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Rhodium Derivatives of Lacunary Heteropolytungstates Illustrate Metalloporphyrin Analogies. Reductive Dimerization to Rh_2-Linked Keggin Moieties

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Abstract: The heteropolyanion $[PW_{11}O_{39}RhCl]^{5-}$ (**1-Cl**) was synthesized by hydrothermal reaction of $[PW_{11}O_{39}]^{7-}$ and $RhCl_3$ at 150 °C for 20 h. The tetramethylammonium salt of **1-Cl** was characterized by elemental analysis, ^{31}P and ^{183}W NMR, and solution molecular weight determination by ultracentrifugation (found 2744 ± 63, calcd 2816). The cyclic voltammogram of **1-Cl** shows an irreversible reduction wave at −0.45 V vs Ag/AgCl, and controlled potential reduction at −0.5 V generates the dimeric metal−metal bonded species $[(PW_{11}O_{39}Rh)_2]^{10-}$ (**2**). The composition and structure of **2** have been confirmed by elemental analysis of the cesium salt, analytical ultracentrifugation (ionic weight 5821 ± 186, calcd 5561), P and W NMR, and a limited structural analysis of the potassium salt, which revealed a Rh−Rh bond length of 2.52(2) Å ($K_{10}[(PW_{11}O_{39}Rh)_2]\cdot xH_2O$, triclinic, $P\bar{1}$; $a = 12.703(6)$, $b = 17.868(8)$, and $c = 19.131(9)$ Å; $\alpha = 96.56(2)$, $\beta = 97.12(2)$, and $\gamma = 91.318(33)°$; $Z = 2$; $V = 4278(3)$ Å^3). Aqueous solutions of **2** show an absorption band at 720 nm attributed to the $\pi^* \rightarrow \sigma^*$ transition of the metal−metal bond. Photolysis ($\lambda > 670$ nm) of acetone solutions of **2** with $PhCH_2Br$ yields $[PW_{11}O_{39}RhBr]^{5-}$ **(1-Br)** and $PhCH_2CH_2Ph$. Oxidation of **2** by air, Br_2, and hypochlorite yields $[PW_{11}O_{39}Rh(H_2O)]^{4-}$ (**1-aq**), **1-Br**, and **1-Cl**, respectively. Photochemical, electrochemical, and ligand substitution routes to other $[PW_{11}O_{39}RhL]^{n-}$ species, L = I^-, CN^-, CH_3COO^-, pyridine, or S-bonded dimethyl sulfoxide, are described. Each of these complexes has a characteristic P NMR resonance, and mixtures are separable by chromatography on Sephadex.

Introduction

Polyoxometalate anions with Keggin, $[(XO_4)M_{12}O_{36}]^{n-}$, or Dawson, $[(XO_4)_2M_{18}O_{56}]^{n-}$, structures, in which a single tungsten or molybdenum atom (M) has been replaced by a lower-valent transition metal cation, are widely investigated as homogeneous oxidation catalysts.[1] Parallels have been drawn with the chemistry of the metalloporphyrins and other macrocyclic complexes. Since the polyoxometalate "ligand" is fully resistant to oxidation, catalyst lifetimes and turnover numbers are high.

We are interested in exploring other reactivity patterns involving polyoxometalates, which also possess a rich *reduction* chemistry (heteropoly blues and browns),[2] and we have initially focused attention on rhodium-substituted polyoxoanions. The chemistry of Rh^{III} is dominated by octahedral (low-spin d^6) complexes and that of Rh^{II} by Rh_2 species, a consequence of the radical-like behavior of the $t_{2g}{}^6e_g$ configuration. It might, therefore, be anticipated that reduction of Rh^{III}-substituted polyoxometalates would lead to novel chemistry for heteropolyanions. We report here the synthesis, characterization, and chemistry of some Keggin-structure-derived Rh^{III} complexes that illustrate this point.

