), and CCDC-160125 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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