

Organometallic Complexes Supported on a Metal-Oxide Cluster. pH-Dependent Interconversion between the Monomeric and Dimeric Species of the Polyoxoanion-Supported $[(arene)Ru]^{2+}$ Complex

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Keggin polyoxometalate (POM)-supported two (arene)Ru^{2+} complexes, i.e., the monomeric species (type-**m**) $[\{(arene)Ru(H_2O)\}PW_{11}O_{39}]^{5-}$ and the dimeric species (type-**d**) $[(\{(arene)Ru\}PW_{11}O_{39})_2(\mu\text{-}WO_2)]^{8-}$, were prepared as water-soluble $Et_2NH_2^+$ salts by pH-controlled reactions in aqueous solutions of the in situ-generated, mono-lacunary Keggin POM $[PW_{11}O_{39}]^{7-}$ with the organometallic precursor $[\{RuCl_2(arene)\}_2]$. The effects of the arene (benzene (**1**), toluene (**2**), *p*-cymene (**3**), and hexamethylbenzene (**4**)) on the proportion of the type-**m** to type-**d** complex produced were examined. pH-Varied ^{31}P NMR spectroscopy showed that there was a pH-dependent interconversion between type-**m** and type-**d** complexes, i.e., the ratio of the dimeric species increased as pH of the solution was lowered. Under the reaction conditions, the dimeric species **d1**, **d3**, and **d4** as water-soluble $Et_2NH_2^+$ salts were successfully isolated as the major products. It was concluded that (1) steric repulsion between the two (arene)Ru^{2+} fragments in the dimeric species was not significant, (2) the proportion was strongly dependent on the pH of the solution rather than the bulkiness of the arene, and (3) the use of the in situ-generated $[PW_{11}O_{39}]^{7-}$, but not the isolated lacunary species, such as $K_7[PW_{11}O_{39}]\cdot nH_2O$, had an effect on the reaction.

Polyoxometalates (POMs) are molecular metal-oxide clusters, which are of current interest as soluble metal oxides and for their application to catalysis, medicine, and material sciences.[1] The incorporation of transition-metal ions into the mono-lacunary Keggin and Dawson POMs is considered to be inorganic analogues of metalloporphyrin complexes,[1a] and in fact, similar catalytic reactions such as olefin epoxidation and aliphatic and aromatic hydroxylations have been realized with POMs.[2] In particular, water-soluble organometallic complexes which are oxidation catalysts in water at ambient temperature, are interesting from the viewpoint of green chemistry based on homogeneous catalysis by organometallic complexes.[3]

Recently, we have prepared two Dawson-type POM-based, water-soluble organometallic ruthenium(II) complexes, $K_8[\{(benzene)Ru(H_2O)\}\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 12H_2O$ and $K_8[\{(p\text{-}cymene)Ru(H_2O)\}\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 16H_2O$,[4a] and determined the molecular structure of one of the polyoxoanions, that is, $[\{(benzene)Ru(H_2O)\}\alpha_2\text{-}P_2W_{17}O_{61}]^{8-}$. We have also found that these two (arene)Ru^{2+} complexes supported on mono-lacunary Dawson POM catalyze the selective oxidation for several alcohols (benzyl alcohol, 1-octanol, 2-octanol, 4-octanol, *p*-methylbenzyl alcohol, cyclohexanol) with 1 atm molecular oxygen in aqueous–organic biphasic media without any additives.[4b] Several examples of the Ru(arene) complexes supported on the lacunary species of the POMs, such as $[\{Ru(dmso)_3(H_2O)\}(XW_{11}O_{39})]^{6-}$ (X = Ge and Si)[5a] and $[(HW_9O_{33})\{Ru_2(dmso)_6\}]^{7-}$,[5b] $[\{Ru(p\text{-}cymene)\}_2Sb_2W_{20}O_{70}]^{10-}$,[5c] $[\{Ru(benzene)\}_2(XW_9O_{34})]^{6-}$ (X = Si and Ge),[5d] $[(HXW_7O_{28})\{Ru(dmso)_3\}]^{6-}$ (X = P and As),[5e] and $[(PW_9O_{34})_2(cis\text{-}WO_2)(cis\text{-}RuLMe_2)]^{13-}$ (LMe = 1,3-dimethylimidazolidine-2-ylidene),[5f] have been reported recently.

As related compounds, the (η^6-arene)Ru^{2+} complexes (arene = benzene (**1**), toluene (**2**), *p*-cymene (**3**), and hexamethylbenzene (**4**)) supported on mono-lacunary Keggin POMs, i.e., the dimeric species (type-**d**) $[(\{(\eta^6\text{-arene})Ru\}PW_{11}O_{39})_2(\mu\text{-}WO_2)]^{8-}$ and the monomeric species (type-**m**) $[\{(\eta^6\text{-arene})Ru(H_2O)\}PW_{11}O_{39}]^{5-}$, have been reported by Proust and coworkers.[6] From the viewpoint of bimetallic active centers in a homogeneous catalyst, such a dimeric species of (arene)Ru^{2+} complexes is expected to be much more active catalysts for alcohol oxidation with molecular oxygen in aqueous media than the monomeric species.[4b] Proust et al. have mentioned that the proportion of the type-**m** complex to the type-**d** complex is strongly dependent on the bulkiness of the arene.[6] In this work, we examined the synthetic conditions in detail using pH-varied ^{31}P NMR spectroscopy and found that a formation of the dimers was not restricted to less-bulky arenes. Abbreviation of compounds is listed in Table 1.

Herein, we report full details of the improved synthesis of the dimeric complexes **Et_2NH_2-d1**, **Et_2NH_2-d3**, and **Et_2NH_2-d4**, and their characterization with elemental analysis, thermogravimetric and differential thermal analyses (TG/DTA), FTIR, solution (^{31}P and ^1H) NMR spectroscopy as well as solution (^{13}C and ^{183}W) NMR of **d3** and the molecular structure of **d1**.