In 1979, Marcu and Ciogolas[3] reported that lacunary polytungstate anions formed 2:1 complexes with Rh^{III}, "$[Rh(PW_{11}O_{39})_2]^{8-}$" and "$[Rh(P_2W_{17}O_{61})_2]^{14-}$" Subsequently, Zonnevijlle, Tourné, and Tourné[4] described five rhodium-coordinated Keggin or Dawson anions: $[XW_{11}O_{39}Rh^{III}(OH)_{1-2}]^{n-}$ (X = B, Si, P) and $[X_2W_{17}O_{61}Rh^{III}(OH_2)]^{n-}$ (X = P, As). Zonnevijlle et al. suggested, based on the reported IR and UV−vis spectra, that the 2:1 complexes of Marcu and Ciogolas were kinetically inert ion associates. Syntheses of the complexes reported by Zonnevijlle et al. were carried out in unbuffered aqueous solutions, and the products were characterized by elemental analysis. It was reported that salts of $[PW_{11}O_{39}Rh^{III}(OH)]^{5-}$ and $[PW_{11}O_{39}Rh^{III}(O)]^{6-}$ rather than $[PW_{11}O_{39}Rh^{III}(OH_2)]^{4-}$ were obtained, and that the presence of an organic solvent provoked partial decomposition of $[PW_{11}O_{39}Rh^{III}(OH)]^{5-}$

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[1] (a) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34. (b) Hill, C. L.; Prosser-McCartha, C. M. *Coord. Chem. Rev.* **1995**, *143*, 407. (c) Hill, C. L., Ed. *J. Mol. Catal. A: Chem.* special edition: Polyoxometalates in Catalysis), **1996**, *114*, 1−365. (d) Mizuno, N.; Nozaki, C.; Hirose, T. O.; Tateishi, M.; Iwamoto, M. *J. Mol. Catal. A: Chem.* **1997**, *117*, 159. (e) Comuzzi, C.; Dolcetti, G.; Trovarelli, A.; Cavani, F.; Trifiro, F.; Llorca, J.; Finke, R. G. *Catal. Lett.* **1996**, *36*, 75. (f) Gall, R. D.; Hill, C. L.; Walker, J. E. *Chem. Mater.* **1996**, *8*, 2523. (g) Zhang, X.; Sasaki, K.; Hill, C. L. *J. Am. Chem. Soc.* **1996**, *118*, 4809. (h) Hill, C. L.; Zhang, X. *Nature* **1995**, *373*, 324. (i) Duncan, D. C.; Chambers, R. C.; Hecht, E.; Hill, C. L. *J. Am. Chem. Soc.* **1995**, 117, 681. (j) Neumann, R.; Khenkin, A. M. *Inorg. Chem.* **1995**, *34*, 5753. (k) Neumann, R.; Gara, M. J. *Am. Chem. Soc.* **1995**, *117*, 5066. (l) Neumann, R.; Khenkin, A. M.; Dahan, M. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1587. (m) Neumann, R.; Khenkin, A. M.; Juwiler, D.; Miller, H.; Gara, M. *J. Mol. Catal. A: Chem.* **1997**, *117*, 169. (n) Neumann, R.; Dahan, M. *Nature* **1997**, *388*, 353. (o) Neumann, R.; Cohen, M. *Angew.Chem., Int. Ed. Engl.* **1997**, *36*, 1738.

[2] (a) Pope, M.T. *Heteropoly and Isopoly Oxometalates;* Springer: New York, 1983; Chapter 6.(b) Piepgrass, K.; Pope, M. T. *J. Am. Chem. Soc.* **1987**, *109*, 1586.(c) Piepgrass, K.; Pope, M. T. *J. Am. Chem. Soc.* **1989**, *111*, 753.(d) Yamase, T.; Ishikawa, E. *J. Chem. Soc., Dalton Trans.* **1996**, 1619.

[3] Marcu, G.; Ciogolas, I. *Rev. Roum. Chim.* **1979**, *24*, 1049.

[4] Zonnevijlle, F.; Tourné, C. M.; Tourné, G. T. *Inorg. Chem.* **1982**, *21*, 2751. Zonnevijlle, F. Ph. D.Thesis, University of Montpellier, France, 1976.

