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·Article

Synthesis, Characterization, and Photochemical Behavior of {Ru(arene)}²⁺ Derivatives of α-[PW₁₁O₃₉]⁷⁻: An Organometallic Way to Ruthenium-Substituted Heteropolytungstates†

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Reaction of [Ru(arene)Cl₂]₂ (arene = benzene, toluene, *p*-cymene, hexamethylbenzene) with K₇[PW₁₁O₃₉]·14H₂O provided two series of organometallic derivatives of heteropolytungstates: type-**1** and type-**2** complexes of general formulas [PW₁₁O₃₉{Ru(arene)(H₂O)}]⁵⁻ and [{PW₁₁O₃₉{Ru(arene)}}₂{WO₂}]⁸⁻, respectively. All compounds were characterized by infrared and multinuclear NMR (¹H, ³¹P, ¹⁸³W) spectroscopies. The crystal structures of Na₄K₄-[{PW₁₁O₃₉{Ru(benzene)}}₂{WO₂}]·6H₂O (NaK-**2a**·6H₂O), K₇H[{PW₁₁O₃₉{Ru(toluene)}}₂{WO₂}]·4H₂O (K-**2b**·4H₂O), and Cs₃K₂[PW₁₁O₃₉{Ru(*p*-cymene)(H₂O)}]·4H₂O (CsK-**1c**·4H₂O) were obtained and revealed that the {Ru(arene)} fragment is supported on the oxometallic framework. Photochemical reactivity of [PW₁₁O₃₉{Ru(arene)(H₂O)}]⁵⁻ (arene = toluene, *p*-cymene) in the presence of various ligands L (L = H₂O, dimethyl sulfoxide, tetramethylene sulfoxide, and diphenyl sulfoxide) was investigated, and led to the formation of [PW₁₁O₃₉{Ru(L)}]⁵⁻, in which the ruthenium is incorporated into the lacunary [PW₁₁O₃₉]⁷⁻ anion.

Introduction

The coordination chemistry of polyoxometalates with transition metal cations (TMC) has been particularly well documented in the past few decades.[1] Indeed the obtention of TMC derivatives of polyoxoanions appeared from the start as attractive in fields such as catalysis[2] and surface science,[3] since polyoxometalates are often considered as molecular analogues of oxides in terms of structural analogy. However, the lack of reactivity of bridging and terminal oxo ligands in a large number of polyoxometalates prevents the formation of TMC derivatives. To improve the nucleophilicity of the oxygen atoms, two synthetic routes have emerged: (i) the use of vacant polyoxoanions in which the most nucleophilic oxygen atoms are those which delimit the lacuna;[4] (ii) the increase of the overall charge of the polyanions. The latter pathway can be achieved either by reduction of the parent anion[5] or by replacement of one or several M^VI centers (M = Mo, W) by cations with a lower charge (V^V, Nb^V, Ti^IV, ...).[6]

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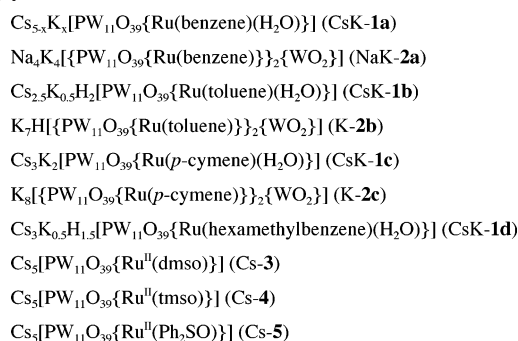† Dedicated to Prof. F. Sécheresse on the occasion of his 60th birthday.
(1) (a) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer: Berlin, 1983. (b) Pope, M. T.; Müller A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 56. (c) Müller A.; Peters F.; Pope M. T.; Gatteschi D. *Chem. Rev.* **1998**, *98*, 239. (d) Gouzerh, P.; Proust, A. *Chem. Rev.* **1998**, *98*, 77.
(2) Adam, W.; Alsters, P. L.; Neumann R.; Saha-Möller, C. R.; Sloboda-Rozner, D.; Zhang, R. *J. Org. Chem.* **2003**, *68*, 1721 and references therein. Hill, C. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 402. Okun, N. M.; Anderson, T. M.; Hill, C. L. *J. Am. Chem. Soc.* **2003**, *125*, 3194. Mizuno, N.; Misono, M. *Chem. Rev.* **1998**, *98*, 199. Kozhevnikov, I. V. *Chem. Rev.* **1998**, *98*, 171.
(3) (a) Okuhara, T.; Mizuno, N.; Misono, M. *Adv. Catal.* **1996**, *41*, 113. (b) Baker, L. C. W. In *Advances in the Chemistry of Coordination Compounds*; Kirschner, S., Ed.; Macmillan: New York, 1961. (c) Day, V. W.; Klemperer, W. G. *Science* **1985**, *228*, 533. (d) Klemperer, W. G.; Marquart, T. A.; Yaghi, O. M. *Angew. Chem.* **1992**, *104*, 51.
(4) (a) *Polyoxometalate Chemistry from Topology via Self-Assembly to Applications*; Pope, M. T., Müller, A., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2001. (b) *Polyoxometalates Chemistry for Nano-Composite Design*; Yamase, T., Pope, M. T., Eds.; Kluwer Academic/Plenum Publishers: Dordrecht, The Netherlands, 2002. (c) *Polyoxometalate Molecular Science*; Borras-Almenar, J. J., Coronado, E., Müller, A., Pope, M. T., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2003. Recent representative papers on the incorporation of TMC into lacunary heteropolytungstates: (d) Hill, C. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 402. (e) Cadot, E.; Pilette, M.-A.; Marrot, J.; Sécheresse, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 2173. (f) Sazani, G.; Pope, M. T. *Dalton Trans.* **2004**, 1989. (g) Keita, B.; Mbomekalle, I.-M.; Nadjo, L.; Anderson, T. M.; Hill, C. L. *Inorg. Chem.* **2004**, *43*, 3257. (h) Bi, L.-H.; Reicke, M.; Kortz, U.; Keita, B.; Nadjo, L.; Clark, R. J. *Inorg. Chem.* **2004**, *43*, 3915. (i) Jabbour, D.; Keita, B.; Mbomekalle, I.-M.; Nadjo, L.; Kortz, U. *Eur. J. Inorg. Chem.* **2004**, 2036. (j) Dablemont, C.; Proust, A.; Thouvenot, R.; Afonso, C.; Fournier, F.; Tabet, J.-C. *Inorg. Chem.* **2004**, *43*, 3514. (k) Ruhlmann, L.; Canny, J.; Vaissermann, J.; Thouvenot, R. *Dalton Trans.* **2004**, 794.

These different routes led to a great number of metallic derivatives of heteropolyoxotungstates incorporating first-row d-TMC or f-TMC.[7] However, examples of d-TMC derivatives from the second and third rows are somewhat scarcer, despite the fact that the introduction in a polyoxometalate of noble cations such as those from the "platinum group" appears to be of fundamental interest in terms of catalytic activity. The case of ruthenium derivatives illustrates this difficulty to synthesize well-defined compounds, and the number of examples of Ru-containing heteropolyanions is abnormally weak.[8−15] For example, only four different studies describe the formation of complexes between ruthenium and the monovacant [α-XW$_{11}$O$_{39}$]$^{n-}$ (X = P, Si, Ge, ...) anions. The formation of various [PW$_{11}$O$_{39}$Ru^{n}L]$^{p-}$ complexes, in which the oxidation state n of ruthenium is in the range +II to +V and L is chosen among various oxygen-, nitrogen-, or sulfur-donor (including dimethyl sulfoxide, DMSO) ligands, was first published by Pope and Rong.[9] An alternate synthesis and the complete characterization of [PW$_{11}$O$_{39}$Ru^{II}-(dmso)]$^{5-}$ was then proposed by Bonchio et al.[12] The synthesis of two ruthenium derivatives of the α-[SiW$_{11}$O$_{39}$]$^{8-}$ anion, [SiW$_{11}$O$_{39}$Ru^{III}(H$_2$O)]$^{5-}$ and [SiW$_{11}$O$_{39}$Ru^{IV}ORu^{III}Si-W$_{11}$O$_{39}$]$^{11-}$, was described by Sadakane and Higashijima.[14] More recently, Kortz reported the synthesis and the characterization of the two {Ru(dmso)$_3$}$^{2+}$ derivatives [XW$_{11}$O$_{39}$-{Ru(dmso)$_3$(H$_2$O)}]$^{6-}$ (X = Ge, Si).[15] Other complexes have been mentioned in the literature, but their characterization is often questionable.

Concerning the ruthenium precursors, Ru^{II} in *cis*-[RuCl$_2$-(dmso)$_4$][11a,12,13,15] and [Ru(H$_2$O)$_6$](C$_7$H$_7$SO$_3$)$_2$[9] and Ru^{III} in [Ru(acac)$_3$][14] and RuCl$_3$·xH$_2$O,[10,11a] which is in fact known