Experimental

Instrumentation/Analytical Procedures. CHN analyses were performed using a Perkin-Elmer PE2400 series II CHNS/

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Table 1. Abbreviation of Compounds

$[\{(arene)Ru(H_2O)\}PW_{11}O_{39}]^{5-}$	(type-**m**)
$[(\{(arene)Ru\}PW_{11}O_{39})_2(\mu\text{-}WO_2)]^{8-}$	(type-**d**)
arene = benzene (**1**), toluene (**2**), *p*-cymene (**3**), hexamethylbenzene (**4**)	
$(Et_2NH_2)_5[\{(benzene)Ru\}PW_{11}O_{39}]\cdot 5H_2O$	**Et_2NH_2-m1**
$(Et_2NH_2)_8[(\{(benzene)Ru\}PW_{11}O_{39})_2(\mu\text{-}WO_2)]\cdot 9H_2O$	**Et_2NH_2-d1**
$(Et_2NH_2)_7H[(\{(p\text{-cymene})Ru\}PW_{11}O_{39})_2(\mu\text{-}WO_2)]\cdot 7H_2O$	**Et_2NH_2-d3**
$(Et_2NH_2)_6H_2[(\{(hexamethylbenzene)Ru\}PW_{11}O_{39})_2(\mu\text{-}WO_2)]\cdot 8H_2O$	**Et_2NH_2-d4**

O Analyzer (Kanagawa University). IR spectra were recorded on a Jasco 4100 FT-IR and/or 300 FT-IR spectrometers in KBr disks at room temperature. Thermogravimetric (TG) and differential thermal analyses (DTA) were acquired using a Rigaku TG8120 and Thermo Plus 2 system. TG/DTA measurements were run in air with a temperature ramp of 4 °C per min between 20 and 500 °C.

^{1}H (399.65 MHz), ^{13}C{^{1}H} (100.40 MHz), and ^{31}P{^{1}H} NMR (161.70 MHz) spectra in D_2O solution were recorded in 5 mm outer diameter tubes on a JEOL JNM-EX 400 FT-NMR spectrometer and a JEOL EX-400 NMR data-processing system. ^{1}H and ^{13}C{^{1}H} NMR spectra of the complexes measured in D_2O were referenced to TSP, and ^{31}P{^{1}H} NMR spectra in D_2O were referenced to an external standard of 25% H_3PO_4 in H_2O in a sealed capillary. ^{31}P NMR signals were shifted to −0.101 ppm by using 85% H_3PO_4 as a reference instead of 25% H_3PO_4. ^{183}W NMR (16.50 MHz) spectra were recorded in 10 mm outer diameter tubes on a JEOL JNM-EX 400 FT-NMR spectrometer equipped with a JEOL NM-40T10L low-frequency tunable probe and a JEOL EX-400 NMR data-processing system. ^{183}W NMR spectra measured in D_2O were referenced to an external standard of saturated Na_2WO_4–D_2O solution. ^{183}W NMR signals were shifted to −0.787 ppm by using 2 M Na_2WO_4 solution as a reference instead of saturated Na_2WO_4 solution.

Materials. The following were used as received: Na_2CO_3, Et_2NH_2Cl, 1 and 0.1 M aqueous HCl solutions (quantitative analysis grade) from Wako; D_2O from Isotec, $[\{RuCl_2(benzene)\}_2]$, $[\{RuCl_2(p\text{-cymene})\}_2]$, and $[\{RuCl_2(hexamethylbenzene)\}_2]$ from Aldrich. $H_3PW_{12}O_{40}\cdot 14H_2O$[7a–c] and $K_7[PW_{11}O_{39}]\cdot 7H_2O$[7d] were prepared according to the literature. The water-soluble precursor $(Et_2NH_2)_6H[PW_{11}O_{39}]\cdot 3H_2O$ was prepared using Et_2NH_2Cl, instead of KCl, in the synthesis of the potassium salt[7d] and identified by using elemental analysis, TG/DTA, FTIR, and ^{31}P NMR.

Preparation of $(Et_2NH_2)_8[(\{(benzene)Ru\}PW_{11}O_{39})_2(\mu\text{-}WO_2)]\cdot 9H_2O$ (Et_2NH_2-d1). A clear colorless solution of $H_3PW_{12}O_{40}\cdot 14H_2O$ (1.00 g, 0.32 mmol) dissolved in water (25 mL) was adjusted to pH 4.9 using Na_2CO_3. To the solution was added $[\{RuCl_2(benzene)\}_2]$ (81.5 mg, 0.16 mmol), followed by vigorous stirring for 1 h. The pH of the brown suspended solution was adjusted to 1.5 with 1 M aqueous HCl solution, and the solution was filtered through a folded filter paper (Whatman #5). To the clear red-brown filtrate was added Et_2NH_2Cl (1.00 g, 9.12 mmol), followed by stirring for 30 min. The red-orange powder that formed was collected on a membrane filter (JG 0.2 μm), washed with MeOH (20 mL × 3) and then Et_2O (50 mL × 3), and dried in vacuo for 2 h. The red-orange powder obtained in 39.3% yield (0.42 g) was soluble in water, DMSO, slightly soluble in CH_3CN, sparingly soluble in MeOH, acetone, and insoluble in EtOH, EtOAc, CH_2Cl_2, $CHCl_3$, benzene.

Microanalysis: Calcd for $C_{44}H_{126}N_8O_{89}P_2Ru_2W_{23}$ or $(Et_2NH_2)_8[(\{(C_6H_6)Ru\}PW_{11}O_{39})_2(\mu\text{-}WO_2)]\cdot 9H_2O$: C, 7.91; H, 1.90; N, 1.68%. Found: C, 7.75; H, 1.44; N, 1.63%. TG/DTA under atmospheric conditions: a weight loss of 2.58% at below 100 °C and a weight loss of 12.18% at between 100 and 500 °C were observed with an exothermic point at 417 °C; calcd 2.43% for $x = 9$ in $(Et_2NH_2)_8[(\{(C_6H_6)Ru\}PW_{11}O_{39})_2(\mu\text{-}WO_2)]\cdot xH_2O$. IR (KBr) (polyoxometalates region): 1635m, 1472m, 1456m, 1436m, 1394m, 1160w, 1101m, 1048m, 955s, 897m, 821vs, 780s, 706s, 620m, 598m, 514m cm^{-1}. ^{31}P NMR (21.9 °C): δ −13.3. ^{1}H NMR (22.0 °C): δ 1.25–1.29 ($CH_3(Et_2NH_2)$, t), 3.09 ($CH_2(Et_2NH_2)$, br), 6.16 (benzene).

Preparation of $(Et_2NH_2)_7H[(\{(p\text{-cymene})Ru\}PW_{11}O_{39})_2(\mu\text{-}WO_2)]\cdot 7H_2O$ (Et_2NH_2-d3). A clear colorless solution of $H_3PW_{12}O_{40}\cdot 14H_2O$ (0.98 g, 0.31 mmol) dissolved in water (25 mL) was adjusted to pH 4.9 using Na_2CO_3. To the solution was added $[\{RuCl_2(p\text{-cymene})\}_2]$ (123 mg, 0.20 mmol), followed by vigorous stirring for 1 h. The pH of the brown suspended solution was adjusted to 1.0 with 1 M aqueous HCl solution, and the solution was filtered through a membrane filter (JG 0.2 μm). To the clear red-orange filtrate was added Et_2NH_2Cl (1.00 g, 9.12 mmol), and the solution was stirred for 30 min. The red-orange precipitate was collected on a membrane filter (JG 0.2 μm), washed with MeOH (20 mL × 3) and then Et_2O (50 mL × 3), and dried in vacuo for 2 h. The red-orange powder obtained in 32.1% yield (0.43 g) was soluble in water, DMSO, slightly soluble in CH_3CN, sparingly soluble in MeOH, acetone, and insoluble in EtOH, EtOAc, CH_2Cl_2, $CHCl_3$, benzene.