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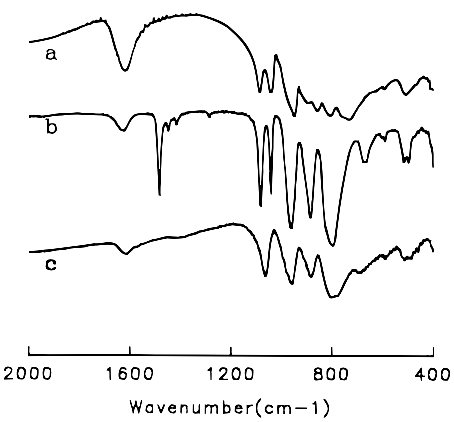

Figure 1. Infrared spectra of (a) $K_7[PW_{11}O_{39}]\cdot xH_2O$, (b) $[(CH_3)_4N]_5[PW_{11}O_{39}RhCl]\cdot H_2O$, and (c) $Cs_{10}[(PW_{11}O_{39}Rh)_2]\cdot 29H_2O$. Spectra of salts of **1-aq, 1-Br, 1-I, 1-CN**, and **1-OAc** are very similar to spectrum b in the region 1100−500 cm^{-1}.

Recently, Rh-containing polytungstates have been reported to act as oxidation catalysts for alkanes ($[SiW_{11}O_{39}Rh(H_2O)]^{5-}$)[5] and alkenes ($[(WZnRh^{III}{}_2)(ZnW_9O_{34})_2]^{10-}$),[6] but only in the latter case has the catalyst been structurally characterized. In our hands, the synthesis of Rh complexes of the lacunary Keggin and Dawson anions by literature methods leads to mixtures of species in relatively low yields, and it is important to discover more reliable and efficient procedures before exploration of possible new reactivity patterns.

Experimental Section

Syntheses. $[(CH_3)_4N]_5[PW_{11}O_{39}RhCl]\cdot H_2O$ (Anion 1-Cl). Lithium carbonate was added in small portions to a solution of 4.3 g of $H_3PW_{12}O_{40}\cdot xH_2O$ (Aldrich; ca. 1.5 mmol) in 36 mL of water until the pH reached 4.8. To this solution was then added 2.0 g of LiCl to produce 1 M [Cl^-]. A solution of 0.391 g of $RhCl_3\cdot xH_2O$ (1.48 mmol) previously dissolved in 14 mL of H_2O was added dropwise to the above solution under constant stirring. At the end, the pH was adjusted to 3.6 by carefully adding solid Li_2CO_3. Between each addition of Li_2CO_3, enough time was allowed for the solution to reach equilibrium. Finally, the mixture was transferred into a Teflon-lined 125-mL Parr acid digestion bomb and kept at 150 °C for 20 h. Addition of 1 g of $(CH_3)_4NCl$ (TMACl) to the resulting solution generated an orange precipitate which was collected by filtering the mixture through a glass-frit funnel. After the product had been washed with three portions of water, it was air-dried. Yield based on $RhCl_3$: 4 g (83%). Elemental analysis, found (calcd for $[(CH_3)_4N]_5[PW_{11}O_{39}RhCl]\cdot H_2O$): C, 7.50 (7.50); N, 2.30 (2.20); P, 0.85 (0.97); W, 63.22 (63.11); Rh, 2.97 (3.21); Cl, 1.00 (1.11). IR (Figure 1): 1084, 1041, 960, 887, 798, 667, 590, 517 cm^{-1}. NMR: ^{31}P, −10.0; ^{183}W, 112.4 (2W), −52.1 (2W), −93.4 (2W), −97.3 (1W), −126.6 (2W), −137.3 (2W).