(5) (a) Chae, H. K.; Klemperer, W. G.; Paez Loyo, D. E. *Inorg. Chem.* **1992**, *31*, 3187. (b) Müller, A.; Koop, M.; Schiffels, P.; Bögge, H. *Chem. Commun.* **1997**, 1715. (c) Müller, A.; Beugholt, C.; Kögerler, P.; Bögge, H.; Bud'ko, S.; Luban, M. *Inorg. Chem.* **2000**, *23*, 5176. (d) Mialane, P.; Dolbecq, A.; Lisnard, L.; Mallard, A.; Marrot, J.; Secheresse, F. *Angew. Chem., Int. Ed.* **2002**, *41*, 2398. (e) Yuan, M.; Li, Y.; Wang, E.; Wang, L.; Hu, C.; Hu, N.; Jia, H. *Inorg. Chem.* **2003**, *42*, 3670.
(6) (a) Day, V. W.; Klemperer, W. G. *Mol. Eng.* **1993**, *3*, 61 and references therein. (b) Weiner, H.; Hayashi, Y.; Finke, R. G. *Inorg. Chem.* **1999**, *38*, 2579 and references therein.
(7) Recent representative papers on the incorporation of block-f cations into polyoxometalates: (a) Cheng, Z.; Howell, R. C.; Scotland, K. B.; Peres, F. G.; Todaro, L.; Francesconi, L. C. *Inorg. Chem.* **2004**, *43*, 7691. (b) Drewes, D.; Limanski, E. M.; Krebs, B. *Dalton Trans.* **2004**, 2087. (c) Dai, L.; Yu, S.; Shan, Y.; He, M. *Eur. J. Inorg. Chem.* **2004**, 237. (d) Mialane, P.; Dolbecq, A.; Rivière, E.; Marrot, J.; Secheresse, F. *Eur. J. Inorg. Chem.* **2004**, 33. (e) Kortz, U.; Holzapfel, C.; Reicke, M. *J. Mol. Struct.* **2003**, *656*, 93. (f) Gaunt, A. J.; May, I.; Sarsfield, M. J.; Collison, D.; Helliwel, M.; Denniss, I. S. *Dalton Trans.* **2003**, 2767. (g) VanPelt, C. E.; Crooks, W. J.; Choppin, G. R. *Inorg. Chim. Acta* **2003**, *346*, 215. (h) Wassermann, K.; Pope, M. T. *Inorg. Chem.* **2001**, *40*, 2763.
(8) Zonnevijlle, F.; Tourné, C. M.; Tourné, G. F. *Inorg. Chem.* **1982**, *23*, 3292.
(9) Rong, C.; Pope M. T. *J. Am. Chem. Soc.* **1992**, *114*, 2932.
(10) Randall, W. J.; Weakley, T. J. R.; Finke, R. *Inorg. Chem.* **1993**, *22*, 1068.
(11) (a) Neumann, R.; Dahan, M. *Polyhedron* **1998**, *17*, 3557. (b) Adam, W.; Alsters, P. L.; Neumann, R.; Saha-Moeller, C. R.; Sloboda-Rozner, D.; Zhang, R. *J. Org. Chem.* **2003**, *68*, 1721.
(12) Bagno, A.; Bonchio, M.; Sartorel, A.; Scorrano, G. *Eur. J. Inorg. Chem.* **2000**, 17.
(13) Nomiya, K.; Torii, H.; Nomura, K.; Sato, Y. *J. Chem. Soc., Dalton Trans.* **2001**, 1506.
(14) Sadakane, M.; Higashijima, M. *Dalton Trans.* **2003**, 659.
(15) Bi, L.-H.; Kortz, U.; Keita, B.; Nadjo, L. *Dalton Trans.* **2004**, 3184.

Chart 1

Cs$_{5-x}$K$_x$[PW$_{11}$O$_{39}${Ru(benzene)(H$_2$O)}] (CsK-**1a**)

Na$_4$K$_4$[{PW$_{11}$O$_{39}${Ru(benzene)}}$_2${WO$_2$}] (NaK-**2a**)

Cs$_{2.5}$K$_{0.5}$H$_2$[PW$_{11}$O$_{39}${Ru(toluene)(H$_2$O)}] (CsK-**1b**)

K$_7$H[{PW$_{11}$O$_{39}${Ru(toluene)}}$_2${WO$_2$}] (K-**2b**)

Cs$_3$K$_2$[PW$_{11}$O$_{39}${Ru(*p*-cymene)(H$_2$O)}] (CsK-**1c**)

K$_8$[{PW$_{11}$O$_{39}${Ru(*p*-cymene)}}$_2${WO$_2$}] (K-**2c**)

Cs$_3$K$_{0.5}$H$_{1.5}$[PW$_{11}$O$_{39}${Ru(hexamethylbenzene)(H$_2$O)}] (CsK-**1d**)

Cs$_5$[PW$_{11}$O$_{39}${Ru^{II}(dmso)}] (Cs-**3**)

Cs$_5$[PW$_{11}$O$_{39}${Ru^{II}(tmso)}] (Cs-**4**)

Cs$_5$[PW$_{11}$O$_{39}${Ru^{II}(Ph$_2$SO)}] (Cs-**5**)

to be a mixture of Ru^{III} and Ru^{IV},[16] appeared to successfully lead to well-defined structures in a certain number of cases. However, the formation of such ruthenium derivatives of polyoxometalates often required special synthetic conditions, such as the oxidation by O$_2$ of the mother solution after addition of [Ru(H$_2$O)$_6$](C$_7$H$_7$SO$_3$)$_2$[9] or microwave and/or hydrothermal techniques.[12,14]

In previous reports, the group of Süss-Fink and our group have described the easy formation of organometallic oxides by self-condensation of simple molybdates or tungstates with {Ru^{II}(arene)}$^{2+}$-containing cations (arene = benzene, toluene, *p*-cymene, mesitylene, durene, or hexamethylbenzene).[17] The Ru^{II} cations played the role of Lewis acids and were responsible for the aggregation of the different metallic fragments in water or in organic solvents. In this work, we report on the synthesis and the structural characterization of water-soluble {Ru(arene)}$^{2+}$ derivatives (Chart 1) of hetero-polytungstates obtained by reaction between the organometallic [Ru^{II}(arene)Cl$_2$]$_2$ precursor and the monovacant α-[PW$_{11}$O$_{39}$]$^{7-}$ anion. The photochemical reactivity of some of the species obtained is also presented, insofar as it appeared to be a new way of access to nonorganometallic ruthenium complexes of α-[PW$_{11}$O$_{39}$]$^{7-}$.

Experimental Section

Materials and Methods. K$_7$[PW$_{11}$O$_{39}$]·14H$_2$O[18] and [Ru(arene)-Cl$_2$]$_2$ complexes[19] were prepared as described in the literature. All reagents and solvents (dimethyl sulfoxide (DMSO), tetramethylene sulfoxide (TMSO), diphenyl sulfoxide (Ph$_2$SO), ethanol, acetonitrile, and diethyl ether) were obtained from commercial sources and used as received. IR spectra were recorded from KBr pellets on a Bio-Rad FT 165 spectrometer. The ^{1}H (300.13 MHz, TMS) and ^{31}P

(16) (a) Seddon, E. A.; Seddon, K. R. *The Chemistry of Ruthenium*; Elsevier: New York, 1984. (b) Rard, J. A. *Chem. Rev.* **1985**, *85*, 1.
(17) (a) Süss-Fink, G.; Plasseraud, L.; Ferrand, V.; Stoeckli-Evans, H. *Chem. Commun.* **1997**, 1657. (b) Süss-Fink, G.; Plasseraud, L.; Ferrand, V.; Stanislas, S.; Neels, A.; Stoeckli-Evans, H. *Polyhedron* **1998**, *17*, 2817. (c) Plasseraud, L.; Stoeckli-Evans, H.; Süss-Fink, G. *Inorg. Chem. Commun.* **1999**, *2*, 344. (d) Artero, V.; Proust, A.; Herson, P.; Thouvenot, R.; Gouzerh, P. *Chem. Commun.* **2000**, 883. (e) Artero, V.; Proust, A.; Herson, P.; Gouzerh, P. *Chem.—Eur. J.* **2001**, *7*, 3901. (f) Villanneau, R.; Artero, V.; Laurencin, D.; Herson, P.; Proust, A.; Gouzerh, P. *J. Mol. Struct.* **2003**, *656*, 67. (g) Laurencin, D.; Garcia Fidalgo, E.; Villanneau, R.; Villain, F.; Herson, P.; Pacifico, J.; Stoeckli-Evans H.; Bénard, M.; Rohmer, M.-M.; Süss-Fink, G.; Proust, A. *Chem.—Eur. J.* **2004**, *10*, 208.
(18) Contant, R. *Can. J. Chem.* **1987**, *65*, 570.
(19) (a) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233. (b) Bennett, M. A.; Huang, T. N.; Matheson, T. W.; Smith, A. K. *Inorg. Synth.* **1982**, *21*, 74.

NMR (121.5 MHz, external 85% H_3PO_4) spectra were obtained in solution on a Bruker AC 300 spectrometer equipped with a QNP probehead. The assignment of the aromatic protons for the toluene derivatives was based on a 2D-COSY experiment. ^{183}W NMR spectra were recorded in 10 mm o.d. tubes at 12.5 MHz on a Bruker AC 300 spectrometer equipped with a low-frequency special VSP probehead. The ^{183}W NMR spectrum of the anion **1c** was recorded on an aqueous saturated solution of CsK-**1c**. The ^{183}W NMR spectrum of the anion **2c** was recorded on the lithium salt obtained by dissolution of a sample of K-**2c** in a saturated aqueous solution of $LiClO_4$ and separation of the precipitated $KClO_4$. The ^{183}W NMR spectrum of the anion **3** was recorded on a 0.1 mol·L^{-1} solution of $Li_5[PW_{11}O_{39}\{Ru(dmso)\}]$ (Li-**3**). This solution was obtained by passing the cesium salt through a Li^+-form resin (Amberlyst 15). 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). It must be noted that in the case of compounds CsK-**1b** and Csk-**1d**, big differences appeared between the experimental and calculated elemental analyses. In particular, the methods used by the Service Central d'Analyse led to a systematic underestimation of the W percentage. Besides, after measurement of the oxygen percentage in both compounds, the total sum of the percentages of the different elements which compose CsK-**1b** and CsK-**1d** does not reach 100%. For the photochemical reactions, the solutions were degassed and transferred into a 5 mm o.d. NMR tube equipped with a tight screw cap and were irradiated with a Heraeus TQ150 Z1 lamp doped with gallium iodide (150 W). Electrochemical data were obtained in a 0.5 M sulfate buffer (pH = 3.0). Cyclic voltammetry at a carbon electrode was carried out with a EG&G model 273A potentiostat instrument. A standard three-electrode cell was used, which consisted of the working electrode, an auxiliary platinum electrode, and an aqueous saturated calomel electrode (SCE) equipped with a double junction. All potentials are relative to SCE. The voltage sweep rate is of 100 mV·s^{-1}.

Synthesis of $Cs_{5-x}K_x[PW_{11}O_{39}\{Ru(benzene)(H_2O)\}]$ (CsK-1a). A mixture of $K_7[PW_{11}O_{39}]\cdot14H_2O$ (0.81 g, 0.25 mmol) and of $[Ru(benzene)Cl_2]_2$ (0.07 g, 0.13 mmol) in 12 mL of water was stirred at room temperature for 1 h. CsCl (0.62 g, 3.69 mmol, 15 equiv) was then added, leading to the precipitation of a brown solid, which was separated by filtration and identified as a mixed potassium and cesium salt of **1a** (CsK-**1a**) (yield: 0.76 g). IR (KBr, cm^{-1}): 3081 (w), 1436 (w), 1260 (w), 1094 (m), 1040 (s), 948 (s), 892 (s), 851 (s), 805 (s), 755 (s), 618 (sh), 593 (w), 511 (m), 410 (w), 358 (s). ^1H NMR (D_2O): $\delta = 6.13$ ppm (s, 6H, Ar-*H*). ^{31}P NMR (D_2O): $\delta = -12.24$ ppm (s).