Microanalysis: Calcd for $C_{48}H_{127}N_7O_{85}P_2Ru_2W_{23}$ or $(Et_2NH_2)_7H[(\{(C_{10}H_{14})Ru\}PW_{11}O_{39})_2(\mu\text{-}WO_2)]\cdot 7H_2O$: C, 8.62; H, 1.91; N, 1.47%. Found: C, 8.53; H, 1.27; N, 1.42%. TG/DTA under atmospheric conditions: a weight loss of 1.76% at below 136 °C and a weight loss of 13.05% at between 136 and 500 °C were observed with exothermic points at 264 and 389 °C; calcd 1.87% for $x = 7$ in $(Et_2NH_2)_7H[(\{(p\text{-cymene})Ru\}PW_{11}O_{39})_2(\mu\text{-}WO_2)]\cdot xH_2O$. IR (polyoxometalates region): 1637w, 1543w, 1508w, 1498w, 1474w, 1449w, 1389w, 1098m, 1081m, 1049m, 956s, 896s, 819vs, 779s, 704m, 599w, 517m cm^{-1}. ^{31}P NMR (22.6 °C): δ −13.1. ^{1}H NMR (21.8 °C): δ 1.27 ($CH_3(Et_2NH_2)$, br), 3.10 ($CH_2(Et_2NH_2)$, br), 1.42–1.44 ($CH_3(i\text{-Pr})$, d, $J = 6.84$ Hz), 1.62–1.64 ($CH_3(i\text{-Pr})$, d, $J = 6.59$ Hz), 2.74 (Me, s), 3.49 (CH(*i*-Pr), sept, $J = 6.59$ Hz), 5.30–5.31 (benzene ring, d, $J = 5.86$ Hz), 5.88–5.89 (benzene ring, d, $J = 5.86$ Hz), 6.34–6.36 (benzene ring, d, $J = 5.86$ Hz), 6.39–6.41 (benzene ring, d, $J = 6.10$ Hz).

^{13}C and ^{183}W NMR spectra in D_2O of **d3** were successfully measured after changing the Cs salt, which has been prepared using CsCl, instead of Et_2NH_2Cl, in the synthesis of **Et_2NH_2-d3**, to the highly soluble Li salt by treatment with $LiClO_4$. ^{13}C NMR (25.8 °C, D_2O): δ 22.44, 23.12, 27.28, 33.77 (C7, C8, C9, and C10), 77.93, 78.11, 87.39, 89.58 (C2, C3, C5, and C6), 101.25, 106.87 (C1 and C4). ^{183}W NMR (21.7 °C): δ −74.26 (2W), −83.66 (2W), −97.19 (2W), −113.83 (2W), −128.79 (2W), −131.21 (2W), −148.35, −148.73 (2W + 2W), −153.56 (2W), −162.40 (2W), −171.63 (1W), −188.67 (2W).

Preparation of $(Et_2NH_2)_6H_2[(\{(hexamethylbenzene)Ru\}PW_{11}O_{39})_2(\mu\text{-}WO_2)]\cdot 8H_2O$ (Et_2NH_2-d4). The pH of a clear colorless solution of $H_3PW_{12}O_{40}\cdot 14H_2O$ (0.98 g, 0.31 mmol) dissolved in water (30 mL) was adjusted 4.9 by adding solid of Na_2CO_3. To the solution was added [{$RuCl_2$(hexamethylbenezene)}$_2$] (104 mg, 0.16 mmol), and the solution was stirred vigorously for 1 h. The pH of the dark-brown suspension was adjusted to 1.5 with 1 M aqueous HCl solution, and the solution was then stirred overnight. To the dark-orange filtrate, which was passed through a folded filter paper (Whatman #5), Et_2NH_2Cl (1.0 g, 9.12 mmol) was added, and the solution was stirred for 30 min. A dark-orange powder that formed was collected on a membrane filter (JG 0.2 μm), washed with MeOH (20 mL × 3) and then Et_2O (50 mL × 3), and dried in vacuo for 2 h. The dark-orange powder obtained in 48.6% yield (0.52 g) was soluble in water, CH_3CN, sparingly soluble in MeOH, acetone, EtOH, CH_2Cl_2, and insoluble in EtOAc, $CHCl_3$.

Microanalysis: Calcd for $C_{48}H_{126}N_6O_{88}P_2Ru_2W_{23}$ or $(Et_2NH_2)_6H_2[(\{(C_{12}H_{18})Ru\}PW_{11}O_{39})_2(\mu\text{-}WO_2)]\cdot 8H_2O$: C, 8.62; H, 1.90; N, 1.26%. Found: C, 8.52; H, 1.02; N, 1.46%. TG/DTA under atmospheric conditions: a weight loss of 2.05% at below 122 °C and a weight loss of 13.59% at between 122 and 500 °C were observed with exothermic points at 357 and 395 °C and an endothermic point at 376 °C; calcd 2.13% for $x = 8$ in $(Et_2NH_2)_6H_2[(\{(hexamethylbenzene)Ru\}PW_{11}O_{39})_2(\mu\text{-}WO_2)]\cdot xH_2O$. IR (polyoxometalates region): 1618w, 1458w, 1389w, 1159w, 1102m, 1080m, 1048m, 953s, 896s, 810vs, 747s, 704s, 595w, 517w cm^{-1}. ^{31}P NMR (22.9 °C): δ −12.9. ^{1}H NMR (22.7 °C): δ 1.27 ($CH_3(Et_2NH_2)$, br), 3.10 ($CH_2(Et_2NH_2)$, br), 2.34 (Me, s).