$[(CH_3)_4N]_5[PW_{11}O_{39}RhBr]$ (Anion 1-Br). The synthetic procedure is similar to that of **1-Cl**, except that 4.1 g of NaBr instead of LiCl was added prior to the hydrothermal reaction. The resulting solution was eluted through a Sephadex G-50 column with 0.1 M pH 4.0 NaOAc/HOAc buffer solution. The first red-brown band was collected, and TMACl was added. The brown precipitate was filtered off and washed three times with a small amount of ice-cold water. The solid was allowed to air-dry. The two byproducts, $[PW_{11}O_{39}RhCl]^{5-}$ (**1-Cl**) and $[PW_{11}O_{39}Rh(H_2O)]^{4-}$ (**1-aq**), moved more slowly than **1-Br** on the Sephadex column and were separated from the main product. Yield based on $RhCl_3$: 3.8 g (80%). Elemental analysis of Br for $(TMA)_5[PW_{11}O_{39}RhBr]$: found (calcd) 2.53 (2).48. NMR: ^{31}P, −10.6.

$Cs_{10}[(PW_{11}O_{39}Rh)_2]\cdot 29H_2O$ (Anion 2). A solution of 1.92 g of tetramethylammonium salt of **1-Cl** in 80 mL of 0.5 M HOAc/NaOAc solution (pH 4.6) was reduced at −0.52 V on a graphite cloth electrode. The electrolysis proceeded quickly and was complete within half an hour, accompanied by a color change from orange to dark red. The progress of reduction was monitored by measuring the cyclic voltammogram of the electrolyzed solution, and the electrolysis was terminated when the intense reduction wave in the cyclic voltammogram of the starting solution had vanished. The number of electrons transferred was approximately one per Keggin anion. Addition of 1 g of CsCl to the resulting solution generated a dark red precipitate which was collected on a glass frit and washed with ice-cold water three times before drying. Yield: 1.95 g (94%). Elemental analysis, found (calcd for $Cs_{10}[(PW_{11}O_{39}Rh)_2]\cdot 29H_2O$): Cs, 18.75 (17.93); P, 0.69 (0.83); W, 54.52 (54.57); Rh, 2.69 (2.78). IR (Figure 1): similar to that of **1-Cl**, except that the two bands at 1084 and 1041 cm^{-1} are coalesced into a single absorption at 1084 cm^{-1}. NMR: ^{31}P, −12.0; ^{183}W, 78.7 (2W), −51.9 (2W), −93.1 (2W), −106.3 (1W), −128.7 (2W), −138.5 (2W).

A tetra-*n*-butylammonium (TBA) salt of **2,** soluble in polar organic solvents, was prepared by addition of 0.7 g of Bu_4NBr to a solution of 1.0 g of the above product in 30 mL of 0.1 M acetate buffer, pH 4.0. The precipitate was separated by filtration and washed with water and ethanol. The product was then placed in a vacuum oven at 60 °C for 3−4 h before further use. Yield: 1.2 g (94%). ^{31}P NMR, fresh (red) solution in acetonitrile: −8.1.

$[(CH_3)_4N]_4[PW_{11}O_{39}Rh(H_2O)]\cdot 4H_2O$ (Anion 1-aq). A solution of 0.4 g of the cesium salt of **2** in 40 mL of 0.1 M acetate buffer, pH 4.0, was heated at 60 °C for 10−15 min until the red solution had turned yellow. The resulting solution, upon cooling to room temperature, showed a single ^{31}P resonance at −9.42 ppm. Addition of TMACl yielded the tetramethylammonium salt. Elemental analysis, found (calcd for $[(CH_3)_4N]_4[PW_{11}O_{39}Rh(H_2O)]\cdot 4H_2O$): N, 1.83 (1.78); C, 6.20 (6.10); P, 0.85 (0.98); W, 64.16 (64.22); Rh, 3.14 (3.27). NMR: ^{31}P, −9.4; ^{183}W, 125 (2W), −44.8 (2W), −93.1 (2W), −97.7 (1W), −126.8 (2W), −137.0 (2W).

Elemental analyses were carried out by E+R Microanalytical Laboratory (Corona, NY).