Preparation of the Crystals Used for the X-ray Structural Determination of $Na_4K_4[\{PW_{11}O_{39}\{Ru(benzene)\}\}_2\{WO_2\}]\cdot6H_2O$ (NaK-2a·6H$_2$O). $[Ru(benzene)Cl_2]_2$ (1.5 g, 3.0 mmol) was dissolved in 45 mL of CH_3CN, and 2.7 g of $AgBF_4$ (13.9 mmol) was added to the solution. The mixture was stirred at 35 °C for 2 h, during which a precipitate of AgCl appeared. After removal of the precipitate, the volume of the filtrate was reduced to a third and cooled at -40 °C. Yellow crystals of $[Ru(benzene)(CH_3CN)_3]$-$(BF_4)_2$ were collected (1.00 g, 70%). A mixture of $[Ru(benzene)$-$(CH_3CN)_3](BF_4)_2$ (0.07 g, 0.15 mmol) and $K_7[PW_{11}O_{39}]\cdot14H_2O$ (0.48 g, 0.15 mmol) in 10 mL of water was refluxed for 3 days, after which a new crop of 0.07 g of $[Ru(benzene)(CH_3CN)_3](BF_4)_2$ was added to the solution. After an extra 3 days of reflux, the suspension was filtered. After addition of KCl to the filtrate, slow evaporation of the solution at room temperature led to the formation of a few crystals of NaK-**2a**·6H$_2$O. The presence of sodium cations in the crystals is due to the use, in this specific preparation, of a

sample of $[PW_{11}O_{39}]^{7-}$, which appeared to be a mixed sodium and potassium salt $Na_xK_{7-x}[PW_{11}O_{39}]\cdot14H_2O$. IR (KBr, cm^{-1}) 3088 (w), 1103 (m), 1047 (m), 958 (s), 898 (m), 837 (s), 784 (m), 744 (m), 700 (s), 597 (w), 510 (m), 484 (w), 372 (s), 328 (m). ^1H NMR (D_2O): $\delta = 6.15$ ppm (s, Ar-*H*). ^{31}P NMR (D_2O): $\delta = -12.86$ ppm (s).

Reaction of $K_7[PW_{11}O_{39}]\cdot14H_2O$ with $[Ru(benzene)Cl_2]_2$ in Refluxing Water. A 3.22 g amount of $K_7[PW_{11}O_{39}]\cdot14H_2O$ (1.0 mmol) was dissolved in 25 mL of distilled water. $[Ru(benzene)$-$Cl_2]_2$ (0.25 g, 0.5 mmol) was added to the solution, and the resulting suspension was refluxed for 1 h. The dark brown solution was allowed to cool at room temperature, and an excess of KCl (1.35 g, 20.0 mmol) was added. The solution was stirred for 2 days leading to the precipitation of an orange powder, which was filtered out and washed with 5 mL of cold water and then dried by ethanol and diethyl ether ($m = 1.16$ g). The solid was identified as a mixture of $[PW_{11}O_{39}\{Ru(benzene)(H_2O)\}]^{5-}$ (**1a**) and $[\{PW_{11}O_{39}\{Ru$-$(benzene)\}\}_2\{WO_2\}]^{8-}$ (**2a**) by IR spectroscopy. The **1a**:**2a** ratio after redissolution of the precipitate in D_2O was estimated to ca. 4:1 by analysis with ^{31}P and ^1H NMR spectroscopies.

Synthesis of $Cs_{2.5}K_{0.5}H_2[PW_{11}O_{39}\{Ru(toluene)(H_2O)\}]$ (CsK-1b). A suspension of $K_7[PW_{11}O_{39}]\cdot14H_2O$ (0.76 g, 0.24 mmol) and $[Ru(toluene)Cl_2]_2$ (0.06 g, 0.11 mmol) in 12 mL of water was stirred at room temperature for 3 h. CsCl (0.62 g, 3.69 mmol, 15 equiv) was then added, leading to the precipitation of a brown solid, which was separated by filtration and identified as a mixed potassium and cesium salt of **1b**, $Cs_{2.5}K_{0.5}H_2[PW_{11}O_{39}\{Ru(toluene)(H_2O)\}]$· $5H_2O$ (CsK-**1b**) (yield: 0.63 g, 78%). IR (KBr, cm^{-1}): 3069 (w), 1449 (w), 1372 (w), 1256 (w), 1094 (m), 1040 (s), 947 (s), 892 (s), 851 (s), 804 (s), 755 (s), 626 (sh), 594 (w), 511 (m), 410 (w), 359 (s). ^1H NMR (D_2O): $\delta = 2.48$ (s, 3H, Ar-C*H$_3$*), 5.74 (d, 1H, $^3J = 6.2$ Hz, $C_6H_5CH_3$, H_{ortho}), 5.89 (d, 1H, $^3J = 6.2$ Hz, $C_6H_5CH_3$, H_{ortho}), 5.97 (t, 1H, $^3J = 5.3$ Hz, $C_6H_5CH_3$, H_{para}), 6.06 (t, 1H, $^3J = 5.5$ Hz, $C_6H_5CH_3$, H_{meta}), 6.35 ppm (t, 1H, $^3J = 5.5$ Hz, $C_6H_5CH_3$, H_{meta}). ^{31}P NMR (D_2O): $\delta = -12.09$ ppm (s). UV (H_2O) [λ_{max} (ϵ)]: 419 (1.3 × 10^4), 341 nm (2.6 × 10^4 mol^{-1}·dm^3·cm^{-1}). Anal. Calcd (found) for $C_7H_{22}Cs_{2.5}K_{0.5}O_{45}PRuW_{11}$: C, 2.52 (2.23); H, 0.67 (0.48); Cs, 9.97 (9.27); K, 0.59 (0.58); P, 0.93 (0.99); Ru, 3.03 (2.43); W 60.69 (50.28).

Synthesis of $K_7H[\{PW_{11}O_{39}\{Ru(toluene)\}\}_2\{WO_2\}]$ (K-2b). A mixture of $K_7[PW_{11}O_{39}]\cdot14H_2O$ (1.61 g, 0.5 mmol) and $[Ru(toluene)Cl_2]_2$ (0.14 g, 0.25 mmol) in 25 mL of water was refluxed for 1 h and then cooled to room temperature and filtered on paper. KCl (0.86 g, 11.5 mmol, 23 equiv) was added, leading to the precipitation of a small amount of an orange solid, which appeared to be a mixture of the potassium salts of **1b** and **2b**, in a 1:7 ratio. The solid was then discarded. After a few days, red crystals of K-**2b**, suitable for X-ray crystallography, were collected from the filtrate (yield: 0.10 g, 6%). IR (KBr, cm^{-1}): 1102 (m), 1050 (m), 956 (s), 900 (m), 838 (s), 786 (s), 777 (s), 745 (m), 704 (s), 597 (w), 510 (m), 371 (s), 331 (m). ^1H NMR (D_2O): $\delta = 2.74$ (s, 3H, Ar-C*H$_3$*), 5.38 (d, 1H, $^3J = 5.7$ Hz, $C_6H_5CH_3$, H_{ortho}), 5.90 (d, 1H, $^3J = 5.3$ Hz, $C_6H_5CH_3$, H_{ortho}), 5.97 (t, 1H, $^3J = 5.7$ Hz, $C_6H_5CH_3$, H_{para}), 6.45 (t, 1H, $^3J = 5.9$ Hz, $C_6H_5CH_3$, H_{meta}), 6.49 ppm (t, 1H, $^3J = 5.7$ Hz, $C_6H_5CH_3$, H_{meta}). ^{31}P NMR (D_2O): $\delta = -12.86$ ppm (s).

Syntheses of $Cs_{3.75}K_{0.25}H[PW_{11}O_{39}\{Ru(toluene)(H_2O)\}]$ and $Cs_{5.25}K_{0.25}H_{2.5}[\{PW_{11}O_{39}\{Ru(toluene)\}\}_2\{WO_2\}]$ (CsK-2b). A suspension of $K_7[PW_{11}O_{39}]\cdot14H_2O$ (1.61 g, 0.5 mmol) and of $[Ru(toluene)Cl_2]_2$ (0.14 g, 0.25 mmol) in 25 mL of water was refluxed for 1 h and then cooled to room temperature and filtered on paper. CsCl (2.00 g, 11.9 mmol, 24 equiv) was added, leading

to the formation of an oily brown precipitate **p**. After filtration and separation of the precipitate **p**, the filtrate was allowed to evaporate at room temperature, which sometimes led to the formation of crystals of $Cs_3K_2[PW_{11}O_{39}\{Ru(toluene)(H_2O)\}]$ (space group $P\bar{1}$; $a = 11.400(1)$, $b = 12.643(1)$, $c = 19.954(2)$ Å; $\alpha = 89.444(7)$, $\beta = 85.220(7)$, $\gamma = 65.856(6)$ °; $V = 2614.3(4)$ Å³). The precipitate **p** was redissolved in a minimum of boiling water. The resulting solution was left to cool to room temperature, leading to the formation of an orange solid, which was separated and identified as a mixed potassium and cesium salt of **2b**, $Cs_{5.25}K_{0.25}H_{2.5}$-$[\{PW_{11}O_{39}\{Ru(toluene)\}\}_2\{WO_2\}]\cdot 18H_2O$ (CsK-**2b**) (yield: 0.19 g, 6%). Slow evaporation of the filtrate at room temperature led to a brown solid, containing a mixed potassium and cesium salt of **1b**, $Cs_{3.75}K_{0.25}H[PW_{11}O_{39}\{Ru(toluene)(H_2O)\}]\cdot 8H_2O$ (CsK-**1b**), according to IR and ³¹P NMR spectroscopies, and 8% of a minor species which was detected and characterized by its ³¹P chemical shift ($\delta = -11.66$ ppm). By comparison with the infrared spectrum of the pure crystals of $Cs_3K_2[PW_{11}O_{39}\{Ru(toluene)(H_2O)\}]$, the impurity is characterized by the presence of a shoulder at 1083 cm⁻¹ on the infrared spectrum of the mixture. The number of water molecules of crystallization was proposed on the basis of the chemical analysis for CsK-**1b** and CsK-**2b**. Anal. Calcd (found) for CsK-**1b**, $C_7H_{27}Cs_{3.75}K_{0.25}O_{48}PRuW_{11}$: C, 2.37 (2.06); H, 0.77 (0.76); Cs, 14.07 (13.71); K, 0.28 (0.24); P, 0.87 (1.13); Ru, 2.85 (2.59); W, 57.10 (52.69). Calcd (found) for CsK-**2b**, $C_{14}H_{54.5}$-$Cs_{5.25}K_{0.25}O_{98}P_2Ru_2W_{23}$: C, 2.41 (2.43); H, 0.79 (1.1); Cs, 9.98 (9.97); K, 0.14 (0.15); P, 0.89 (1.14); Ru, 2.89 (2.80); W, 60.48 (57.65).