X-ray Crystallography of Et_2NH_2-d1. A dark orange needle of **Et_2NH_2-d1** (0.20 × 0.04 × 0.02 mm^3) was surrounded by liquid paraffin (Paratone-N) to prevent its degradation. Data collection was done on a Bruker SMART APEX CCD diffractometer at 90 K in the range of $0.93° < 2\theta < 56.76°$. The intensity data were automatically corrected for Lorentz and polarization effects during integration. The structure was solved by direct methods (SHELXS-97)[8a] followed by subsequent difference Fourier calculation and refined by full-matrix least-square procedure on F^2 (SHELXL-97).[8b] Absorption correction was performed with SADABS (empirical absorption correction).[8c]

Crystal data for $C_{44}H_{126}N_8O_{89}P_2Ru_2W_{23}$: $M_r = 6684.16$, monoclinic, space group $P2_1/n$, $a = 13.3163(8)$, $b = 43.992(3)$, $c = 20.9541(13)$ Å, $\beta = 102.6310(10)°$, $V = 11978.1(13)$ Å^3, $Z = 4$, $D_{calcd} = 3.707$ Mg m^{-3}, μ(Mo Kα) = 22.359 mm^{-1}, $R1 = 0.0680$, $wR2 = 0.1113$ (for all data), $R_{int} = 0.0852$, $R1 = 0.0458$, $wR2 = 0.0982$, GOF = 1.072 (137961 total reflections, 29849 unique reflections where $I > 2\sigma(I)$). The maximum and minimum residual density (3.663 and −1.838 eÅ^{-3}) holes were located at 0.79 Å from W11A and 1.90 Å from O1B, respectively. The O25A, O2B, O32A, C2A atoms were refined isotropically.

The main features of the molecular structure of the polyoxoanion were clear. However, it is frequently impossible in POM chemistry due to disorder to locate and assign all counteractions and water molecules of crystallization unequivocally by single-crystal X-ray diffraction.[9]

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-601876 for **Et_2NH_2-d1**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Control Experiments for Synthesis of d1, d3, and d4 by pH-Varied ^{31}P NMR. The pH-varied ^{31}P NMR measurements revealed that the ratio of the dimeric species (**d1**, **d3**, and **d4**) of the polyoxoanion-suppored [(arene)Ru]$^{2+}$ complex increased as pH of the solution decreased.

For Synthesis of d1. The pH of a clear colorless solution of $H_3PW_{12}O_{40}\cdot 14H_2O$ (1.00 g, 0.32 mmol) dissolved in 20 mL water was adjusted to 4.9 using Na_2CO_3. To the solution was added 81.5 mg (0.16 mmol) of [{$RuCl_2$(benzene)}$_2$], and the solution was vigorously stirred for 1 h. The pH of the brown suspended solution was 4.68. By adding drops of 1 M aqueous HCl solution, the pH of the solution was adjusted to 2.99, 1.98, and 1.48, respectively. The pH of the last solution (pH 1.48) was readjusted to 4.44 using Na_2CO_3. ^{31}P NMR spectra of these solutions are shown in Fig. 1, and the numerical data are summarized in Table 2.

In the ^{31}P NMR spectrum of the pH 4.68 solution, there were two organometallic complexes present, i.e., the monomer **m1** (δ −12.6) as a main product and the dimer **d1** (δ −13.3) as a minor product, as well as $[PW_{11}O_{39}]^{7-}$ (δ −10.6) as a minor

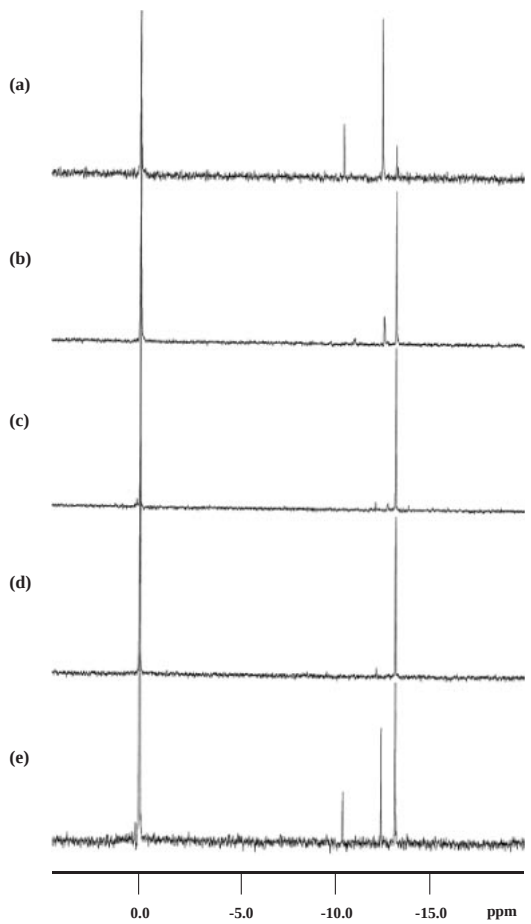


Fig. 1. pH-Varided ^{31}P NMR spectra in water of the reaction solution containing the in situ-generated $[PW_{11}O_{39}]^{7-}$ (0.32 mmol) and [{$RuCl_2$(benzene)}$_2$] (0.16 mmol) of (a) pH 4.68, (b) pH 2.99, (c) pH 1.98, (d) pH 1.48, and (e) readjusted to pH 4.44 after ^{31}P NMR measurement of the pH 1.48 solution.

Table 2. Control Experiments for Synthesis of **d1**, **d3**, and **d4** Using pH-Varied ^{31}P NMR in H_2O

For synthesis of **d1**

pH 4.68 (23.7 °C): δ −10.6 (minor peak due to $[PW_{11}O_{39}]^{7-}$), −12.6 (major peak due to **m1**), −13.3 (minor peak due to **d1**).
pH 2.99 (23.4 °C): δ −12.7 (minor peak due to **m1**), −13.3 (major peak due to **d1**).
pH 1.98 (24.3 °C): δ −12.9 (minor peak due to **m1**), −13.3 (major peak due to **d1**).
pH 1.48 (23.8 °C): δ −13.3 (single peak due to **d1**).
Readjusted to pH 4.44 after ^{31}P NMR measurement of the pH 1.48 solution (23.7 °C):
δ −10.6 (minor peak due to $[PW_{11}O_{39}]^{7-}$), −12.6 (major peak due to **m1**), −13.3 (major peak due to **d1**).

For synthesis of **d3**

(1) The reactions using in situ-generated $[PW_{11}O_{39}]^{7-}$

pH 4.64 (22.8 °C): δ −12.4 (peak due to only **m3**).
pH 3.51 (22.5 °C): δ −12.4 (major peak due to **m3**), −13.3 (minor peak due to **d3**).
pH 2.51 (22.3 °C): δ −12.5 (minor peak due to **m3**), −13.2 (major peak due to **d3**).
pH 0.96 (22.8 °C): δ −13.1 (single peak due to **d3**).

(2) Reactions using the separately prepared $K_7[PW_{11}O_{39}]\cdot 7H_2O$

pH 4.63 (22.5 °C): δ −12.3 (peak due to only **m3**).
pH 3.53 (22.3 °C): δ −12.3 (peak due to only **m3**).
pH 2.54 (22.7 °C): δ ca. −12.4 (multiple peaks due to **m3** and others).
pH 2.00 (22.5 °C): δ −12.3 (minor peak due to **m3**), −12.8 (major peak due to the unidentified species), −13.2 (minor peak due to **d3**).
pH 1.00 (22.5 °C): δ −12.4 (peak due to **m3**), −12.5 and −12.7 (peaks due to the unidentified species), −13.2 (peak due to **d3**). These peaks were observed with approximately equal intensities.

