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Synthesis and Characterization of Two Novel, Mono-Lacunary Dawson Polyoxometalate-Based, Water-Soluble Organometallic Ruthenium(II) Complexes: Molecular Structure of $[\{(C_6H_6)Ru(H_2O)\}(\alpha_2\text{-}P_2W_{17}O_{61})]^{8-}$

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The synthesis and structural characterization of a novel class of mono-lacunary Dawson polyoxometalate-(POM-)based, water-soluble organometallic complexes, which are expected to be effective homogeneous oxidation catalyst precursors in water, is described. The organometallic complexes $K_8[\{(C_6H_6)Ru(H_2O)\}(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot12H_2O$ (**1**) and $K_8[\{(p\text{-cymene})Ru(H_2O)\}(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot16H_2O$ (**2**) were successfully prepared by direct reactions of the mono-lacunary Dawson POM $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot19H_2O$ with the organometallic precursors $[(C_6H_6)RuCl_2]_2$ and $[(p\text{-cymene})RuCl_2]_2$, respectively, in aqueous media and characterized by complete elemental analysis, thermogravimetric and differential thermal analyses (TG/DTA), and FT-IR and solution (^1H, ^{13}C, ^{31}P, and ^{183}W) NMR spectroscopy. The molecular structure of $[\{(C_6H_6)Ru(H_2O)\}(\alpha_2\text{-}P_2W_{17}O_{61})]^{8-}$ (**1a**), in which the binding of the cationic organometallic group $\{(C_6H_6)Ru(H_2O)\}^{2+}$ occurs through two oxygen atoms of the four available oxygen atoms in the mono-lacunary site of the POM, resulting in overall C_1 symmetry, was successfully determined by single-crystal X-ray analysis. Interestingly, the hydrophilicity of the organometallic precursors is greatly enhanced by binding to a mono-lacunary Dawson POM with higher hydrophilicity.

Introduction

Polyoxometalates (POMs) are molecular metal oxide clusters that are of current interest as soluble metal oxides and for their application in catalysis, medicine, and materials science.[1] It has been stressed that it is important to discover more reliable and efficient procedures of synthesis before exploration of any possible new reactivity patterns.[2] The incorporation of transition metal ions into mono-lacunary Keggin and Dawson POMs has been found to give inorganic analogs of metalloporphyrin complexes[1a] and, in fact, metalloporphyrin-like catalysts that promote olefin epoxidation and aliphatic and aromatic hydroxylations have been realized.[3] The 4d or 5d transition metal ion substituted Keggin and Dawson POMs have been pointed out from the viewpoints of anticipated catalysis, in which the lacunary POM species work as π-acceptor ligands.[2]

In a separate area, water-soluble organometallic complexes that work as oxidation catalysts in water at ambient temperature are interesting from the viewpoint of green chemistry based on homogeneous catalysis by organometallic complexes.[4]

Recently, we have prepared the mono-Ru^{III}-substituted Dawson POM $K_7[\alpha_2\text{-}P_2W_{17}O_{61}Ru^{III}(H_2O)]\cdot19H_2O$ as a black crystalline solid from the reaction of the mono-lacunary Dawson POM $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot19H_2O$ with *cis*-$[RuCl_2(DMSO)_4]$ as the ruthenium source.[5] The purity of the POM obtained here was less than 95%, which has been attributed to a serious issue involving the starting ruthenium source, i.e. some of the coordinating DMSO molecules are difficult to remove because of their strong bonding to the Ru^{II} atom. Ruthenium complexes without coordinated DMSO molecules are also desirable because these DMSO molecules act as a catalyst poison during the homogeneous catalysis by the ruthenium center. POM-supported ruthenium(II) complexes such as $[Ru(DMSO)_3(H_2O)XW_{11}O_{39}]^{6-}$ (X = Ge, Si)[6a] and $[HW_9O_{33}Ru_2(DMSO)_6]^{7-}$,[6b] prepared from *cis*-$[RuCl_2(DMSO)_4]$, have been reported and also contain some DMSO molecules coordinated to the Ru^{II} atoms. For preparation of POMs that do not contain any coordinated DMSO molecules, we therefore sought other ruthenium(II) precursors without DMSO molecules, and selected the organometallic ruthenium(II) complexes $[(C_6H_6)RuCl_2]_2$ and $[(p\text{-cymene})RuCl_2]_2$.

In this work, we have obtained the novel, POM-based, diamagnetic ruthenium(II) complexes $K_8[\{(C_6H_6)Ru(H_2O)\}(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot12H_2O$ (**1**) and $K_8[\{(p\text{-cymene})Ru(H_2O)\}(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot16H_2O$ (**2**) by the direct reaction of $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ with the organometallic ruthenium(II) complexes in aqueous media, and unexpectedly found that the products **1** and **2** are water-soluble. The molecular structure

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of the polyoxo anion $[\{(C_6H_6)Ru(H_2O)\}(\alpha_2\text{-}P_2W_{17}O_{61})]^{8-}$ (**1a**) was successfully determined by single-crystal X-ray analysis. The cationic organometallic group $\{(C_6H_6)\text{-}Ru(H_2O)\}^{2+}$ was found to be attached to two oxygen atoms of the four available oxygen atoms in the mono-lacunary site of the POM, resulting in overall C_1 symmetry.

Organometallic complexes supported on mono-lacunary Keggin and Dawson POMs have until now only been reported without X-ray structure analysis, such as $[(CpTi)\text{-}PW_{11}O_{39}]^{4-}$ ($Cp = C_5H_5$),[8a,8b] $[\{(C_6H_5)Sn\}PW_{11}O_{39}]^{4-}$,[8b] $[\{(RSi)_2O\}SiW_{11}O_{39}]^{4-}$ $\{R = C_2H_5, C_6H_5, NC(CH_2)_3, C_3H_5\}$,[8b] $[(C_6H_5Sn)P_2W_{17}O_{61}]^{7-}$,[8b] metal–metal bonded derivatives[8c] such as $[\{CpFe(CO)_2Sn\}SiMo_{11}O_{39}]^{5-}$, $[\{[(OC)_3CoGe]_2OSiW_{11}O_{39}\}^{5-}]_n$, and $[\{(C_7H_8)_2RhSn\}\text{-}PW_{11}O_{39}]^{4-}$, and water-soluble organometallic complexes supported on tri-lacunary Keggin POM $[(CpTi)_3\text{-}XW_9O_{37}]^{7-}$ (X = Si, Ge).[8e]

As for X-ray structure analysis, POM-supported (η^6-arene)Ru^{2+} complexes have been recently reported by Proust and co-workers,[7] including (η^6-arene)Ru^{2+} complexes (arene = benzene, toluene, *p*-cymene, hexamethylbenzene) supported on mono-lacunary Keggin POMs such as $[\{[Ru(\eta^6\text{-arene})]PW_{11}O_{39}\}_2(WO_2)]^{8-}$ and $[\{Ru(\eta^6\text{-arene})(H_2O)\}\text{-}PW_{11}O_{39}]^{5-}$.[7e]