Synthesis of Cs₅[PW₁₁O₃₉{Ru(p-cymene)(H₂O)}] (Cs-1c). $[Ru(p\text{-}cymene)Cl_2]_2$ (0.31 g, 0.5 mmol) was added to a solution of $K_7[PW_{11}O_{39}]\cdot 14H_2O$ (3.22 g, 1.0 mmol) in 50 mL of water. The resulting suspension was refluxed for 1 h and then filtered on paper. Addition of an excess of CsCl (4.00 g, 23.8 mmol) resulted in the formation of an oily red-orange precipitate and was sometimes followed by the formation of crystals of $Cs_3K_2[PW_{11}O_{39}\{Ru(p\text{-}cymene)(H_2O)\}]\cdot 4H_2O$ (CsK-**1c**·4H₂O), which were analyzed by X-ray crystallography. The oily solid was recrystallized in a minimum of boiling water: thin orange crystals of $Cs_5[PW_{11}O_{39}$-$\{Ru(p\text{-}cymene)(H_2O)\}]\cdot 6H_2O$ (Cs-**1c**·6H₂O) settled in 1 day. They were filtered out and dried with ethanol and diethyl ether (yield: 2.75 g, 79%, based on Ru). IR (KBr, cm⁻¹): 3088 (w), 2965 (w), 2929 (w), 2872 (w), 1095 (m), 1047 (m), 949 (s), 883 (m), 849 (s), 804 (vs), 752 (sh), 714 (sh), 597 (w), 585 (w), 516 (w), 411 (w), 363 (s). ¹H NMR (D₂O): $\delta = 1.35$ (d, 3H, $^3J = 6.9$ Hz, Ar−CH(CH_3)₂), 1.44 (d, 3H, $^3J = 6.8$ Hz, Ar−CH(CH_3)₂), 2.47 (s, 3H, Ar−CH_3), 3.05 (sept, 1H, $^3J = 7.0$ Hz, Ar−CH(CH₃)₂), 5.66 (d, 1H, $^3J = 6.1$ Hz, Ar-H), 5.81 (d, 1H, $^3J = 5.7$ Hz, Ar-H), 5.87 (d, 1H, $^3J = 6.1$ Hz, Ar-H), 6.22 ppm (d, 1H, $^3J = 5.8$ Hz, Ar-H). ³¹P NMR (D₂O): $\delta = -12.05$ ppm (s). ¹⁸³W NMR (saturated aqueous solution): $\delta = -75.8$ (s, 1W), −97.3 (s, 1W), −105.5 (s, 1W), −107.2 (s, 1W), −117.2 (s, 1W), −128.3 (s, 1W), −136,6 (s, 1W), −148.0 (s, 1W), −148.8 (s, 1W), −153.6 (s, 1W), −157.3 ppm (s, 1 W). UV (H₂O) [λ_{max} (ϵ)]: 419 (1.6 × 10⁴), 341 nm (3.4 × 10⁴ mol⁻¹·dm³·cm⁻¹). Anal. Calcd (found) for $C_{10}H_{28}Cs_5O_{46}PRuW_{11}$: C, 3.24 (3.32); H, 0.76 (0.78); Cs, 17.94 (16.25); Ru, 2.59 (2.73); W, 53.01 (54.61).

Synthesis of K₈[{PW₁₁O₃₉{Ru(p-cymene)}}₂{WO₂}] (K-2c). A 0.61 g (1.0 mmol) amount of $[Ru(p\text{-}cymene)Cl_2]_2$ and 0.78 g (4.0 mmol) of AgBF₄ were dissolved in 10 mL of CH₃CN and heated at 40 °C for 2 h. The precipitate of AgCl was then removed and the solvent evaporated. The resulting red oil was dissolved in 10 mL of water, and then the solution was added to a solution of $K_7[PW_{11}O_{39}]\cdot 14H_2O$ (3.22 g, 1.0 mmol) in 20 mL of water. The

mixture was refluxed for 1 day. After filtration of a white solid, a large excess of KCl (2 g, 26.8 mmol) was added to the brown solution. Precipitation of $K_8[\{PW_{11}O_{39}\{Ru(p\text{-}cymene)\}\}_2\{WO_2\}]\cdot$ 15H₂O (K-**2c**·15H₂O) immediately occurred (yield: 1.70 g, 50%, based on {PW₁₁}). Nevertheless, the sample appeared to be contaminated by ca. 3 equiv of residual KCl, as judged by the results of the elemental analysis on the crude product. IR (KBr, cm⁻¹): 1101 (s), 1050 (s), 956 (s), 896 (m), 837 (vs), 795 (sh), 780 (sh), 745 (sh), 705 (s), 514 (m), 372 (s). ¹H NMR (D₂O): $\delta = 1.45$ (d, 3H, $^3J = 6.9$ Hz, Ar−CH(CH_3)₂), 1.62 (d, 3H, $^3J = 6.6$ Hz, Ar−CH(CH_3)₂), 2.77 (s, 3H, Ar−CH_3), 3.48 (sept, 1H, $^3J = 6.8$ Hz, Ar−CH(CH₃)₂), 5.34 (d, 1H, $^3J = 6.1$ Hz, Ar-H), 5.93 (d, 1H, $^3J = 5.9$ Hz, Ar-H), 6.38 (d, 1H, $^3J = 5,6$ Hz, Ar-H), 6.42 ppm (d, 1H, $^3J = 6.2$ Hz, Ar-H). ³¹P NMR (H₂O): $\delta = -12.70$ ppm (s). ¹⁸³W NMR (LiClO₄ saturated aqueous solution): $\delta = -73.5$ (s, 2W), −84.3 (s, 2W), −97.4 (s, 2W), −114.5 (s, 2W), −129.3 (s, 2W), −131.3 (s, 2W), −148.8 (s, 4W), −154.0 (s, 2W), −163.1 (s, 2W), −167.25 (s, 1W, large), −189.7 ppm (s, 2 W). Anal. Calcd (found) for $C_{20}H_{58}Cl_3K_{11}O_{95}P_2Ru_2W_{23}$: C, 3.51 (3.52); H, 0.85 (0.87); P, 0.90 (0.92); K, 6.28 (6.57); Ru, 2.95 (3.09); W, 61.75 (58.60).

Synthesis of Cs₃K₀.₅H₁.₅[PW₁₁O₃₉{Ru(hexamethylbenzene)-(H₂O)}] (CsK-1d). $K_7[PW_{11}O_{39}]\cdot 14H_2O$ (0.48 g, 0.15 mmol) was dissolved in 10 mL of distilled water. [Ru(hexamethylbenzene)-Cl₂]₂ (0.05 g, 0.075 mmol) was added to the solution, and the resulting suspension was refluxed for 1 h. The mixture was then allowed to cool at room temperature. Unreacted [Ru(hexamethyl-benzene)Cl₂]₂ was filtered off, and an excess of solid CsCl was added. Precipitation of an orange microcrystalline powder immediately occurred. The closest formula for the precipitate is $Cs_3K_{0.5}H_{1.5}[PW_{11}O_{39}\{Ru(hexamethylbenzene)(H_2O)\}]\cdot 4H_2O$ (CsK-**1d**·4H₂O), according to the chemical analysis (yield: 0.5 g, 90.6%, based on Ru). IR (KBr, cm⁻¹): 2924 (w), 2856 (w) 1091 (s), 1044 (s), 948 (s), 892 (m), 852 (s), 808 (s), 763 (sh), 723 (sh), 595 (w), 510 (m), 409 (w), 358 (s). ¹H NMR (D₂O): $\delta = 2.29$ ppm (s, Ar−CH_3). ³¹P NMR (H₂O): $\delta = -11.67$ ppm (s). Anal. Calcd (found) for $C_{12}H_{29.5}Cs_3K_{0.5}O_{44}P_1Ru_1W_{11}$: C, 4.18 (3.90); H, 0.86 (0.85); Cs, 11.56 (11.15); P, 0.90 (0.89); K, 0.57 (0.43); Ru, 2.93 (2.43); W, 58.61 (52.50).

Synthesis of Cs₅[PW₁₁O₃₉{Ruᴵᴵ(dmso)}] (Cs-3). DMSO (0.045 mL) was added to a degassed deuterated aqueous solution (2 mL) of $Cs_5[PW_{11}O_{39}\{Ru(p\text{-}cymene)(H_2O)\}]$ (Cs-**1c**) (0.16 g, 0.05 mmol) in a screw-capped 5 mm o.d. NMR tube. Irradiation of the sample for 3 days led to the complete disappearance of **1c**, as monitored by ³¹P and ¹H NMR spectroscopy, and to the formation of $[PW_{11}O_{39}\{Ru^{II}(dmso)\}]^{5-}$ (anion **3**). The formation of a minor byproduct sometimes occurred. This compound was characterized by ³¹P NMR ($\delta = -8.4$ ppm), but the ratio byproduct:[PW₁₁O₃₉-{Ruᴵᴵ(dmso)}]⁵⁻ never exceeded 1:15. The cesium salt of the [PW₁₁O₃₉{Ruᴵᴵ(dmso)}]⁵⁻ anion (Cs-**3**) was isolated by addition of 0.10 g of CsCl to the very dark solution (yield: 0.12 g, 77%, based on Ru). IR (KBr, cm⁻¹): 2925 (w), 1095 (sh), 1066 (s), 1049 (m), 1017 (w), 958 (br), 877 (s), 795 (br), 695 (m), 520 (w), 375 (m). ¹H NMR (D₂O): $\delta = 3.34$ (s, (CH_3)₂SO). ³¹P NMR (H₂O): $\delta = -10.76$ ppm (s). ¹⁸³W NMR (Li₅[PW₁₁O₃₉{Ruᴵᴵ(dmso)}] solution in D₂O): $\delta = 117.5$ (s, 2W), −1.7 (s, 2W), −94.6 (s,2W), −105.3 (s, 1W), −133.0 (s, 2W), −145.2 (s, 2W). Cyclic voltammetry: $E(Ru^{III}/Ru^{II}) = 0.32$ V vs SCE.