For synthesis of **d4**

pH 4.86 (23.6 °C): δ −10.5 (major peak due to $[PW_{11}O_{39}]^{7-}$), −12.0 (minor peak due to **m4**).
pH 3.52 (22.5 °C): δ −10.6 (major peak due to $[PW_{11}O_{39}]^{7-}$), −12.1 (minor peak due to **m4**), −12.9 (minor peak due to **d4**).
pH 2.52 (22.4 °C): δ −11.1 (major peak due to unidentified species), −12.8 (minor peak due to **d4**).
pH 1.49 (22.2 °C): δ −12.3 (major peak due to **m4**), −12.9 (minor peak due to **d4**).
pH 1.01 (22.6 °C): δ −12.4 (minor peak due to **m4**), −12.8 (major peak due to **d4**), −15.1 (minor peak due to $[PW_{12}O_{40}]^{3-}$).

species (Eq. 2). As the pH of the solution was lowered, the amount of **m1** decreased, while that of **d1** increased (Eq. 3). In the ^{31}P NMR spectrum of the pH 1.48 solution, only **d1** was observed. In the ^{31}P NMR spectrum of the pH 4.44 solution that was readjusted by adding an aqueous Na_2CO_3 solution to the pH 1.48 solution **m1** and $[PW_{11}O_{39}]^{7-}$ were observed. This showed that **m1** could be recovered from the dimer.

Thus, the behavior of the (benzene)Ru^{2+} complexes in solution can be represented with the following Eqs. 1–3.

$$2[PW_{12}O_{40}]^{3-} + 6OH^- \rightarrow 2[PW_{11}O_{39}]^{7-} + 2[WO_4]^{2-} + 6H^+ \quad (1)$$

$$4[PW_{12}O_{40}]^{3-} + 12OH^- + 4[(\text{benzene})Ru]^{2+} \rightarrow 2[\{(\text{benzene})Ru(H_2O)\}PW_{11}O_{39}]^{5-}\ (\mathbf{m1}) + [(\{(\text{benzene})Ru\}PW_{11}O_{39})_2(\mu\text{-}WO_2)]^{8-}\ (\mathbf{d1}) + 8H^+ + 3[WO_4]^{2-} \quad (2)$$

$$2[\{(\text{benzene})Ru(H_2O)\}PW_{11}O_{39}]^{5-}\ (\mathbf{m1}) + 4H^+ + WO_4{}^{2-} \rightleftharpoons [(\{(\text{benzene})Ru\}PW_{11}O_{39})_2(\mu\text{-}WO_2)]^{8-}\ (\mathbf{d1}) + 4H_2O \quad (3)$$

In these reactions, the key factors were (1) the pH of the solution and (2) the use of the in situ-generated $[PW_{11}O_{39}]^{7-}$, but not the use of the isolated lacunary species $K_7[PW_{11}O_{39}]\cdot 14H_2O$. The same was observed in the cases with arene = *p*-cymene (**3**) and hexamethylbenzene (**4**).

For Synthesis of d3. The pH-varied reactions of $[\{RuCl_2(p\text{-cymene})\}_2]$ with in situ-generated $[PW_{11}O_{39}]^{7-}$ in solution and the separately prepared $K_7[PW_{11}O_{39}]\cdot 7H_2O$, were examined.

The Reactions Using In Situ-Generated $[PW_{11}O_{39}]^{7-}$: The pH of a clear colorless solution of $H_3PW_{12}O_{40}\cdot 14H_2O$ (0.98 g, 0.31 mmol) dissolved in 25 mL water was adjusted to 4.9 using Na_2CO_3. To the solution was added 123 mg (0.20 mmol) of $[\{RuCl_2(p\text{-cymene})\}_2]$, and the solution was vigorously stirred for 1 h. The pH of the brown suspended solution was 4.64. By adding drops of 1 or 0.1 M aqueous HCl solution, the pH of the solution was adjusted to 3.51, 2.51, and 0.96, respectively. ^{31}P NMR spectra of these solutions are shown in Fig. 2 (Table 2).

Reactions Using the Isolated $K_7[PW_{11}O_{39}]\cdot 7H_2O$: To a clear colorless solution of $K_7[PW_{11}O_{39}]\cdot 7H_2O$ (1.0 g, 0.32 mmol) dissolved in 25 mL water was added 123 mg (0.20 mmol) of $[\{RuCl_2(p\text{-cymene})\}_2]$. After vigorously stirring for 1 h, the pH of the brown suspended solution was 4.63. By adding drops of 1 or 0.1 M aqueous HCl solution, the pH of the solution was adjusted to 3.53, 2.54, 2.00, and 1.00. ^{31}P NMR data of these solutions are listed in Table 2.

The two control experiments gave different results: the former reactions showed formation of only **d3** (δ −13.1) in solu-

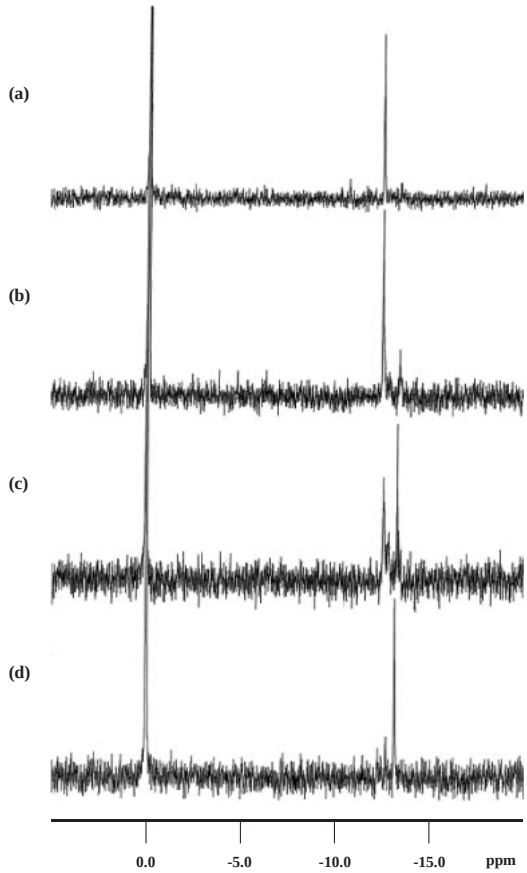


Fig. 2. pH-Varided ^{31}P NMR spectra in water of the reaction solution containing the in situ-generated $[PW_{11}O_{39}]^{7-}$ (0.31 mmol) and $[\{RuCl_2(p\text{-cymene})\}_2]$ (0.20 mmol) of (a) pH 4.64, (b) pH 3.51, (c) pH 2.51, and (d) pH 0.96.