On the other hand, several saturated POMs, for example the triniobium(v)- and trivanadium(v)-substituted Keggin and Dawson POMs $[XW_9M_3O_{40}]^{n-}$ (M = Nb, V; X = Si, P) and $[P_2W_{15}M_3O_{62}]^{9-}$, have been used as molecular oxide supports for various cationic organometallic groups such as $CpTi^{3+}$, Cp^*Rh^{2+}, $(C_6H_6)Ru^{2+}$, $(cod)Pt^{2+}$, $(cod)Ir^+$, $(cod)\text{-}Rh^+$, $Re(CO)_3^+$, $Ir(CO)_2^+$, $Rh(CO)_2^+$, etc.[9–12] However, only a few successful X-ray structure analyses have been reported, such as $(Bu_4N)_6Na[(Cp^*Rh)(\alpha\text{-}1,2,3\text{-}P_2W_{15}Nb_3O_{62})]\cdot 10CH_3CN\cdot 10Me_2CO$[9a] and $[\{[Ag(2,2'\text{-}bpy)]_2[Ag_2(2,2'\text{-}bpy)_3]_2\}\alpha\text{-}PW_9V_3O_{40}]$.[10e]

Herein we report full details of the synthesis and unequivocal characterization of **1** and **2**, with complete elemental analysis, thermogravimetric and differential thermal analyses (TG/DTA), and FT-IR and solution (^1H, ^{13}C, ^{31}P, and ^{183}W) NMR spectroscopy, and the molecular structure of **1a**.

Results and Discussion

Synthesis and Compositional Characterization

The two novel 1:1-type complexes of the cationic organometallic groups with the POM (**1** and **2**) were formed by direct reaction of the organometallic precursors $[(L)\text{-}RuCl_2]_2$ ($L = C_6H_6$, *p*-cymene) with the mono-lacunary POM $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$, in aqueous solution, at room temperature, under air. They were isolated as analytically pure, orange and yellow-brown powders in 24.5% (0.49 g scale) and 33.2% (0.67 g scale) yields, respectively.

The formation of **1** and **2** is represented in Equation (1).

$$1/2\ [(L)RuCl_2]_2 + K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}] + H_2O \rightarrow K_8[\{(L)Ru(H_2O)\}(\alpha_2\text{-}P_2W_{17}O_{61})] + 2\ KCl \qquad (1)$$

Although the organometallic precursors $[(L)RuCl_2]_2$ are insoluble in water, complexes **1** and **2** containing the organometallic fragments are water-soluble.

The molecular formulae and the 1:1-type compositions of **1** and **2** were established by complete elemental analyses (all elements, including oxygen, 100.06 and 99.7% total observed, respectively), which were carried out for the samples dried at room temperature at 10^{-3}–10^{-4} Torr overnight. The weight losses observed during drying before analysis were 3.79% for **1**, which corresponds to 10–11 adsorbed and/or hydrated water molecules, and 4.2% for **2**, which corresponds to 11–12 water molecules. In the TG/DTA measurements under atmospheric conditions, the weight loss of 3.90% observed below 124 °C in **1** corresponds to 12 water molecules and that of 6.24% observed below 189 °C in **2** corresponds to 17 water molecules, in accordance with the findings of elemental analyses plus the weight losses found before analysis (see Exp. Sect.). In these complexes, the Cl analysis (calcd. 0; found <0.1% for **1** and <0.05% for **2**) indicated no contamination by Cl atoms, thus suggesting that the reaction of Equation (1) progresses completely; complexes **1** and **2** were isolated with high purity. The diamagnetic nature of **1** and **2** was supported by solution (^1H, ^{13}C, ^{31}P, and ^{183}W) NMR spectra; all signals were found in the region usually observed in the diamagnetic POMs.

The solid-state FT-IR measurements of $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$, **1**, and **2** (Figures 1a, 1b, and 1c, respectively) show the spectral patterns characteristic of the Dawson POM framework.[13] The FT-IR spectra of **1** and **2** in the polyoxometalate region are very similar to that of $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$, especially with regards to the multiple P–O bands (1086, 1054, and 1017 cm^{-1} for **1**; 1086, 1055, and

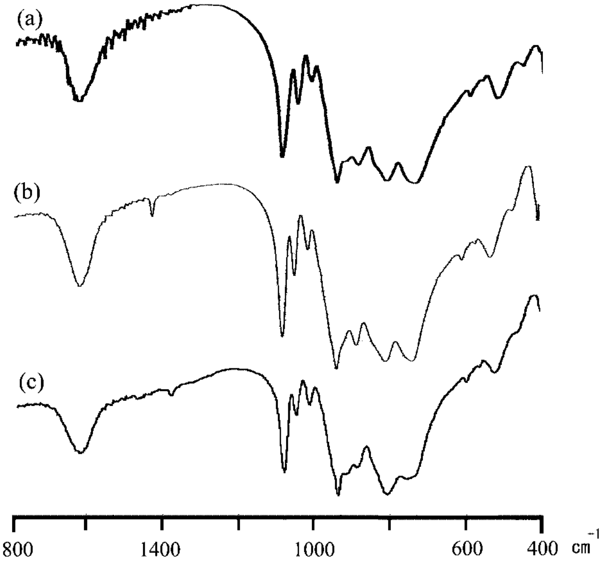


Figure 1. FT-IR spectra in the polyoxo anion regions, measured as KBr disks, of (a) $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 19H_2O$, (b) $K_8[\{(C_6H_6)\text{-}Ru(H_2O)\}(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot 12H_2O$ (**1**), and (c) $K_8[\{(p\text{-cymene})\text{-}Ru(H_2O)\}(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot 16H_2O$ (**2**).

1016 cm^{-1} for **2**; 1085, 1052, and 1016 cm^{-1} for $K_{10}[α_2\text{-}P_2W_{17}O_{61}]$), the bands assignable to M–O$_{terminal}$ oxygen atoms (940 cm^{-1} for **1**, 941 cm^{-1} for **2**, and 939 cm^{-1} for $K_{10}[α_2\text{-}P_2W_{17}O_{61}]$) and in the bands assignable to edge-sharing M–O–M oxygen atoms (810 and 741 cm^{-1} for **1**; 809 and 742 cm^{-1} for **2**; 810 and 737 cm^{-1} for $K_{10}[α_2\text{-}P_2W_{17}O_{61}]$). No change was seen in the bands assignable to corner-sharing M–O–M oxygen atoms (885 cm^{-1} for **1**, **2**, and $K_{10}[α_2\text{-}P_2W_{17}O_{61}]$). Compared with the spectrum of $K_{10}[α_2\text{-}P_2W_{17}O_{61}]$, the FT-IR spectra of **1** and **2** show weaker bands due to the presence of the coordinating aromatic rings at 1434 cm^{-1} for **1** and 1473 and 1389 cm^{-1} for **2**. The aromatic–Ru vibrational data of the precursors are observed at 1433 cm^{-1} for $[(C_6H_6)RuCl_2]_2$ and at 1496, 1471, 1458, 1448, 1408, 1389, and 1362 cm^{-1} for [(*p*-cymene)$RuCl_2]_2$.