Synthesis of Cs₅[PW₁₁O₃₉{Ruᴵᴵ(tmso)}] (Cs-4). Tetramethylene sulfoxide (TMSO) (0.065 mL, 0.065 mmol) was added to a deuterated aqueous solution (2.5 mL) of CsK-**1b** (0.16 g, 0.05 mmol) in a screw-capped 5 mm o.d. NMR tube. The irradiation of the sample for 50 h led to the complete disappearance of **1b**, as

Table 1. Crystal Data for Compounds NaK-**2a**·6H$_2$O, K-**2b**·4H$_2$O, and CsK-**1c**·4H$_2$O

	NaK-**2a**·6H$_2$O	K-**2b**·4H$_2$O	CsK-**1c**·4H$_2$O
formula	C$_{12}$H$_{24}$K$_4$Na$_4$O$_{86}$P$_2$Ru$_2$W$_{23}$	C$_{14}$H$_{24}$K$_7$O$_{84}$P$_2$Ru$_2$W$_{23}$	C$_{10}$H$_{24}$Cs$_3$K$_2$O$_{44}$PRuW$_{11}$
M_r	6262.27	6302.62	3479.58
color	red	red	red
cryst system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/a$
T (K)	ambient	ambient	ambient
a (Å)	13.387(13)	23.130(6)	21.631(6)
b (Å)	19.829(3)	19.726(5)	12.0258(17)
c (Å)	20.249(3)	24.537(8)	21.9892(4)
α (deg)	95.20(1)	90	90
β (deg)	97.82(4)	117.69(2)	95.85(2)
γ (deg)	97.33(3)	90	90
V (Å^3)	5249(5)	9913(5)	5665(2)
Z	2	4	4
μ (cm^{-1})	256.57	272.83	247.34
ρ_{calcd} (g cm^{-3})	3.96	4.22	4.12
$\theta_{min}-\theta_{max}$ (deg)	1−25	2−30	2−30
octants collcd	0, 15; −23, 23; −24, 24	−28, 32; −22, 27; −34, 28	−29, 15; −16, 14; −30, 27
reflcns measd	19 290	57 523	32 088
unique reflcns (R_{int})	18 420 (0.076)	27 144 (0.08)	15 053 (0.09)
obsd reflcns	8070, $(F_o)^2 > 3\sigma(F_o)^2$	9655, $(F_o)^2 > 3\sigma(F_o)^2$	6377, $(F_o)^2 > 3\sigma(F_o)^2$
refined params	668	654	357
R	0.0684	0.0572	0.0820
R_w	0.0744^a	0.0643	0.0914
goodness of fit S	1.0801	1.0885	1.0958
$\Delta\rho$(max/min) (e·Å^{-3})	4.06/−3.70	4.05/−3.66	16.63/−5.84

^{a} Weighting scheme of the form $w = w'[1 - ((|F_o| - |F_c|)/6\sigma(F_o))^2]^2$, with $w' = 1/\Sigma_r A_r T_r(X)$ with coefficients 7.11, −2.40, 5.34 (NaK-**2a**·6H$_2$O), 0.231, 0.161, 0.074 (K-**2b**·4H$_2$O), and 0.546, 0.476, 0.266 (CsK-**1c**·10H$_2$O) for a Chebychev series for which $X = F_c/F_c$(max).

monitored by ^{31}P NMR and ^{1}H NMR, and to the formation of [PW$_{11}$O$_{39}${Ru^{II}(tmso)}]$^{5-}$ (**4**). The cesium salt of the [PW$_{11}$O$_{39}$-{Ru^{II}(tmso)}]$^{5-}$ anion (Cs-**4**) was isolated by addition of 0.70 g of CsCl to the solution, leading to the formation of a dark brown precipitate which was filtered out, washed with diethyl ether, and dried under vacuum (yield: 0.05 g, 35%, based on Ru). IR (KBr, cm^{-1}): 2930 (w), 1101 (sh), 1066 (s), 1047 (m), 959 (br), 878 (s), 789 (br), 698 (m), 591 (w), 512 (w), 372 (m). ^{1}H NMR (D$_2$O): δ = 2.31 (m, 2H, (C*H*$_2$)$_2$(CH$_2$)$_2$SO), 2.47 (m, 2H, (C*H*$_2$)$_2$(CH$_2$)$_2$SO), 3.51 (m, 2H, (CH$_2$)$_2$(C*H*$_2$)$_2$SO), 3.72 (m, 2H, (CH$_2$)$_2$(C*H*$_2$)$_2$SO). ^{31}P NMR (H$_2$O): δ = −10.82 ppm. Cyclic voltammetry: E(Ru^{III}/Ru^{II}) = 0.35 V vs SCE.

Synthesis of Cs$_5$[PW$_{11}$O$_{39}${Ru^{II}(Ph$_2$SO)}] (Cs-5). CsK-**1b** (0.09 g, 0.027 mmol) and diphenyl sulfoxide (0.07 g, 0.35 mmol) were dissolved in 1.7 mL of D$_2$O in a sealed 5 mm o.d. NMR tube. The irradiation of the suspension for 42 h led to the complete disappearance of **1b**, as monitored by ^{31}P NMR and ^{1}H NMR, and to the formation of [PW$_{11}$O$_{39}${Ru^{II}(Ph$_2$SO)}]$^{5-}$ (**5**). The cesium salt of the [PW$_{11}$O$_{39}${Ru^{II}(Ph$_2$SO)}]$^{5-}$ anion (Cs-**5**) was isolated by addition of 0.42 g of CsCl to the solution, leading to the formation of a dark brown precipitate, which was filtered out, washed with acetone and diethyl ether, and dried under vacuum (yield: 0.05 g, 57%, based on Ru). IR (KBr, cm^{-1}): 3058 (w), 1070 (s), 1045 (m), 964 (br), 881 (s), 795 (br), 697 (m), 591 (w), 562 (w), 513 (w), 376 (m). ^{1}H NMR (D$_2$O): δ = 7.58 (m, 6H, Ar-*H*, *H*$_{meta}$, *H*$_{para}$), 7.74 ppm (m, 4H, Ar-*H*, *H*$_{ortho}$). ^{31}P NMR (D$_2$O): δ = −10.79 ppm (s). Cyclic voltammetry: E(Ru^{III}/Ru^{II}) = 0.36 V vs SCE.

Crystallographic Data for NaK-2a·6H$_2$O, K-2b·4H$_2$O, and CsK-1c·4H$_2$O. Crystal structure data for NaK-**2a**·6H$_2$O, K-**2b**·4H$_2$O, and CsK-**1c**·4H$_2$O are summarized in Table 1. Data for NaK-**2a**·6H$_2$O were recorded at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Data for K-**2b**·4H$_2$O and CsK-**1c**·4H$_2$O were recorded at room temperature on a Kappa-CCD Bruker diffractometer with graphite monochromated Mo Kα radiation (λ = 0.710 73 Å) and using the ω-scan technique. All crystals were

mounted on glass fibers and sealed with an epoxy cement, except for NaK-**2a**·6H$_2$O, which was set in a Lindeman tube and coated with paraffin oil. Lattice parameters and the orientation matrix were obtained from a least-squares fit of 25 automatically centered reflections in the range 11−11.3° for NaK-**2a**·6H$_2$O, 4.1− 16.8° for K-**2b**·4H$_2$O, and 3.2−21.9° for CsK-**1c**·4H$_2$O. For NaK-**2a**·6H$_2$O, references were periodically monitored for intensity and orientation control. Intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied.[20] For all complexes, all the measured independent reflections were used in the analysis, and only those with $I > 3\sigma(I)$ were used in calculations. The structures were solved by direct methods and subsequent electron density maps. They were refined with the full-matrix least-squares technique on F using the SHELXS-97[21] and CRYSTALS programs.[22] Only the tungsten, ruthenium, and phosphorus atoms were refined anisotropically, and hydrogen atoms were not included in the refinements. Molecular structures were drawn with CAMERON[23] and are shown in Figures 1−3. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC 245934−245936. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, +44-1223/336-033; E-mail, deposit@ccdc.cam.ac.uk).

Results and Discussion

Syntheses of the {Ru(arene)}$^{2+}$ Derivatives. By reaction of K$_7$[PW$_{11}$O$_{39}$]·14H$_2$O and various [Ru(arene)Cl$_2$]$_2$ dimeric

(20) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.
(21) Sheldrick, G. M. *SHELXS-97*; University of Göttingen: Göttingen, Germany, 1997.
(22) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS*; Chemical Crystallography Laboratory, University of Oxford: Oxford, U.K., 1996.
(23) Pearce, L. J.; Watkin, D. J. *CAMERON*; Chemical Crystallography Laboratory, University of Oxford: Oxford, U.K., 1996.

Table 2. Distribution of Type-**1** and Type-**2** Compounds in Water after 1 h of Reflux

	benzene	toluene	*p*-cymene	hexamethylbenzene
type-**1** (%)	75	85	100	100
type-**2** (%)	25	15	0	0

precursors in water, two different products were formed in solution: $[PW_{11}O_{39}\{Ru(arene)(H_2O)\}]^{5-}$ (type-**1** complex) and $[\{PW_{11}O_{39}\{Ru(arene)\}\}_2\{WO_2\}]^{8-}$ (type-**2** complex). The proportion of **1** to **2** after a prolonged reflux is strongly dependent on the arene (Table 2).