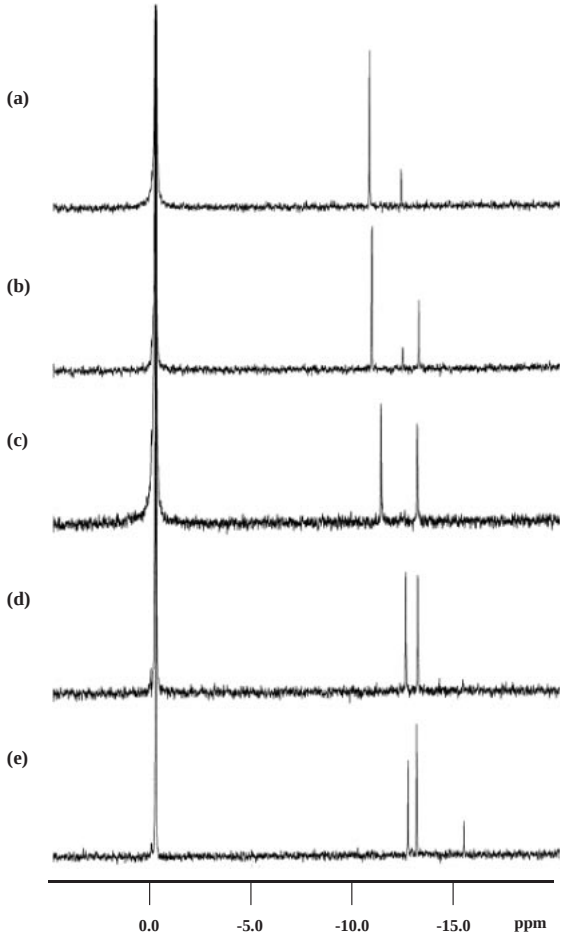


Fig. 3. pH-Varided ^{31}P NMR spectra in water of the reaction solution containing the in situ-generated $[PW_{11}O_{39}]^{7-}$ (0.31 mmol) and $[\{RuCl_2(hexamethylbenzene)\}_2]$ (0.16 mmol) of (a) pH 4.86, (b) pH 3.52, (c) pH 2.52, (d) pH 1.49, and (e) pH 1.01.

tion at pH 0.96, while the latter reactions gave multiple peaks in the ^{31}P NMR spectrum due to a mixture of the monomer (δ −12.4), dimer (δ −13.2), and an unidentified species (δ −12.5 and −12.7) in solution at pH 1.00. Thus, it is clear that the μ-WO_2 group in the dimeric species originated from the tungstate ion coexisting in the solution containing in situ-generated $[PW_{11}O_{39}]^{7-}$. These experiments showed that the proportion in solution of the monomer **m3** to the dimer **d3** was also strongly pH-dependent.

For Synthesis of d4. The pH of a clear colorless solution of $H_3PW_{12}O_{40}\cdot 14H_2O$ (0.98 g, 0.31 mmol) dissolved in 25-mL water was adjusted to 4.9 by adding a solid of Na_2CO_3. To the solution containing the in situ-generated $[PW_{11}O_{39}]^{7-}$ was added 104 mg (0.16 mmol) of $[\{RuCl_2(hexamethylbenzene)\}_2]$. After vigorously stirring for 1 h, the pH of the black-brown suspension was 4.86. By adding drops of 1 or 0.1 M aqueous HCl solution, the pH of the solution was adjusted to 3.52, 2.52, 1.49, and 1.01. ^{31}P NMR spectra of these solutions are shown in Fig. 3 (Table 2).

Compared to the complexes with arene = benzene and *p*-cymene, the effect of the arene could not be completely ruled out. Nevertheless, at low pH values, the dimeric species **d4** (δ −12.8) was present as the main species in solution.

Synthesis, Compositional and Solution NMR Characterization of d1, d3, and d4. The three 2:2-type complexes linked through the μ-WO_2 group, composed of (arene)Ru^{2+} (arene = benzene, *p*-cymene, and hexamethylbenzene) and the mono-lacunary Keggin POM $[PW_{11}O_{39}]^{7-}$, i.e., water-soluble Et_2NH_2 salts of **d1**, **d3**, and **d4**, were prepared as analytically pure compounds by the reactions of the organometallic precursors $[\{RuCl_2(arene)\}_2]$ with the solution containing in situ-generated $[PW_{11}O_{39}]^{7-}$ under acidic conditions at room temperature in air. Their synthetic conditions were determined on the basis of pH-varied ^{31}P NMR spectroscopy in the control experiments.

The number of hydrated water molecules and that of Et_2NH_2 counter ions in the formulas of **Et_2NH_2-d1**, **Et_2NH_2-d3**, and **Et_2NH_2-d4** (Table 1) changed with the arene. In particular, the number of Et_2NH_2 counter ions decreased according to bulkiness of the arene: benzene > *p*-cymene > hexamethylbenzene.

FTIR spectra (Fig. S1) of **Et_2NH_2-d1**, **Et_2NH_2-d3**, and **Et_2NH_2-d4** showed the characteristic vibrational bands for the Keggin-type "$XW_{12}O_{40}{}^{n-}$" polyoxotungstate framework.[10] The vibrational bands at 1100–700 cm^{-1} originated from the mono-lacunary α-Keggin POM, $[\alpha\text{-}PW_{11}O_{39}]^{7-}$, but the vibrational bands due to the aromatic groups coordinated to

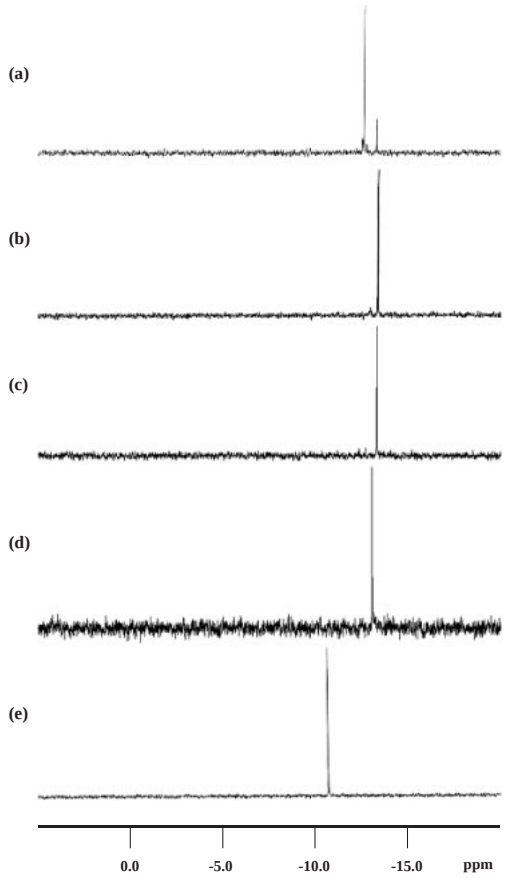


Fig. 4. ^{31}P NMR spectra in D_2O of (a) **m1** contaminated with **d1** of minor species (see Supporting Information, Experimental S1), (b) **Et_2NH_2-d1**, (c) **Et_2NH_2-d3**, (d) **Et_2NH_2-d4**, and (e) $(Et_2NH_2)_6H[PW_{11}O_{39}]\cdot 3H_2O$.

the Ru^{2+} atom were hidden under the intense bands of counter cations.