Solution NMR Spectra

The ^{31}P NMR spectra in D_2O show clean, two-line spectra with resonances at $δ$ = –8.36 and –14.02 ppm for **1** (Figure 2b) and at $δ$ = –8.28 and –14.08 ppm for **2** (Figure 2c), which are different from those of $K_{10}[α_2\text{-}P_2W_{17}O_{61}]$ at $δ$ = –7.00 and –14.17 ppm (Figure 2a). The upfield resonance is known to be due to the phosphorus P(1) atom closer to the W_3O_6 cap (Figure 6b), whereas the downfield resonance is assigned to the phosphorus P(2) atom closest to the opposite site. The two-line, impressively clean ^{31}P NMR spectra strongly suggest the presence of a single species in solution, thereby precluding the presence of even minor, phosphorus-containing impurities in **1**, **2**, and $K_{10}[α_2\text{-}P_2W_{17}O_{61}]$. Further, the observed ^{31}P chemical shifts are in the usual region for diamagnetic species of various Dawson POMs,[5,9,12b,12c] supporting the suggestion that **1** and **2** are diamagnetic Ru^{II} complexes.

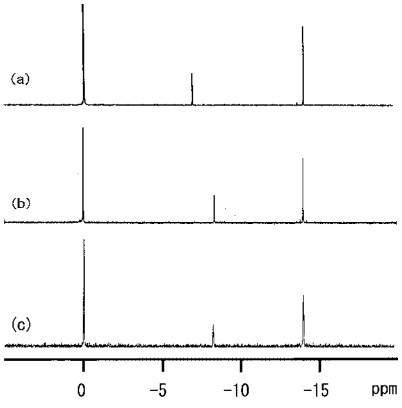


Figure 2. ^{31}P NMR spectra (in D_2O) of (a) $K_{10}[α_2\text{-}P_2W_{17}O_{61}]·19H_2O$, (b) $K_8[\{(C_6H_6)Ru(H_2O)\}(α_2\text{-}P_2W_{17}O_{61})]·12H_2O$ (**1**), and (c) $K_8[\{(p\text{-cymene})Ru(H_2O)\}(α_2\text{-}P_2W_{17}O_{61})]·16H_2O$ (**2**). In each case a very high level of purity is indicated (i.e., with respect to any other P-containing polyoxo anions or other materials).

The ^{183}W NMR spectrum of $K_{10}[α_2\text{-}P_2W_{17}O_{61}]$ in D_2O (Figure 3a) shows nine primary resonances at $δ$ = –117.1, –140.4, –151.7, –181.0, –183.1, –218.1, –220.5, –224.0, and –242.6 with integration intensities of 2:2:2:2:1:2:2:2:2, consistent with the overall C_s symmetry of the mono-lacunary Dawson structure. The ^{183}W NMR measurements of **1** in D_2O were unsuccessful because of an insufficient concentration of the aqueous solution (see Exp. Sect.). On the other hand, the ^{183}W NMR spectrum of **2a**, which was derived by cation exchange of the potassium salt **2** with an excess of $NaClO_4$ (see Exp. Sect.), in D_2O consists of virtually 17 lines at $δ$ = –117.6, –125.1, –138.6, –139.0, –163.8, –177.1, –177.3, –186.5, –207.6, –217.3 (1 + 1), –218.2, –219.5, –220.6, –221.9, –239.6, and –241.6. The relative intensity of all signals, except the signals at $δ$ = –217.3 ppm, is one (Figure 3b), thus suggesting its overall C_1 symmetry. These resonances are substantially different from those of $[α_2\text{-}P_2W_{17}O_{61}]^{10–}$.

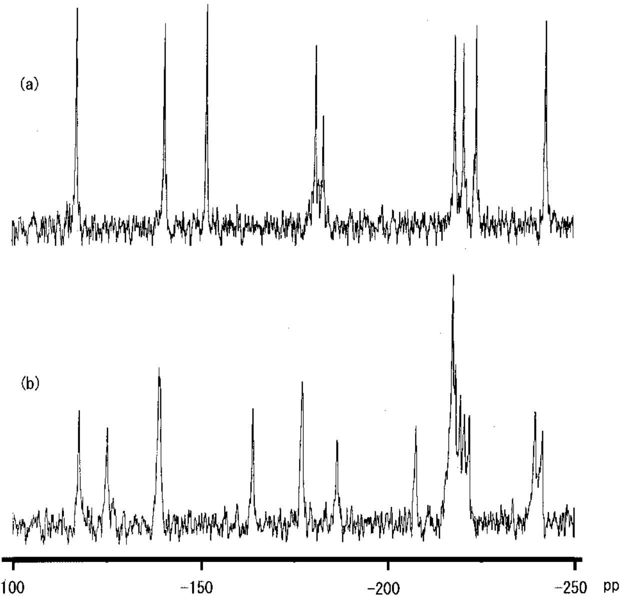


Figure 3. ^{183}W NMR spectra (in D_2O) of (a) $K_{10}[α_2\text{-}P_2W_{17}O_{61}]·19H_2O$ and (b) $[\{(p\text{-cymene})Ru(H_2O)\}(α_2\text{-}P_2W_{17}O_{61})]^{8–}$ (**2a**), which was prepared by cation exchange of **2** using an excess amount of $NaClO_4$.

The ^{1}H (Figure 4a) and ^{13}C NMR (Figure 5a) spectra of **1** in D_2O show single peaks at $δ$ = 6.18 and 82.98 ppm, respectively, due to the benzene ring coordinated to the Ru atom. On the other hand, the ^{13}C NMR spectrum of **2** in D_2O (Figure 5b) shows 10 lines due to the *p*-cymene ring coordinated to the Ru atom, thus suggesting that all carbon atoms of the coordinated *p*-cymene are inequivalent, i.e. C_1 symmetry. Correspondingly, the ^{1}H NMR spectrum of **2** in D_2O (Figure 4b) shows that the ring protons (H2, H3, H5, H6) are inequivalent; they were actually observed as apparent three-line signals with a 1:2:1 intensity ratio. The ^{1}H and ^{13}C NMR spectra show the local symmetry around the coordinated benzene and the coordinated *p*-cymene, whereas the ^{31}P and ^{183}W NMR spectra show the overall symmetry of **1a** and **2a**. In the coordinated *p*-cymene ligand, all the carbon atoms are inequivalent (local symmetry

C_1) as its rotational movement is probably restricted, whereas in the coordinated benzene all the carbon atoms seem equivalent because of its free rotation on the NMR timescale. Similar observations have recently been made by the Proust group.[7e] On the other hand, the overall symmetry of **1a** is C_1, as revealed by single-crystal X-ray structure analysis, and that of **2a** should also be C_1, as suggested by the 17-line ^{183}W NMR spectrum.