With the less bulky arenes (benzene and toluene), both compounds **1** and **2** were obtained after 1 h of reflux in the ratio ca. 3:1 for benzene and 6:1 for toluene in solution, as determined by ³¹P NMR spectroscopy. Isolation of type-**1** complexes was possible for both arenes, by reacting [Ru(arene)Cl₂]₂ with K₇[PW₁₁O₃₉]·14H₂O at room temperature. Indeed, in the case of benzene, the mixed potassium and cesium salt (CsK-**1a**) was isolated by addition of an excess of CsCl to the solution after 1 h of reaction at room temperature. In the same way, in the case of toluene, addition of an excess of CsCl to the solution after 3 h of reaction at room temperature allowed the isolation of the mixed cesium and potassium salt CsK-**1b**. Isolation of type-**2** complexes is more difficult, insofar as the compounds were never observed alone in solution. In the case of benzene, we were not able to establish a procedure to isolate the anion **2a** in the solid state. Only once did we by serendipity isolate crystals of Na₄K₄[{PW₁₁O₃₉{Ru(benzene)}}₂{WO₂}]·6H₂O (NaK-**2a**·6H₂O), suitable for an X-ray analysis, by reaction in refluxing water of [Ru(benzene)(CH₃CN)₃](BF₄)₂ with a sample of Na$_x$K$_{7-x}$[PW₁₁O₃₉]·14H₂O for 3 days. On the contrary, in the case of toluene, it was possible to separate the anions **1b** and **2b** in a low yield. The addition after 1 h of reflux of respectively potassium chloride or cesium chloride, followed by further treatments (see Experimental Section), led to the crystallization or precipitation of potassium or mixed potassium and cesium salts of **2b**. The crystal structure of the anion **2b** was determined after an X-ray analysis of one crystal of the potassium salt (K-**2b**·4H₂O).

With the more bulky arenes (*p*-cymene and hexamethylbenzene), only type-**1** complexes are formed after 1 h of reflux. These compounds can be precipitated as cesium or mixed potassium and cesium salts (Cs-**1c** for *p*-cymene and CsK-**1d** for hexamethylbenzene) and recrystallized in hot water. Cs-**1c** and CsK-**1d** are remarkably stable in water since no decomposition of the species is observed after 2 days of reflux. On the contrary, the behavior of **1c** and **1d** in the mother liquor is quite different: indeed, when the heating of the solution exceeds 1 day, different byproducts appear, as shown by ³¹P NMR spectroscopy. Among these products, only type-**2** complexes [{PW₁₁O₃₉{Ru(arene)}}₂{WO₂}]⁸⁻ could be identified by ³¹P NMR ($\delta = -12.70$ ppm for *p*-cymene, and $\delta = -12.48$ ppm for hexamethylbenzene), even though they remain in both cases a minor component in such conditions. However, unlike in the case of toluene, the subsequent addition of potassium chloride to the solution did not allow us to obtain the pure type-**2** compound, since it led to the coprecipitation of the potassium salts of **1** and

2. In the case of *p*-cymene, we were able to isolate a pure potassium salt of **2c** using [Ru(*p*-cymene)(CH₃CN)₃](BF₄)₂ instead of [Ru(*p*-cymene)Cl₂]₂ and refluxing for 1 day. However, the crystals obtained with this method were not suitable for X-ray crystallography.

Experimental Conditions for the Photolysis of Complexes 1. Decoordination of arenes upon UV irradiation of (η^6-arene)Ru^{II}-containing complexes is well documented.[24] This led us to explore the potential of complexes **1** for the synthesis of nonorganometallic ruthenium derivatives of [PW₁₁O₃₉]⁷⁻. UV irradiation of a deuterated aqueous solution of **1b** or **1c** in the presence of an excess of DMSO was followed by ¹H and ³¹P NMR spectroscopy, which showed the disappearance of **1** along with the formation of $[PW_{11}O_{39}\{Ru^{II}(dmso)\}]^{5-}$ (**3**). The latter was identified by its characteristic signals in ¹H (3.34 ppm) and ³¹P (−10.76 ppm) NMR spectroscopy[9] and by cyclic voltammetry ($E(Ru^{III}/Ru^{II}) = 0.32$ V vs SCE). It was precipitated as a cesium salt (Cs-**3**) by addition of CsCl. The tetramethylene sulfoxide (Cs-**4**) and diphenyl sulfoxide (Cs-**5**) analogues of Cs-**3** were obtained in the same way, using TMSO and Ph₂SO in place of DMSO.

A qualitative study of the formation of **3** from **1** was done. The reaction rate increases with the temperature. Formation of **3**, however, does not occur in the absence of irradiation. Not unexpectedly, the choice of the glassware acted upon the rate of decomplexation: transformation of **1b** (**1c**) was complete within 8 (16) h in quartz glassware instead of several days in standard glassware, but this higher efficiency was reached at the expense of selectivity. Indeed, ³¹P and ¹H NMR spectroscopies showed the formation of other products along with **3**: although some free dimethyl sulfide was also characterized, the known complex [PW₁₁O₃₉-{Ru^{II}(SMe₂)}]⁵⁻ was not detected.[9] The cause of the formation of dimethyl sulfide remains unclear, so as the nature of the phosphorus-containing byproducts.

Several experiments revealed that strictly degassed solutions should be used to avoid the oxidation of some Ru^{II} centers into paramagnetic Ru^{III}. The formation of a small amount of oxidized species was first proved by ¹⁸³W NMR since we observed in that case the broadening of some peaks on the NMR spectrum. Indeed, in paramagnetic species, the nuclear relaxation rate increases dramatically as the distance to the paramagnetic center decreases, resulting in a severe broadening of the NMR signals. Moreover these signals exhibit large paramagnetic shifts, either to high or low frequencies, and outside the normal spectral range of diamagnetic species. When the paramagnetic species is present as a minor compound in equilibrium (rapid exchange) with a major diamagnetic one, the spectrum only changes with respect to that of the pure diamagnetic species only by the broadening of the signals.[25] The closest nuclei to the dia/paramagnetic center are, in that case, the most affected by this.

(24) (a) Gill, T. P.; Mann, K. R. O*rganometallics* **1982**, *1*, 485. (b) Karlen, T.; Hauser, A.; Ludi, A. *Inorg. Chem.* **1994**, *33*, 2213.
(25) Kozik, M.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1986**, *108*, 7627.
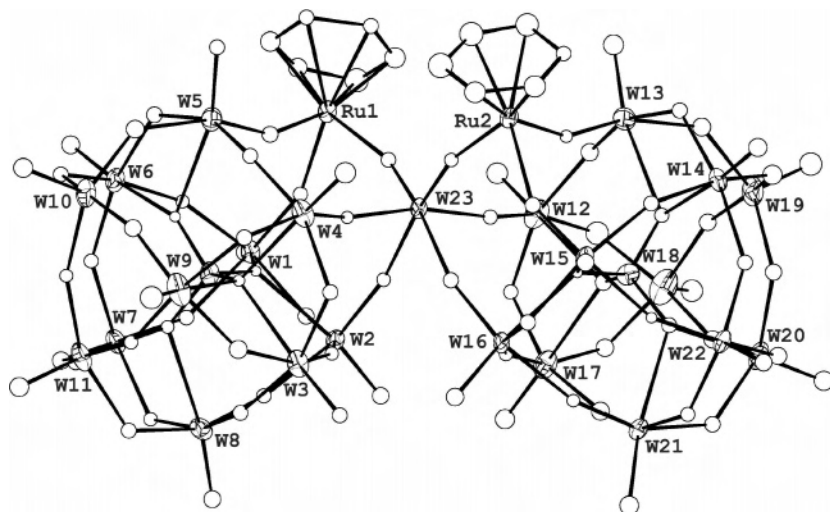
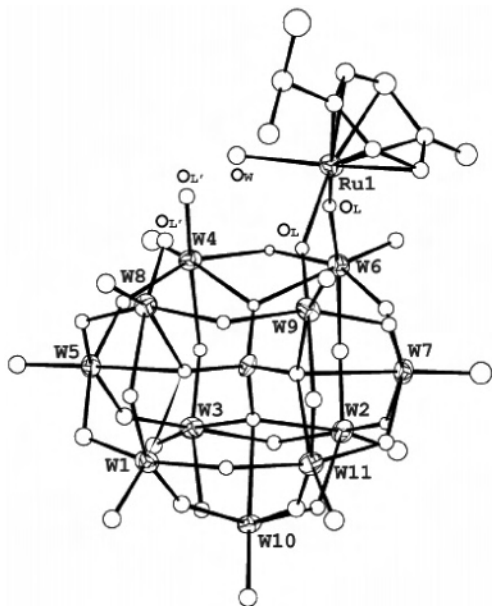**Figure 1.** Molecular structure of the $[\{PW_{11}O_{39}\{Ru(benzene)\}\}_2\{WO_2\}]^{8-}$ anion **2a**.
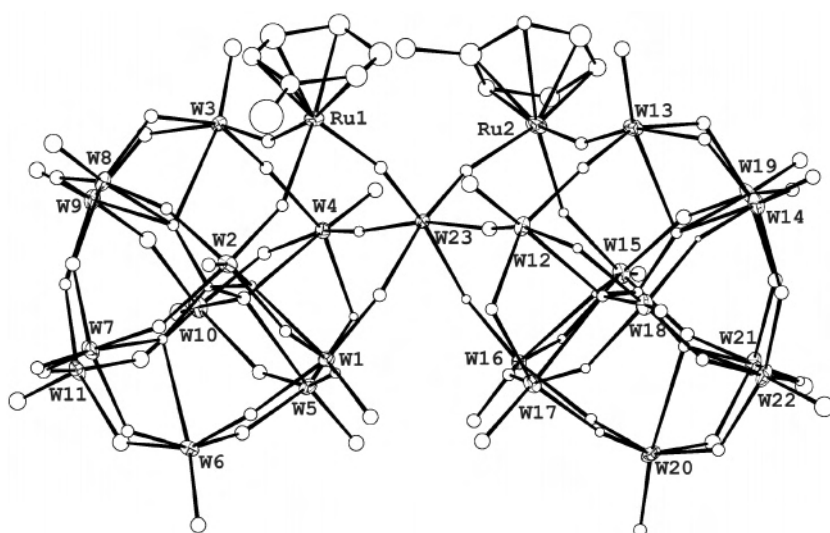
Figure 2. Molecular structure of the $[\{PW_{11}O_{39}\{Ru(toluene)\}\}_2\{WO_2\}]^{8-}$ anion **2b**.

Irradiation of **1** in pure D_2O, i.e. in the absence of DMSO, leads to a mixture of products, according to ^{31}P NMR spectroscopy. The major product could be identified as $[PW_{11}O_{39}\{Ru^{II}(H_2O)\}]^{5-}$ previously described by Rong and Pope.[9] However, while the observed chemical shift (-8.7 ppm) is in agreement with that reported for $[PW_{11}O_{39}-\{Ru^{II}(H_2O)\}]^{5-}$ at pH 3 (-8.7 ppm), the signal is much broader ($\Delta\nu_{1/2} = 110$ Hz) than expected ($\Delta\nu_{1/2} = 2.6$ Hz).[9] This could indicate a fast exchange between the diamagnetic $[PW_{11}O_{39}\{Ru^{II}(H_2O)\}]^{5-}$ and the paramagnetic $[PW_{11}O_{39}-\{Ru^{III}(H_2O)\}]^{4-}$ formed (in small amount) by oxidation of the quite oxygen-sensitive Ru^{II} product.