^{31}P NMR in D_2O (Fig. 4) showed a single peak at δ −13.3 for **d1**, at δ −13.1 for **d3**, and at δ −12.9 for **d4**, suggesting a very high level of purity in aqueous solution in each case. For comparison, ^{31}P NMR of the powder sample containing **m1** as major species and **d1** as minor species (see Supporting Information, Experimental S1) and that of the mono-lacunary Keggin POM as precursor are also shown in Fig. 4.

In the ^{1}H NMR spectrum of **d1**, a single peak due to benzene coordinated to Ru^{2+} was observed at δ 6.16, and the signals due to the ethyl group in Et_2NH_2 counter ions were observed at around δ 1.27 and 3.09. ^{1}H NMR spectrum of **d3**, the two methyl protons at around δ 1.43 and 1.63, the –CH– proton at δ 3.49 of *i*-Pr group, the methyl proton at δ 2.74, and the ring protons at δ 5.31, 5.89, 6.35, and 6.40 of the *p*-cymene coordinated to Ru^{2+} were observed as well as the ethyl protons in Et_2NH_2 counter ions at around δ 1.27 and 3.10. Thus, the ^{1}H NMR spectrum of **d3** showed that the two methyl groups of the *i*-Pr group and four ring protons are inequivalent, probably due to the restricted rotation of the coordinated *p*-cymene. Similar phenomenon has been also observed in a related compound, $K_8[\{(p\text{-cymene})Ru(H_2O)\}\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 16H_2O$.[4a] On the other hand, in the ^{1}H NMR spectrum of **d4**, a single peak due to the methyl group of the hexamethylbenzene coordinated to Ru^{2+} at δ 2.34 and the ethyl protons in Et_2NH_2 group at around δ 1.27 and 3.10 were observed.

^{13}C and ^{183}W NMR spectra in D_2O of **d3** could be obtained after changing the separately prepared Cs salt (see the Experimental section) to the highly soluble Li salt by treatment with $LiClO_4$. The 10 inequivalent signals were observed in the ^{13}C NMR spectrum (Fig. S2), which was consistent with the ^{1}H NMR spectrum. The ^{183}W NMR spectrum (Fig. S3) showed a 12-line spectrum due to the $(PW_{11})_2(\mu\text{-}WO_2)$ unit, which is consistent with that of the Li salt of **d3** reported by Proust's group.[6] The NMR spectra indicated that the molecular structure of **d3** was maintained in water.

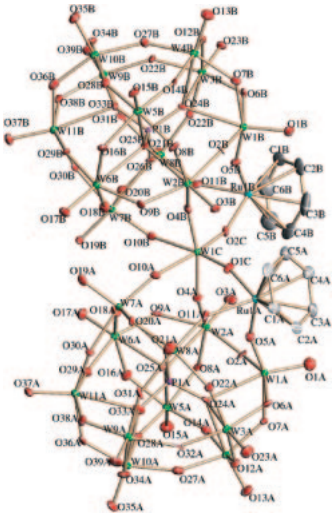
Crystallization of **Et_2NH_2-d1** was much more easier than **Et_2NH_2-m1** (see Supporting Information, Experimental S1 and S2).

Molecular Structure of d1. The crystal of **Et_2NH_2-d1** contained discrete cluster anions, Et_2NH_2 counter cations and lattice water molecules, all on general positions in the monoclinic space group $P2_1/n$. The observed electron densities of the Ru and W atoms were quite different, and the data unequivocally distinguished and defined the Ru and W atoms. The 23 tungsten atoms, two ruthenium atoms, two P atoms and eight Et_2NH_2 counter cations were clearly identified. Thus, the main features of the molecular structure of the POM were elucidated.

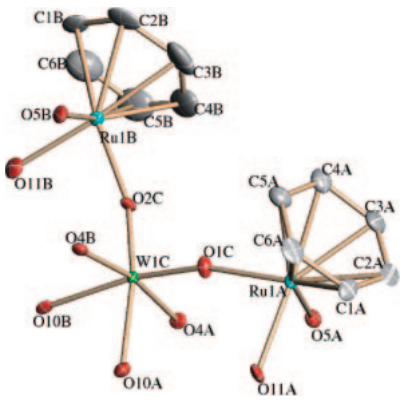
The molecular structure of **d1** and its local structure around the $\{(benzene)Ru\}_2(\mu\text{-}WO_2)$ moiety are depicted in Figs. 5a and 5b, respectively. The molecular structure was composed of the two mono-lacunary Keggin POM units A and B, the bridging μ-WO_2 group and the two $[(benzene)Ru]^{2+}$ units. The $[(benzene)Ru]^{2+}$ group in **d1** was not coordinated by the water molecule, as seen in the monomeric species $[\{(benzene)\text{-}Ru(H_2O)\}PW_{11}O_{39}]^{5-}$ **m1**[6] and the Dawson POM $[\{(benzene)Ru(H_2O)\}\alpha_2\text{-}P_2W_{17}O_{61}]^{8-}$[4a] and, instead, it bonded to the oxygen atom of the μ-WO_2 group. The two $[(benzene)\text{-}Ru]^{2+}$ groups were arranged in a *cis* fashion to the μ-WO_2 group. The molecular structure of **d1** was essentially consistent with that of the Proust's POM, Na_4K_4 salt.[6]

It should be noted that steric repulsion between the two $(benzene)Ru^{2+}$ fragments in **d1** should not be significantly large because of the longer Ru···Ru distance (Ru1A···Ru1B 6.267 Å) and wider angle between two lines through the atom W1C (the bridging μ-WO_2 group) and Ru^{2+} atom (Ru1A···W1C···Ru1B 113.63°). Moreover, the shortest C···C distance between the two $(benzene)Ru^{2+}$ groups (C(4A)···C(3B)) was 5.195 Å.