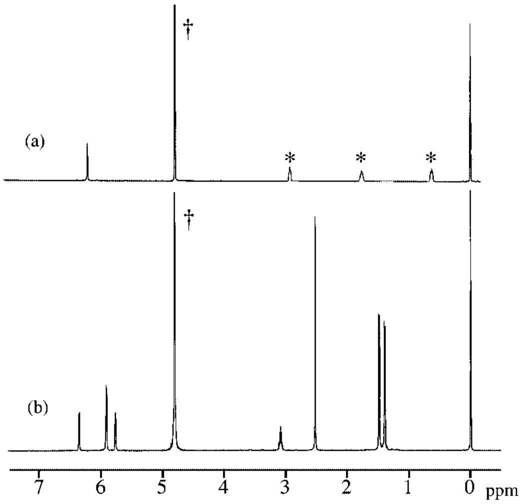


Figure 4. ^{1}H NMR spectra (in D_2O) of (a) $K_8[\{(C_6H_6)Ru(H_2O)\}(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot 12H_2O$ (**1**), with an internal reference of DSS, and (b) $K_8[\{(p\text{-cymene})Ru(H_2O)\}(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot 16H_2O$ (**2**) with an internal reference of TSP. The proton signals denoted by an asterisk in (a) are from the methylene groups of the DSS, and in both (a) and (b) the proton signals denoted by a dagger are from H_2O.

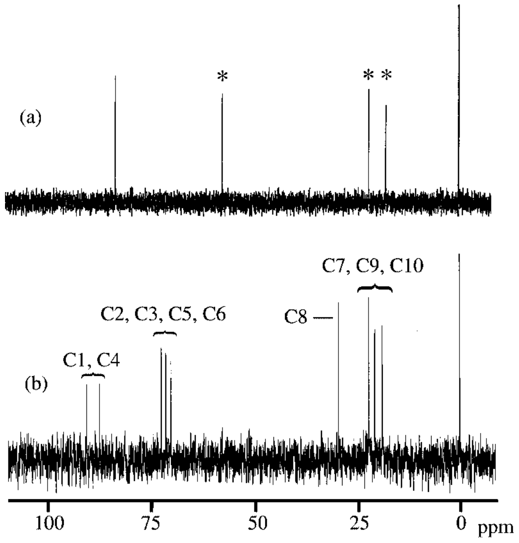
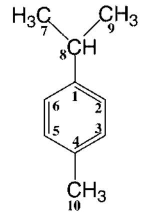


Figure 5. ^{13}C NMR spectra (in D_2O) of (a) $K_8[\{(C_6H_6)Ru(H_2O)\}(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot 12H_2O$ (**1**), with an internal reference of DSS, and (b) $K_8[\{(p\text{-cymene})Ru(H_2O)\}(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot 16H_2O$ (**2**), with an internal reference of TSP. The carbon signals denoted by an asterisk in (a) are from the methylene groups of the DSS.



p-cymene ligand and its numbering

Molecular Structure of 1a

The crystal of **1** contains discrete cluster anions, potassium cations, and lattice water molecules, all at general positions in the triclinic space group ($P\bar{1}$), except for three water oxygen atoms at special positions with a site occupancy factor fixed at 0.5. The solid-state packing of the polyoxo anion **1a** is shown in Figure 6a. The observed electron densities of the Ru and W atoms are quite different, and the data unequivocally distinguished and defined the Ru and W atoms. The 17 tungsten atoms, the one ruthenium atom, and the two P atoms were clearly identified. Thus, the main features of the molecular structure of the POM were clarified. However, the resolution obtained for the structure of the salt was limited by the poor quality of the available crystals and by the considerable disorder of the countercations and the solvent of crystallization. These features are all too common in POM crystallography.[14]

The molecular structure of **1a** is composed of the mono-lacunary Dawson POM unit $\alpha_2\text{-}P_2W_{17}O_{61}$ and the $\{(C_6H_6)Ru\}^{2+}$ unit, to which one oxygen atom is bonded in the form of a water molecule [Ru1A–O62A = 2.067(17) Å]. The benzene ring is disordered [C–C distances: 1.35(4)–1.47(4) Å; Ru–C distances: 2.12(3)–2.20(3) Å]. The $[(C_6H_6)Ru(H_2O)]^{2+}$ group is coordinated to only two [Ru1A–O56A (cap W) = 2.090(17) Å; Ru1A–O52A (belt W) = 2.056(18) Å] of the four available oxygen atoms (O47A, O52A, O55A, O56A) in the lacunary site of the POM support, resulting in the chiral configuration of **1a** based on C_1 symmetry. Thus, the polyoxo anion is found as a set of enantiomeric pairs in the unit cell (Figure 6a). As a matter of fact, there are four polyoxo anion units, denoted as units A, A′, B, and B′, in the unit cell ($Z = 4$). The relative configurations of the benzene ring and the water molecule coordinated to the ruthenium(II) center are somewhat different between units A and B, although their polyoxo anion moieties have the same structure. Thus, the units A/A′ and B/B′ are actually the different set of enantiomeric pairs, respectively, and therefore the unit cell contains two types of the racemic mixture.

The molecular structure of unit A is depicted in Figure 6b, and that of unit B is deposited in the Supporting Information as Figure S1. Figure 6c shows a polyhedral representation of the polyoxo anion **1a**.

A few examples where only two of the four available oxygen atoms in the mono-lacunary site in the Keggin POM are utilized for coordination to the organometallic center are known. These include $[\{C_6H_5P(O)\}_2PW_{11}O_{39}]^{3-}$,[15]