Crystal Structures of NaK-2a·6H₂O, K-2b·4H₂O, and CsK-1c·4H₂O. Compounds $Na_4K_4[\{PW_{11}O_{39}\{Ru(benzene)\}\}_2-\{WO_2\}]\cdot 6H_2O$ (NaK-**2a**·6H₂O) (Figure 1), $K_7H[\{PW_{11}O_{39}-\{Ru(toluene)\}\}_2\{WO_2\}]\cdot 4H_2O$ (K-**2b**·4H₂O) (Figure 2), and $Cs_3K_2[PW_{11}O_{39}\{Ru(p\text{-cymene})(H_2O)\}]\cdot 4H_2O$ (CsK-**1c**·4H₂O) (Figure 3) were characterized by X-ray crystallography. NaK-**2a**·6H₂O crystallizes in the triclinic $P\bar{1}$ space group. The asymmetric unit contains one anion, eight cations, and six molecules of water, all in general positions. K-**2b**·4H₂O crystallizes in the monoclinic $P2_1/c$ space group. The

asymmetric unit contains one anion, seven potassium cations, and four molecules of water, all in general positions. CsK-**1c**·4H₂O crystallizes in the monoclinic $P2_1/a$ space group. The asymmetric unit contains one anion, four molecules of water, three cesium cations, and three potassium cations, two of them with 50% occupancy; all atoms are in general positions.

The anion **1c** consists on a lacunary $[PW_{11}O_{39}]^{7-}$ anion supporting a $\{Ru(p\text{-cymene})\}^{2+}$ fragment which is only bound to two oxygen atoms O_L of the lacuna. The Ru^{II} cation achieves an 18-electron configuration through coordination to the oxygen atom O_W of a water molecule. Furthermore, the water molecule is involved in hydrogen bonds with the two uncoordinated oxygen atoms $O_L{}'$ of the lacuna as characterized by the two short $O_W\cdots O_L{}'$ distances (respectively 2.63(4) and 2.59(4) Å). It is noteworthy that, for **1c**, the coordination of $\{Ru(p\text{-cymene})\}^{2+}$ onto the lacuna leads to the loss of the C_s symmetry of the parent anion $[PW_{11}O_{39}]^{7-}$. Indeed, the ruthenium fragment in **1c** is bound to two chemically unequivalent oxygen atoms: the first one belongs to a complete $\{W_3O_{13}\}$ triad, while the second one is part of the lacunary $\{W_2O_{12}\}$ moiety. Accordingly, the

Figure 3. Molecular structure of the [PW$_{11}$O$_{39}${Ru(*p*-cymene)(H$_2$O)}]$^{5-}$ anion **1c**.

anion **1c** is chiral, and as the synthesis is not enantioselective, both enantiomers are obtained and are actually present in the crystal, because of the existence of an inversion center in the $P2_1/a$ space group.

The coordination mode of the organometallic unit in **1** is reminiscent of that observed in several supported complexes derived from lacunary Lindqvist-type polyoxometalates, e.g. [{Ru(arene)}$_2$M$_5$O$_{16}${Ru(arene)(H$_2$O)}] (arene = C$_6$Me$_6$, M = Mo or W),[17e] [Mo$_5$O$_{13}$(OMe)$_4$(NO){Rh(C$_5$Me$_5$)(H$_2$O)}]$^{2-}$,[26] and [Mo$_5$O$_{13}$(OMe)$_4$(NO){M(CO)$_3$(H$_2$O)}]$^{2-}$ (M = Mn, Re).[27]

The anions **2a,b** are constituted from the assembly of two [PW$_{11}$O$_{39}${Ru(arene)}]$^{5-}$ units connected through a *cis*-dioxo {WO$_2$}$^{2+}$ fragment. The overall symmetry of the oxoanion is C_2, the binary axis being located in the bisecting plane of the {WO$_2$}$^{2+}$ group. However, in the crystal, while the C_2 axis is still present in **2a**, a nonequivalency between the two toluene ligands appears in the structure of K-**2b**·4H$_2$O, leading to the loss of the element of symmetry. [Nevertheless, in solution, the toluene ligands become equivalent.] It is noteworthy that, in type-**2** complexes, the environment around the tungsten atom W$_{23}$ of the {WO$_2$}$^{2+}$ group is strongly distorted, compared to that of the tungsten atoms of the {PW$_{11}$O$_{39}$} subunits. The binding mode of each {Ru(arene)}$^{2+}$ group in type-**2** complexes is essentially the same as in **1a**, the main difference being that the ruthenium is linked to an oxo ligand of the {WO$_2$}$^{2+}$ group instead of the water molecule. However, despite this difference, the geometric characteristics of the Ru−O−W bridges are similar: the Ru−O distances fall in the range 2.03(4)−2.08(4) Å for **1c** and 2.00(3)−2.14(3) for **2a**, while the Ru−O−W angles for both compounds are all in the range 150.3(17)−161.3(17)°.

(26) Villanneau, R.; Proust, A.; Robert, F.; Villain, F.; Verdaguer, M.; Gouzerh, P. *Polyhedron* **2003**, *22*, 1157.
(27) Villanneau, R.; Proust, A.; Robert, F.; Gouzerh, P. *Chem.−Eur. J.* **2003**, *9*, 1982.

Table 3. Infrared Data (cm⁻¹) for the Anions **1a−d** and **2a−c**

	[PW₁₁O₃₉]⁷⁻	1a	1b	1c	1d	2a	2b	2c
ν(PO)	1086	1094	1094	1095	1091	1103	1102	1101
	1045	1040	1040	1047	1044	1047	1050	1050
ν(W=O$_t$)	952	948	947	949	948	958	956	956
ν(W−O$_b$)	904	892	892	883	892	898	900	896
	861	851	851	849	852	837	838	837
	808	805	804	804	808	784	786	795
	735	755	755	752	763		777	780
		618	626	714	723	744	745	745
		593	594	597	595	700	704	705
	511	511	511	516	510	510	510	514
		410	410	411	409			
	360	358	359	363	358	372	371	372

The families of complexes **1** and **2** described above are rare examples of well crystallographically characterized supported metallic derivatives of the lacunary [α-XW$_{11}$O$_{39}$]$^{n-}$ anions. It must be noted that the structural types of type-**1** complexes and [XW$_{11}$O$_{39}${Ru^{II}(dmso)$_3$(H$_2$O)}]$^{n-}$ (X = Si, Ge, n = 6; X = P, n = 5)[15,28] are identical with respect to the central heteroatom and to the Ru^{II} fragments bound to the polyanion. The side-on coordination mode of an electrophilic fragment onto the lacuna of the anion [PW$_{11}$O$_{39}$]$^{7-}$ had also been described in the phosphonate derivative [{PhPO}$_2$PW$_{11}$O$_{39}$]$^{3-}$, which presented a disordered structure because of the location of the anion on a symmetry element of the crystal.[29]

Infrared Spectra. The IR spectra of complexes **1−5** display the characteristic features of subunits which derive from the Keggin structure (Table 3). With respect to the lacunary anion [PW$_{11}$O$_{39}$]$^{7-}$, the splitting of the ν(P−O) band is not significantly reduced in **1** and **2** ($\Delta\nu$(P−O) ≈ 50 cm^{-1}), contrary to [PW$_{11}$O$_{39}${Ru(dmso)}]$^{5-}$ ($\Delta\nu$(P−O) = 23 cm^{-1}). This is not surprising as Ru does not interact with the central PO$_4$ unit in either **1** or **2**. Indeed, d^6 *fac*-ML$_3$ fragments such as {Ru(η^6-arene)}$^{2+}$ are not complementary to monovacant Keggin anions. The formation of [PW$_{11}$O$_{39}${ML$_3$}]$^{n-}$ species where M would be incorporated into the polyanion is thus unlikely and, in fact, has not been observed. For complexes **1** and **2**, the number of bands due to stretching vibrations involving bridging oxo ligands is larger than in [PW$_{11}$O$_{39}$]$^{7-}$, which is consistent with the symmetry lowering from C_s to C_1 and the presence of dissymmetric W−O$_b$−Ru bridges. This leads to characteristic patterns which are clear fingerprints of **1** and **2**. On the contrary, the higher symmetry of [PW$_{11}$O$_{39}${Ru(dmso)}]$^{5-}$ (**3**) results in considerable simplification of its IR spectrum, despite the existence of W−O$_b$−Ru bonds.

NMR Spectra. According to the crystal structures of complexes **1** and **2**, the ^{1}H NMR spectra of **1** and **2** should display several signals owing to the dissymmetrical grafting of the {Ru(arene)}$^{2+}$ units. Actually, only one signal is observed for **1a** and **2a**, which indicates fast rotation of the C$_6$H$_6$ ligand around the C_6 axis in solution, as it usually observed for η^n-C$_n$H$_n$ ligands. A single signal is also observed for **1d**, which indicates equivalence of the six methyl groups (δ = 2.29 ppm), due to rapid rotation. However, because of

(28) Laurencin, D.; Villanneau, R.; Gérard, H.; Proust, A. To be published.
(29) Kim, G. S.; Hagen, K. S.; Hill, C. L. *Inorg. Chem.* **1992**, *31*, 5316.
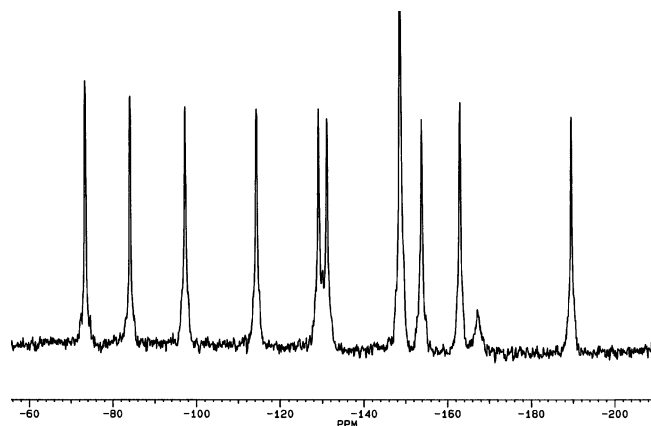
Figure 4. ^{183}W NMR spectrum of an aqueous solution of the lithium salt of [{PW$_{11}$O$_{39}${Ru(p-cymene)}}$_2${WO$_2$}]$^{8-}$ (**2c**) (see Experimental Section).

the side-on coordination of the {Ru(arene)}$^{2+}$ moiety, all aromatic protons remain nonequivalent in **1b,c**, giving rise to respectively five and four ^{1}H signals.