There was no disorder in the benzene ring (C–C distances 1.40(2)–1.437(19) Å for unit A and 1.33(3)–1.46(3) Å for unit B, where the difference of C–C distances in the units A and B is due to different temperature factor, Ru–C distances 2.137(14)–2.186(12) Å for unit A and 2.138(17)–2.174(13) Å for unit B). The $[(benzene)Ru]^{2+}$ group was coordinated by one oxygen atom (O1C) of the μ-WO_2 group (Ru1A–O1C 2.031(9) Å) and by two oxygen atoms (O5A and O11A) of the four available oxygen atoms (O5A, O11A, O10A, and O4A) in the mono-lacunary Keggin POM (Ru1A–O5A 2.068(8) Å and Ru1A–O11A 2.073(8) Å), resulting in overall C_2 symmetry. Selected bond distances and angles around the



(a)



(b)

Fig. 5. (a) Molecular structure of the polyoxoanion **d1** with 50% probability ellipsoids and (b) the partial structure around the two [(benzene)Ru]$^{2+}$ units linked by μ-WO_2 group.

ruthenium(II) centers (Table S1) and average bond distances and angles (Table S2) for **d1** are given.

In the lacunary site, the important W–O distances are: W8A–O11A (bonding to Ru atom) 1.741(8) Å, W8A–O21A (terminal) 1.735(8) Å; W1A–O5A (bonding to Ru atom) 1.763(9) Å, W1A–O1A (terminal) 1.722(9) Å; W2A–O4A (μ-WO_2) 1.836(7) Å, W2A–O3A (terminal) 1.686(9) Å; W1C–O1C (bonding to Ru) 1.760(8) Å. These bond distances indicate the double bond character of the W–O (terminal) bonds. It is likely that the coordination of the Ru atom by the two oxygen atoms (O11A and O5A) in the lacunary site has only a small influence on the W–O distances from a comparison with the distances (W8A–O21A and W1A–O1A). Similar feature has been observed in the related POM [{(C_6H_6)Ru(H_2O)}-(α_2-$P_2W_{17}O_{61}$)]$^{8-}$.[4a]

On the other hand, the average W–O distances for two Keggin units A and B, i.e., the W–Ot (Ot = terminal oxygen) 1.713 Å (unit A) and 1.717 Å (unit B), W–Oe (Oe = edge-sharing oxygen) 1.931 Å (unit A) and 1.926 Å (unit B), W–Oc (W belt) (Oc = corner-sharing oxygen) 1.913 Å (unit A) and 1.915 Å (unit B), and W–Oa (Oa = oxygen coordinated to P atom) 2.419 Å (unit A) and 2.418 Å (unit B) were in the normal range.[1b] Each Keggin unit contained one central P atom in an almost regular tetrahedral environment of PO_4: unit A [P–O distances 1.523(8)–1.560(9) Å; O–P–O angles 107.1(4)–110.9(5)°] and unit B [P–O distances 1.515(8)–1.553(8) Å; O–P–O angles 107.8(4)–111.7(5)°].

The bond valence sums (BVS, Table S3) of W and P atoms,[11] calculated using the observed bond distances for **d1**, were in the ranges of 6.035–6.220 for the W(1A–11A) atoms and 5.978–6.173 for the W(1B–11B) atoms, 4.876 for P(1A) atom and 4.953 for P(1B), which reasonably correspond to the formal valences of W^{6+} and P^{5+}, respectively. The BVS values of oxygen atoms (O5A, O11A, and O1C) and (O5B, O11B, and O2C) around the (benzene)Ru groups in the units A and B and the μ-WO_2 group suggest that they are not protonated. Furthermore, the BVS values (1.635–2.136) for oxygen atoms (O1A–O39A) and those (1.635–2.136) for (O1B–O39B) also suggest that they are not protonated.

The molecular structure of **d1** is consistent with the results of solution (^{31}P and ^{1}H) NMR spectra, suggesting that the solid-state structure of **d1** is maintained in aqueous solution.

Conclusion

As for the two types of the (η^6-arene)Ru^{2+} complexes (arene = benzene (**1**), toluene (**2**), *p*-cymene (**3**), and hexamethylbenzene (**4**)) supported on mono-lacunary Keggin POMs, i.e., the dimeric species (type-**d**) [({(η^6-arene)Ru}-$PW_{11}O_{39}$)$_2$(μ-WO_2)]$^{8-}$ and the monomeric species (type-**m**) [{(η^6-arene)Ru(H_2O)}$PW_{11}O_{39}$]$^{5-}$,[6] the dimeric species possessing a bimetallic active center in a molecule is much more interesting than the monomeric species in the viewpoint of a homogeneous oxidation catalyst which works with molecular oxygen in water.[4b] In this work, synthetic conditions to obtain the dimeric species as the main products were examined in detail, and the improved syntheses were presented. X-ray crystallography revealed that the steric repulsion between the two (benzene)Ru^{2+} fragments in **d1** should not be significantly large. The two key factors for formation of the dimeric species were concluded to be (1) the smaller pH (1.0–1.5) of the reaction solutions and (2) the use of in situ-generated $[PW_{11}O_{39}]^{7-}$ coexisting with free tungstate ion in solution, but not the isolated mono-lacunary species, such as $K_7[PW_{11}O_{39}]\cdot nH_2O$. Keggin POM-supported dimeric species **d1**, **d3**, and **d4** were successfully obtained in good yields as water-soluble $Et_2NH_2^+$ salts. The data of their oxidation catalysis with molecular oxygen in water will be reported in due course.

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Supporting Information

Preparation of powder sample containing **m1** as major species and **d1** as minor species (Experimental S1), crystallization of **Et_2NH_2-d1** from the aqueous solution of the powder sample containing **m1** (major species) and **d1** (minor species) (Experimental S2), the FTIR spectra of **Et_2NH_2-m1**, **Et_2NH_2-d1**, **Et_2NH_2-d3**, **Et_2NH_2-d4**, and $(Et_2NH_2)_6H[PW_{11}O_{39}]\cdot 3H_2O$ (Fig. S1), ^{13}C NMR

spectrum in D_2O of **d3** (Fig. S2), ^{183}W NMR spectrum in D_2O of **d3** (Fig. S3), selected bond distances (Å) and angles (°) around the ruthenium(II) centers in $\mathbf{Et_2NH_2}$**-d1** (Table S1), average bond distances (Å) and angles (°) [range] for the Keggin POM moiety in $\mathbf{Et_2NH_2}$**-d1** (Table S2) and bond valence sum (BVS) calculations of W, P, and O atoms in $\mathbf{Et_2NH_2}$**-d1** (Table S3). This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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