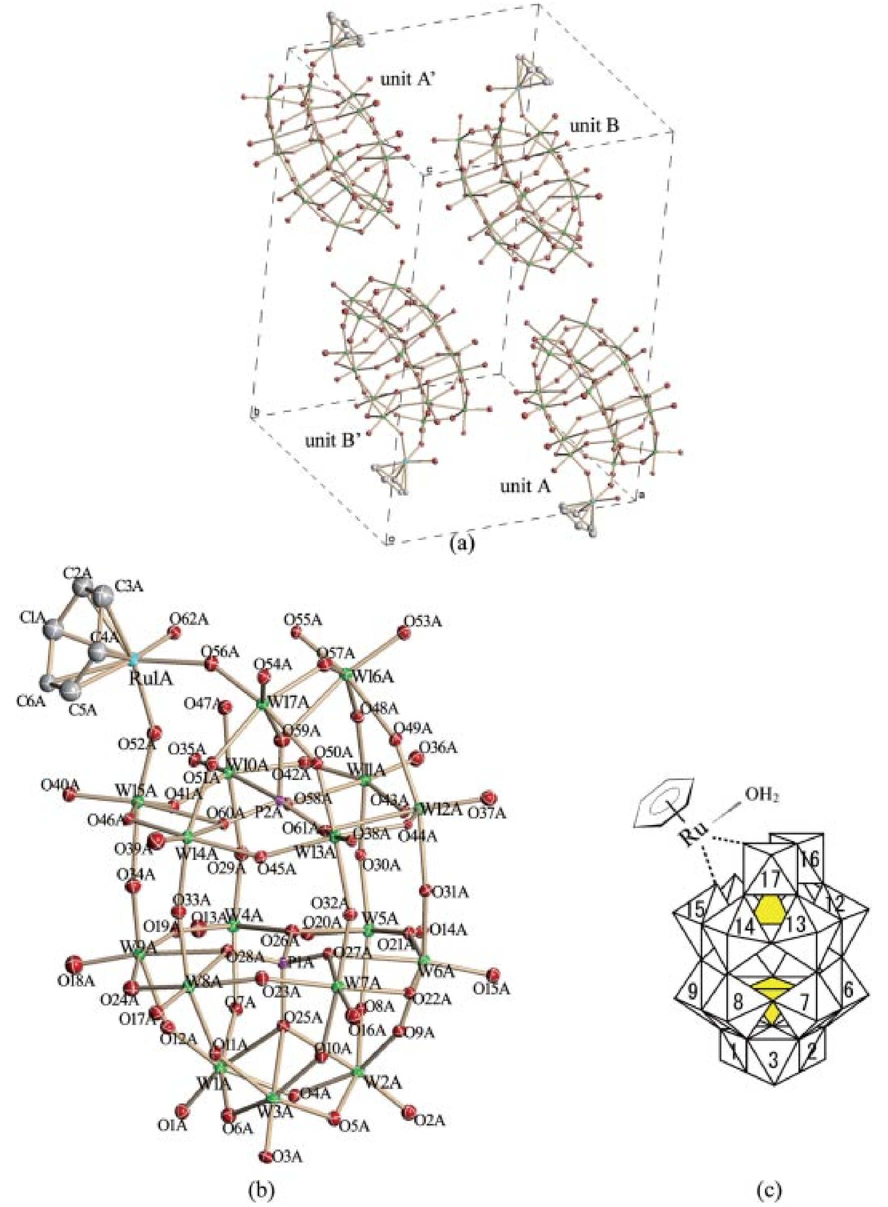


Figure 6. (a) Solid-state packing of the polyoxo anion $[\{(C_6H_6)Ru(H_2O)\}(\alpha_2\text{-}P_2W_{17}O_{61})]^{8-}$ (**1a**) (Z = 4). (b) Molecular structure of unit A in **1a** with 50% probability ellipsoids. (c) Polyhedral representation of the polyoxo anion **1a**. In (a), the units (A, A′) and (B, B′) are the different sets of enantiomeric pairs, and the relative configurations of the benzene ring and the water molecule coordinated to the ruthenium(II) center are somewhat different between the units (A and B), although their polyoxo anion moieties take the same structure. Thus, the unit cell contains two types of the racemic mixture. The molecular structure of unit A is depicted in (b); that of unit B is deposited in Supporting Information as Figure S1. In (c), the internal yellow tetrahedra represent the PO_4^{3-} core, while the white octahedra represent the WO_6 fragment with a tungsten atom in the center of the octahedra and oxygen atoms at each corner. The cationic $[(C_6H_6)Ru(H_2O)]^{2+}$ group binds to two terminal oxygen atoms in the lacunary site. The two phosphorus atoms, P(2) and P(1), are defined as "close to Ru (north)" and "far from Ru (south)", respectively.

$[Ru(DMSO)_3(H_2O)XW_{11}O_{39}]^{6-}$ (X = Ge, Si),[6a] and $[\{Ru(\eta^6\text{-arene})(H_2O)\}PW_{11}O_{39}]^{5-}$.[7e]

Selected bond lengths and angles around the ruthenium(II) atom in **1a** are given in Table 1 and Table S1, with average bond lengths and angles for the Dawson POM unit in Table S2.

In the lacunary site, the W–O distances should be noted: W15A–O52A (bonding to Ru atom) = 1.775(18) Å; W15A–O40A (terminal) = 1.739(17) Å; W17A–O56A (bonding to Ru atom) = 1.772(17) Å; W17A–O54A (terminal) = 1.738(17) Å; W10A–O47A (terminal) = 1.767(17) Å; W10A–O35A (terminal) = 1.714(16) Å; W16A–O55A (terminal) = 1.728(16) Å; W16A–O53A (terminal) = 1.743(17) Å. These bond lengths indicate the double-bond character of the W–O (terminal) bonds. It is likely that the coordination of the Ru atom to the two oxygen atoms (O52A, O56A) in the lacunary site influences the W–O distances less than the distances W10A–O47A and W16A–O55A. On the other hand, the W–O distances in the W_3 cap and the two W_6 belts, i.e. the W–Ot (Ot: terminal oxy-

Table 1. Selected bond lengths [Å] and angles [°] around the ruthenium(II) atom in the unit A of **1a**.

Ru1A–O62A (H_2O)	2.067(17)	W15A–O52A (bonding Ru)	1.775(18)
Ru1A–O56A (bonding cap W)	2.090(17)	W10A–O47A (terminal)	1.767(17)
Ru1A–O52A (bonding belt W)	2.056(18)	W17A–O56A (bonding Ru)	1.772(17)
		W16A–O55A (terminal)	1.728(16)
Ru1A–C1A	2.15(3)	C1A–C2A	1.44(4)
Ru1A–C2A	2.16(3)	C2A–C3A	1.37(4)
Ru1A–C3A	2.20(3)	C3A–C4A	1.47(4)
Ru1A–C4A	2.15(3)	C4A–C5A	1.35(4)
Ru1A–C5A	2.12(3)	C5A–C6A	1.42(4)
Ru1A–C6A	2.15(3)	C6A–C1A	1.41(4)
O52A–Ru1A–O56A	83.4(7)	O47B–Ru1B–O57B	83.6(6)
O62A–Ru1A–O52A	79.7(7)	O62B–Ru1B–O47B	85.1(7)
O62A–Ru1A–O56A	84.0(7)	O62B–Ru1B–O57B	79.5(7)
W15A–O52A–Ru1A	149.7(10)	W10B–O47B–Ru1B	145.3(9)
W17A–O56A–Ru1A	148.3(10)	W16B–O57B–Ru1B	150.6(10)

gen atom), W–Oe (Oe: edge-sharing oxygen atom), W–Oc (W belt) (Oc: corner-sharing oxygen atom), and W–Oa (Oa: oxygen atom coordinated to P atom) distances, are in the normal range.[1b] The Dawson unit contains two central P atoms in an almost regular tetrahedral environment of PO_4: the PO_4 unit closest to the lacunary site [P–O distances: 1.534(19)–1.571(17) Å; O–P–O angles: 107.7(9)–111.3(9)°] and the PO_4 unit closest to the W_3 cap [P–O distances: 1.516(17)–1.568(17) Å; O–P–O angles: 106.3(9)–112.6(9) °].