The ^{31}P NMR spectra have been systematically recorded to check the purity of any sample. The chemical shifts for **1** (from −11.65 to −12.24 ppm) are higher than for **2** (from −12.48 to −12.86 ppm). In addition, they are arene dependent: the less bulky the arene, the lower the chemical shift is. More generally, all signals for both series of complexes are shifted toward lower frequency with respect to the free [α-PW$_{11}$O$_{39}$]$^{7-}$ anion but also to [PW$_{11}$O$_{39}${Ru^{II}(dmso)}]$^{5-}$ in which the lacuna of the [PW$_{11}$O$_{39}$]$^{7-}$ unit appeared to be filled by the Ru^{II} cation.

The ^{183}W NMR spectrum of **1c** was recorded on an aqueous solution of the cesium salt. Due to the low solubility of Cs-**1c**, the spectrum was not well defined; nevertheless it unambiguously showed 11 lines, which is in agreement with the asymmetric grafting of the {Ru(arene)}$^{2+}$ fragment onto the [α-PW$_{11}$O$_{39}$]$^{7-}$ unit. Attempts to replace Cs$^+$ by Li$^+$ or Na$^+$ to increase the solubility resulted in the partial transformation of **1c** into **2c**. The ^{183}W NMR spectrum of **2c** was recorded on a solution prepared by addition of K-**2c** to a saturated aqueous solution of LiClO$_4$, followed by filtration of precipitated KClO$_4$. The spectrum consists of a 11-line pattern with approximate relative intensities 2:2:2:2:2:2:(2 + 2):2:2:1:2 (Figure 4). It agrees with the C_2 symmetry of the whole anion, the C_2 axis passing through W$_{23}$. The signal of relative intensity 1 is unambiguously assigned to the unique tungsten atom of the {WO$_2$}$^{2+}$ unit, and it appears markedly broader than the other ones. This can be related to the lower local symmetry of the tungsten atom (C_{2v} instead of ca. C_{4v} for the tungsten atoms in the [PW$_{11}$O$_{39}$]$^{7-}$ framework). The 10 other signals correspond to the tungsten atoms of the {PW$_{11}$O$_{39}$} moiety, with an accidental degeneracy of two of the signals with relative intensity of 2. No attempt was made to assign these lines.

Thermal vs Photochemical Behavior of 1. The expected redox chemistry and catalytic activity of noble metal-containing heteropolyoxotungstates, especially ruthenium-containing species, have given an impetus to the study of these compounds.[9,11,12] The observation that organometallic

oxides are readily formed by self-assembly reactions between [Ru(arene)Cl$_2$]$_2$ and simple molybdates or tungstates in various solvents, including water, led us to extend these reactions to heteropolyoxometalates. We have found that [Ru(arene)Cl$_2$]$_2$ reacts with [α-PW$_{11}$O$_{39}$]$^{7-}$ to give the complexes [PW$_{11}$O$_{39}${Ru(arene)(H$_2$O)}]$^{5-}$ (**1**) and [{PW$_{11}$O$_{39}$-{Ru(arene)}}$_2$WO$_2$]$^{8-}$ (**2**). The formation of **1** likely occurs through reaction of the nucleophilic polyanion [PW$_{11}$O$_{39}$]$^{7-}$ with the electrophilic cations [Ru(arene)Cl(H$_2$O)$_2$]$^+$ or [Ru(arene)(H$_2$O)$_3$]$^{2+}$ arising from hydrolysis of [Ru(arene)-Cl$_2$]$_2$.[30] The formation of **2** requires additional tungstate, which is provided by degradation of part of [PW$_{11}$O$_{39}$]$^{7-}$ units. During the course of the study, we showed that the evolution of **1** into **2** in the mother liquor was hindered by increasing the bulkiness of the arene. For example, after 1 h of reflux, no presence of **2** was detected for bulky arenes such as p-cymene or hexamethylbenzene (Table 2), and 1 whole day of reflux was necessary to observe the presence of **2c** or **2d** in the mother liquor. This could be due to the fact that the formation of **2** requires the bringing together of two [PW$_{11}$O$_{39}${Ru(arene)(H$_2$O)}]$^{5-}$ ions to form a species in which the two {Ru(arene)}$^{2+}$ moieties are close to one another. It seems clear that the bulkier the arene is, the harder it will be to find a way of approaching the type **1** complexes which minimizes the steric repulsion between the arenes.

As the ruthenium center in **1** is coordinatively and electronically saturated, its participation in a catalytic transformation would be facilitated by an initial activation. Indeed, during a catalytic cycle, the transformation of the substrate into the product requires, temporarily at least, the release of one (or more) coordination site(s) on the metal, to allow the coordination of the substrate. Complexes **1** were found to be fairly thermally stable in aqueous solutions, except for the (partial) transformation in **2** observed in the mother liquor. Since a simple thermal activation of the complex did not seem efficient, we considered the possibility of releasing, simultaneously, three coordination sites on the ruthenium, by using a photochemical displacement of the arene. Indeed the photolabilization of the coordinated arene in various ruthenium complexes has been reported[24] and used for synthetic purposes, such as the formation of [Ru(H$_2$O)$_6$]$^{2+}$ by irradiation of [Ru(arene)(H$_2$O)$_3$]$^{2+}$ in water,[31] and the generation of catalytically active species in photoinduced ring-opening metathesis polymerization (PROMP)[32] and ring-closing metathesis (RCM).[33] The UV spectra of complexes **1b,c** both present two bands (341 and 419 nm) which were attributed to charge-transfer transitions by comparison with the spectrum of [Ru(C$_6$H$_6$)(H$_2$O)$_3$]$^{2+}$.[31] According to the literature, irradiation of the compounds at such wavelengths should favor the decoordination of the arene. This was indeed observed: the use of the Heraeus TQ150 Z1, whose emission

(30) Zelonka, R. A.; Baird, M. C. *Can. J. Chem.* **1972**, *50*, 3063.

(31) Weber, W.; Ford, P. C. *Inorg. Chem.* **1986**, *25*, 1088.

(32) (a) Karle, T.; Ludi, A.; Mühlebach, A.; Bernhard, P.; Pharisa, C. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 1665. (b) Van der Schaaf, P. A.; Hafner, A.; Mühlebach, A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1845.

(33) (a) Picquet, M.; Bruneau, C.; Dixneuf, P. H. *Chem. Commun.* **1998**, 2249. (b) Fürstner, A.; Ackermann, L. *Chem. Commun.* **1999**, 95.

profile displays two strong lines with wavelengths at 417 and 366 nm, was successful, even though the emission line does not quite correspond to the maximum of absorption of the highest energy band ($\lambda = 341$ nm), which could have been more interesting to irradiate.[31]

UV irradiation of [PW$_{11}$O$_{39}${Ru(arene)(H$_2$O)}]$^{5-}$ (arene = toluene, *p*-cymene) in aqueous solution in the presence of DMSO provides a new synthetic route to [PW$_{11}$O$_{39}${Ru-(dmso)}]$^{5-}$ which adds further to those previously described: Pope's group synthesized **3** by heating a solution of [PW$_{11}$O$_{39}${Ru^{II}(H$_2$O)}]$^{5-}$ in the presence of DMSO,[9] whereas Bonchio's group obtained the complex by reacting [RuCl$_2$-(dmso)$_4$] with [PW$_{11}$O$_{39}$]$^{7-}$ in water at 200 °C under microwave irradiation.[12] Even though this mode of synthesis of **3** is not as interesting as that proposed by Bonchio in terms of time of reaction and number of steps, in principle it should give access, like in the case of Pope, to the family complexes of the type [PW$_{11}$O$_{39}$(Ru^{II}L)]$^{n-}$, and we have indeed extended this approach to other ligands such as TMSO, Ph$_2$SO, and H$_2$O. The main difference of the approach presented in this work, compared to that described by Pope, is that it avoids the synthesis and subsequent reduction of the precursor [PW$_{11}$O$_{39}${Ru^{III}(H$_2$O)}]$^{4-}$, necessary for obtaining most [PW$_{11}$O$_{39}${Ru(L)}]$^{5-}$ derivatives.

Conclusion. Throughout this study, we have described the easy formation of organometallic derivatives of the monovacant α-[PW$_{11}$O$_{39}$]$^{7-}$ anion by bonding {Ru(arene)}$^{2+}$ cations (arene = benzene, toluene, *p*-cymene, hexamethyl-benzene) to the oxygen atoms of the lacuna of the polyoxometalate. Two families of compounds were obtained by reaction of K$_7$[PW$_{11}$O$_{39}$]·14H$_2$O with [Ru(arene)Cl$_2$]$_2$, which both result of the association of [PW$_{11}$O$_{39}${Ru(arene)}]$^{5-}$ subunits. The formation of such complexes once again underscores that the organometallic [Ru(arene)Cl$_2$]$_2$ compounds are convenient precursors for the synthesis of ruthenium derivatives of heteropolytungstates. The nature of the arene ligand plays a role in the formation of such compounds, since bulky arene ligands appeared to disfavor the formation of the dimeric [{PW$_{11}$O$_{39}${Ru(arene)}}$_2$-{WO$_2$}]$^{8-}$-type anions. Furthermore, we have shown that the Ru^{II} cation can go from a side-on coordination mode involving only two oxygen atoms of the lacuna to a complete integration into the structure, involving the five oxygen atoms: this process occurs after the photolabilization of the arene of [PW$_{11}$O$_{39}${Ru(toluene)(H$_2$O)}]$^{5-}$ and [PW$_{11}$O$_{39}${Ru-(*p*-cymene)(H$_2$O)}]$^{5-}$, in the presence of a coordinating ligand such as DMSO.

Supporting Information Available: X-ray crystallographic files in CIF format for compounds NaK-**2a**·6H$_2$O, K-**2b**·4H$_2$O, and CsK-**1c**·4H$_2$O, a ^{183}W NMR spectrum of CsK-**1c**, and a cyclic voltamogram of compound Cs-**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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