The bond valence sums (BVS),[16] calculated using the observed bond lengths for **1a**, are in the range of 5.97–6.33 for the 17 W atoms and 4.84–5.00 for the two P atoms, which reasonably correspond to the formal valences of W^{6+} and P^{5+}. Furthermore, the BVS values (2.17–1.50) of all oxygen atoms, except the O(62A) atom (0.45), which is bonded to the Ru^{II} atom, show that they are not protonated. The BVS value of the O(62A) atom (0.45) suggests that this oxygen atom is part of a water molecule. These results are in good agreement with those of the related compounds, $[Ru(DMSO)_3(H_2O)XW_{11}O_{39}]^{6-}$ (X = Ge, Si)[6a] and $[\{Ru(p\text{-cymene})(H_2O)\}PW_{11}O_{39}]^{5-}$.[7e]

The molecular structure of **1a** is consistent with the results of the solution NMR spectra, and suggests that the solid-state structure of **1a** is maintained in aqueous solution.

Bonding of the Organometallic Groups to the Mono-Lacunary POM

The $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ POM support, the formula of which can also be rewritten as $[(PO_4{}^{3-})_2(W_{17}O_{53}{}^{4-})]$, suggests that it possesses enough basicity of the surface oxygen atoms, i.e. an extra four-minus negative charge in comparison with the saturated Dawson POM $[P_2W_{18}O_{62}]^{6-}$ $[(PO_4{}^{3-})_2(W_{18}O_{54}{}^{0})]$, and, therefore, the cationic organometallic groups can be covalently bonded to this POM. The present work shows that the higher hydrophilicity of the mono-lacunary POM is kept even after attachment of the cationic organometallic groups.

These features can be compared with the formation of the previously reported cationic organometallic complexes supported on the trivanadium(V)- and triniobium(V)-substituted Dawson POMs $[P_2W_{15}M_3O_{62}]^{9-}$ (M = V^V and Nb^V; $[P_2W_{15}M_3O_{62}]^{9-} = [(PO_4{}^{3-})_2(W_{15}M_3O_{54}{}^{3-})]$), which have an extra three-minus negative charge in comparison with the parent POM $[P_2W_{18}O_{62}]^{6-}$.[9,10] It should be noted that the all-sodium salts of organometallic complexes supported on Dawson and Keggin POMs, namely $Na_7[(Cp^*Rh)(\alpha\text{-}1,2,3\text{-}P_2W_{15}Nb_3O_{62})]\cdot7DMSO\cdot5H_2O$[9c] and $Na_5[(Cp^*Rh)(\beta\text{-}1,2,3\text{-}SiW_9Nb_3O_{40})]\cdot3DMSO\cdot2H_2O$,[11d] have been prepared by crystallization from aqueous media. However, these compounds are relatively unstable in water.

The present complexes **1** and **2** can also be compared with our previous $[\alpha_2\text{-}P_2W_{17}O_{61}]$-based 1:2-type Ru^{II} complex $K_{18}[Ru^{II}(DMSO)_2(\alpha_2\text{-}P_2W_{17}O_{61})_2]$, which was obtained from the reaction of *cis*-$[RuCl_2(DMSO)_4]$ with $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$ in ice-cooled, aqueous HCl solution.[5] Oxidation of the 1:2-type compound with Br_2 gave the 1:1-type Ru^{III} compound $K_7[P_2W_{17}Ru^{III}(H_2O)O_{61}]$, without DMSO molecules. There are several factors in the formation of the 1:2- and 1:1-type complexes: (1) the ionic radius of the Ru^{II} atom is much larger than that of the Ru^{III} atom (0.82 Å for the six-coordinate, low-spin geometry[17]), and (2) the binding of several DMSO molecules to the Ru^{II} atom is so strong that removal of all DMSO molecules is not easy.

Conclusions

The cationic organometallic groups $\{(C_6H_6)Ru(H_2O)\}^{2+}$ and $\{(p\text{-cymene})Ru(H_2O)\}^{2+}$ have been covalently bound to the lacunary site of the mono-lacunary Dawson POM $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$. These complexes are water-soluble and stable in water. The molecular structure of $[\{(C_6H_6)Ru(H_2O)\}(\alpha_2\text{-}P_2W_{17}O_{61})]^{8-}$ (**1a**) was successfully determined. These POM complexes can be compared with the previously reported organometallic complexes supported on the multicenter active sites in the triniobium(V)- and trivanadium(V)-substituted Dawson POMs $[\alpha\text{-}1,2,3\text{-}P_2W_{15}M_3O_{62}]^{9-}$ (M = Nb, V).[9–12] The formation of complexes $K_8[\{(C_6H_6)Ru(H_2O)\}(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot12H_2O$ (**1**) and $K_8[\{(p\text{-cymene})Ru(H_2O)\}(\alpha_2\text{-}P_2W_{17}O_{61})]\cdot16H_2O$ (**2**) brings up several interesting points: (1) the hydrophilicity of the organometallic precursors is greatly enhanced by binding to the mono-lacunary

Dawson POM with higher hydrophilicity, (2) the mono-lacunary POM has enough basicity of the surface oxygen atoms for the cationic species, suggesting the possible formation of other water-soluble organometallic complexes, (3) the mono-lacunary POM works as a bidentate O-donor ligand to the ruthenium centers, resulting in the formation of a chiral configuration (overall C_1 symmetry), and (4) the catalytic oxidation behaviors of the ruthenium(II) centers can be anticipated in water at ambient temperature. Thus, POMs **1** and **2** will be of interest as water-soluble, organometallic ruthenium(II) complexes, oxidation catalysis by which is anticipated in water.[3n] Studies in this direction are in progress and the data will be reported in due course.

Experimental Section

Materials: The following were obtained as reagent grade and used as received: KCl, 85% aq. H_3PO_4, $Na_2WO_4{\cdot}2H_2O$, $KHCO_3$, CH_3CN, MeOH, EtOH, Et_2O (all from Wako); D_2O (Isotec); $[(p\text{-cymene})Ru^{II}Cl_2]_2$ and $[(C_6H_6)RuCl_2]_2$ (both from Aldrich). The mono-lacunary POM $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]{\cdot}19H_2O$ was prepared according to the literature and characterized accordingly.[3b,18]

Instrumentation/Analytical Procedures: Complete elemental analyses were carried out by Mikroanalytisches Labor Pascher (Remagen, Germany). The samples were dried at room temperature at 10^{-3}–10^{-4} Torr overnight before analysis. The C,H,N analyses were performed with a Perkin–Elmer PE2400 series II CHNS/O Analyzer (Kanagawa University). Infrared spectra were recorded with a Jasco 300 FT-IR spectrometer in KBr disks at room temperature. TG/DTA data were acquired with a Rigaku TG8101D and TAS 300 data-processing system. TG/DTA measurements were run under air with a temperature ramp of 4 °C/min between 30 and 500 °C. ^{1}H (399.65 MHz), ^{13}C{^{1}H} (100.40 MHz), and ^{31}P{^{1}H} (161.70 MHz) NMR spectra in solution were recorded in 5-mm outer-diameter tubes with a Jeol JNM-EX 400 FT NMR spectrometer using a Jeol EX-400 NMR spectroscopic data processing system. ^{31}P{^{1}H} (202.47 MHz) NMR spectra in solution were also recorded in 5-mm outer-diameter tubes with a Jeol ECP 500 FT NMR spectrometer using a Jeol ECP-500 NMR spectroscopic data processing system. ^{1}H and ^{13}C{^{1}H} NMR spectra of the complexes were measured in D_2O solution with reference to internal DSS or TSP {sodium [2,2,3,3-D_4]-3-(trimethylsilyl)propionate}. Chemical shifts are reported as positive for resonances downfield of DSS or TSP (δ = 0 ppm). ^{31}P{^{1}H} NMR spectra were measured in D_2O solution with reference to an external standard of 25% H_3PO_4 in H_2O in a sealed capillary. Chemical shifts are reported as negative for resonances upfield of H_3PO_4 (δ = 0 ppm). ^{183}W NMR (16.50 MHz) spectra were recorded in 10-mm outer-diameter tubes with a Jeol JNM-EX 400 FT NMR spectrometer equipped with a Jeol NM-40T10L low-frequency tunable probe and a Jeol EX-400 NMR spectroscopic data-processing system. These spectra, measured in D_2O, were referenced to an external standard of a saturated Na_2WO_4/D_2O solution. Chemical shifts are reported as negative for resonances upfield of Na_2WO_4 (δ = 0 ppm).

Preparation of $K_8[\{(C_6H_6)Ru^{II}(H_2O)\}(\alpha_2\text{-}P_2W_{17}O_{61})]{\cdot}12H_2O$ (1): $[(C_6H_6)RuCl_2]_2$ (0.10 g, 0.20 mmol) was added to a stirred solution of $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]{\cdot}19H_2O$ (2.00 g, 0.41 mmol) in 50 mL of water. The brown suspension was stirred at room temperature for 1 h and then the brown powder was filtered off through a folded filter paper (Whatman No. 2). The clear brown filtrate was concentrated to a volume of about 15 mL in a rotary evaporator at 35 °C, and then placed in a refrigerator at 5 °C overnight. The brown powder formed was collected on a membrane filter (JG, 0.2 µm) and washed with CH_3CN (2 × 5 mL) and then Et_2O (3 × 50 mL). At this stage the yield was 1.0–1.5 g. All the brown powder was suspended in 15 mL of water at 60 °C. The suspension was cooled to room temperature and then placed in a refrigerator at 5 °C for 1 h. The yellow-brown powder that deposited was filtered off through a membrane filter (JG, 0.2 µm) and the clear brown filtrate was concentrated to about 7 mL in a rotary evaporator at 30 °C. After standing at room temperature for 30 min, the solution was passed through a folded filter paper (Whatman No. 2). The filtrate was slowly concentrated at room temperature in the dark. The orange plate-like crystals formed were collected on a membrane filter (JG, 0.2 µm), washed with CH_3CN (2 × 5 mL) and Et_2O (3 × 50 mL), and dried in vacuo for 2 h. The orange powder, obtained in 24.5% (0.49 g scale) yield, was soluble in water and DMSO, but insoluble in CH_3CN, MeOH, EtOH, and Et_2O. $K_8[\{(C_6H_6)Ru(H_2O)\}\text{-}P_2W_{17}O_{61}]{\cdot}2H_2O$ = $C_6H_{12}O_{64}K_8P_2W_{17}Ru$ (4709.4): calcd. C 1.53, H 0.26, Cl 0.00, K 6.64, O 21.74, P 1.32, Ru 2.15, W 66.37; found (repeat trials for C,H analysis) C 1.49 (1.47), H 0.33 (0.41), Cl < 0.1, K 6.26, O 22.1, P 1.25, Ru 2.23, W 66.4; total 100.06%. A weight loss of 3.79% was observed during the course of drying at room temperature at 10^{-3}–10^{-4} Torr overnight before analysis, suggesting the presence of 10–11 weakly solvated or adsorbed water molecules. TG/DTA data under atmospheric conditions: weight losses of 3.90% below 124 °C and 3.12% between 124 and 500 °C were observed with endothermic peaks at 30, 101, 147, and 185 °C and an exothermic peak at 481 °C; calcd. 3.71% for x = 12 in $K_8[\{(C_6H_6)Ru(H_2O)\}P_2W_{17}O_{61}]{\cdot}xH_2O$. FT-IR (KBr disk, polyoxometalate region): $\tilde{\nu}$ = 1434 w, 1086 s, 1054 m, 1017 m, 940 vs, 885 s, 810 s, 741 s, 601 w, 528 w cm^{-1}. ^{31}P NMR (D_2O, 22.9 °C): δ = –8.36 (1 P), –14.02 (1 P) ppm. ^{1}H NMR (D_2O, 23.7 °C): δ = 6.18 (s, 6 H, C_6H_6) ppm. ^{13}C NMR (D_2O, 24.5 °C): δ = 82.98 ppm. Preparation of an aqueous solution of **1a** for ^{183}W NMR measurements was attempted by methods (1)–(3) described below, but a sufficient concentration of the pure form of **1a** was not attained. (1) A saturated D_2O solution of **1** was prepared at 70 °C and the ^{183}W NMR spectrum was measured at this temperature over about 12 h. Clean signals of **1a** were not observed because of partial decomposition. Decomposition of **1** after 12 h at this temperature was also confirmed by a ^{31}P NMR measurement at room temperature. (2) The sodium salt of **1a** was generated in situ by reaction of the potassium salt of **1a** in aqueous solution with an excess amount of $NaClO_4$. After filtering the $KClO_4$ produced, the ^{31}P NMR spectrum of the filtrate was measured, which showed the two signals of **1a** as well as those due to the mono-lacunary POM $[P_2W_{17}O_{61}]^{10-}$. Partial dissociation of the supported organometallic group takes place during the metathesis reaction. On the other hand, complex **2a** was stable during the metathesis and a clean, two-line ^{31}P NMR spectrum of the in situ generated sodium salt of **2a** was observed. (3) The sodium salt of $[P_2W_{17}O_{61}]^{10-}$ was generated by a metathesis reaction of the potassium salt, $K_{10}[P_2W_{17}O_{61}]{\cdot}19H_2O$, with an excess amount of $NaClO_4$. Thus, an excess amount of $[(C_6H_6)\text{-}RuCl_2]_2$ was added to a stirred solution of the in situ generated sodium salt in water. The brown suspension was stirred at room temperature. for 1 h After filtration, the ^{31}P NMR spectrum of the filtrate was measured, which showed four signals due to **1a** and unreacted $[P_2W_{17}O_{61}]^{10-}$.

Preparation of $K_8[\{(p\text{-cymene})Ru^{II}(H_2O)\}(\alpha_2\text{-}P_2W_{17}O_{61})]{\cdot}16H_2O$ (2): $[(p\text{-cymene})RuCl_2]_2$ (0.125 g, 0.20 mmol) was added to a stirred solution of $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]{\cdot}19H_2O$ (2.00 g, 0.41 mmol) in 50 mL of water and the brown suspension was stirred at room temperature for 1 h. The greenish powder was then filtered off through a folded filter paper (Whatman No. 2). The clear brown filtrate was concentrated to a volume of about 10 mL in a rotary evaporator at 30 °C and then placed in a refrigerator at 5 °C overnight. The yellow-brown powder formed was collected on a membrane filter (JG, 0.2 µm) and washed with CH_3CN (3 × 30 mL) and then Et_2O (3 × 50 mL). All the yellow-brown powder was suspended in 10 mL of ice-cooled water. The suspension was stirred for 30 min and then placed in a refrigerator at 5 °C for 30 min. The gray powder that deposited was filtered off through a membrane filter (JG, 0.2 µm) and the clear brown filtrate was added dropwise to 500 mL of ice-cooled MeOH. After stirring for 30 min, the yellow-brown powder was collected on a membrane filter (JG, 0.2 µm), washed with MeOH (3 × 50 mL) and then Et_2O (3 × 50 mL), and dried in vacuo for 2 h. The yellow-brown powder, obtained in 32.7% (0.67 g scale) yield, was hygroscopic, soluble in water, but insoluble in MeOH, CH_3CN, and Et_2O. $K_8[\{(p\text{-cymene})Ru(H_2O)\}P_2W_{17}O_{61}]$ = $C_{10}H_{16}O_{62}K_8P_2W_{17}Ru$ (4729.5): calcd. C 2.54, H 0.34, Cl 0.00, K 6.61, O 21.0, P 1.31, Ru 2.14, W 66.1; found C 2.64, H 0.32, Cl < 0.05, K 6.49, O 20.6, P 1.29, Ru 2.07, W 66.3; total 99.7%. A weight loss of 4.2% was observed during the course of drying at room temperature at 10^{-3}–10^{-4} Torr overnight before analysis, suggesting the presence of 11–12 weakly solvated or adsorbed water molecules. TG/DTA data under atmospheric conditions: a weight loss of 6.24% below 189 °C with exothermic peaks at 206 and 265 °C; calcd. 6.11% for $x = 16$ in $K_8[\{(p\text{-cymene})Ru(H_2O)\}P_2W_{17}O_{61}]\cdot xH_2O$. FT-IR (KBr disk, polyoxometalate region): $\tilde{\nu}$ = 1086 s, 1055 m, 1016 m, 941 vs, 885 s, 809 vs, 742 s, 670 w, 661 w, 601 w, 527 m, 420 w cm^{-1}. ^{31}P NMR (D_2O, 21.9 °C): δ = –8.28 (1 P), –14.08 (1 P) ppm. ^1H NMR (D_2O, 23.3 °C): δ = 1.40 (d, J = 6.87 Hz, 3 H), 1.48 (d, J = 6.87 Hz, 3 H) (H7 and H9), 2.51 (H10), 3.07 [m (7), J = 6.87 Hz 3 H] (H8), 5.73 (d, J = 5.96 Hz, 1 H), 5.88 (d, J = 6.42 Hz, 2 H), 6.32 (d, J = 5.96, 1 H) (relative intensity ratio 1:2:1, H2, H3, H5 and H6) ppm. ^{13}C NMR (D_2O, 25.8 °C): δ = 21.5, 23.5, 25.2 (C7, C9, C10), 33.6 (C8), 80.2, 81.5, 81.6, 82.9 (C2, C3, C5, C6), 99.9, 103.5 (C1, C4) ppm. ^{183}W NMR of **2a** as the sodium salt (D_2O, 22.6 °C): δ = –117.6, –125.1, –138.6, –139.0, –163.8, –177.1, –177.3, –186.5, –207.6, –217.3 (1 + 1), –218.2, –219.5, –220.6, –221.9, –239.6, –241.6 ppm; the relative intensity of all signals, except the signals at δ = –217.3 ppm, is one. The sodium salt of **2a** was prepared in 70.6% yield (0.56 g scale) by a cation-exchange reaction of the potassium salt **2** in aqueous solution with an excess amount of $NaClO_4$, followed by concentration of the filtrate in a rotary evaporator after filtering off the produced $KClO_4$ and then re-precipitation with ice-cooled ethanol. The characterization data of the sodium salt (IR and ^1H and ^{31}P NMR spectra) are in good agreement with those of **2**. On the other hand, for ^{183}W NMR measurements, a cation-exchange reaction of **2** performed using an excess amount of $LiClO_4$ was unsuccessful because of partial dissociation of the supported organometallic group.

X-ray Crystallography of 1: An orange plate crystal (0.18 × 0.06 × 0.02 mm) was surrounded by liquid paraffin (Paratone-N) to prevent its degradation. Data collection was performed with a Bruker SMART APEX CCD diffractometer at 90 K in the range $1.86° < 2\theta < 56.42°$. The intensity data were automatically corrected for Lorentz and polarization effects during integration. The structure was solved by direct methods (SHELXS-97)[19a] followed by subsequent difference Fourier calculation and refined by a full-matrix, least-squares procedure (SHELXL-97).[19b] Absorption correction was performed with SADABS (empirical absorption correction).[19c] Crystal data for $C_6H_{30}K_8O_{74}P_2RuW_{17}$: M = 4887.56, triclinic, space group $P\bar{1}$, a = 18.972(3), b = 19.175(4), c = 24.569(6) Å, α = 67.522(3)°, β = 76.297(5)°, γ = 88.825(3)°, V = 7999(3) $Å^3$, Z = 4, D_c = 4.058 $g\,cm^{-3}$, $\mu(\text{Mo-}K_\alpha)$ = 25.080 mm^{-1}. $R1$ = 0.1093, $wR2$ = 0.1779 (for all data). R_{int} = 0.0595, $R1$ = 0.0773, $wR2$ = 0.1651, GOF = 1.160 [85964 total reflections, 39013 unique reflections where $I > 2\sigma(I)$]. The maximum and minimum residual densities (7.075 and –4.137 $e\,Å^{-3}$) were located at 0.61 Å from K8 and 0.61 Å from K10, respectively. Three water oxygen atoms (O1S, O2S and O3S) were in special position and their site occupancy factors were fixed at 0.5. The site occupancy factors of five water oxygen atoms (O24S, O25S, O26S, O27S, and O28S) and eight potassium atoms (K11, K12, K13, K14, K15, K16, K17, and K18) were also fixed at 0.5. CCDC-270035 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Molecular structure (Figure S1) of unit B of **1a** shown in Figure 6a in the text, and its bond lengths and angles around the ruthenium(II) atom (Table S1) and average bond lengths and angles for **1a** (Table S2).

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