Spectroscopy. The following instruments were used. Infrared: Nicolet 170SX FTIR spectrophotometer (KBr disks). UV−visible: Hewlett-Packard 8451A diode array spectrophotometer (1-cm quartz cuvettes). NMR: Bruker AM-300WB spectrometer operating at a magnetic field of 7.05 T (300.13 MHz for proton). The frequencies (MHz) and chemical shift references employed were as follos: ^{13}C, 75.469, TMS; ^{31}P, 121.496, 85% H_3PO_4; ^{183}W, 12.504, saturated Na_2WO_4. All aqueous ^{183}W NMR spectra were collected on solutions of lithium salts which were obtained by means of ion exchange: 1 g of polyoxotungstate (Cs, K, or TMA salt) was mixed with 2 g of $LiClO_4$ and moistened with a few drops of water. The paste formed was thoroughly stirred, 1 mL of D_2O was added, the insoluble white solid ($CsClO_4$, etc) was removed, and the filtrate was used for NMR measurements. Unless otherwise noted, all ^1H and ^{13}C NMR spectra were taken in D_2O; all other NMR spectra were measured in 0.1 M acetate buffer solution with pH 4.0.

Photochemistry. Photochemical experiments were carried out using a 100-W incandescent lamp filtered to ensure wavelengths greater than 670 nm (SHOTT filters 2-60 and 7-59) for excitation into the 710-nm band of **2**. All photolyzed solutions were subjected to 10 N_2-purge−evacuation cycles before irradiation and were contained in a Schlenk flask that had been partially wrapped in Al foil. The flask was immersed in a water bath at room temperature, and the solution was stirred continuously during irradiation. Parallel dark control experiments were performed in all cases.

Electrochemistry. Cyclic voltammograms (CV) were recorded on a BAS-100A electroanalyzer, using a glassy carbon working electrode, a platinum wire counter electrode, and a standard Ag/AgCl reference electrode (+0.22 V vs NHE). Hanging mercury drop electrode CVs were performed on a static mercury drop electrode (EG & G PARC model 303A). In organic solvents, a nonaqueous reference electrode (BAS MF-2062) which consists of a silver wire immersed in 0.1 M TBAP solution containing 0.01 M $AgNO_3$ was used. The voltage scan was always initiated at the rest potential of the solution. Controlled potential electrolyses were performed using a Brinkmann/Wenking model 70 TS1 potentiostat equipped with a Koslow Scientific Co. model

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(5) Matsumoto, Y.; Asami, M.; Hashimoto, M.; Misono, M. *J. Mol. Catal.* **1996**, *114*, 161.

(6) Neumann, R.; Khenkin, A. M. *J. Mol. Catal.* **1996**, *114*, 167.

541 digital coulometer. The reference and counter electrodes were the same as above; the working electrode was either a piece of graphite cloth (National Electrical Carbon Corp.) or a mercury pool. The counter electrode compartment was a glass tube with a frit bottom and was filled with the supporting electrolyte.

Equilibrium Ultracentrifugation. This was performed with a Beckman XL-A Optima analytical ultracentrifuge equipped with a four-hole An-55 rotor. The concentration distribution of the compound at sedimentation equilibrium was acquired as an average of 25 measurements of absorbance at each radial position, with nominal spacing of 0.001 cm between radial positions. Average molecular weights were estimated assuming a single, homogeneous species according to

$$c_r = B + c_m \exp\frac{M(1 - \bar{v}\rho)\omega^2(r^2 - r_m{}^2)}{2RT}$$

where c_r is the concentration of the sample at a given radial position, c_m is the concentration at some reference position (e.g., the meniscus), M is the molecular weight, $\bar{v}$ is the partial specific volume, ρ is the solvent density, ω is the angular velocity, r is the radial position in centimeters from the center of rotation, r_m is the distance in centimeters from the center of rotation to the meniscus, R and T have their usual meanings, and B is a correction term for a nonzero baseline. Parameters were evaluated using nonlinear least-squares analysis[7,8] or by using a modified version of IGOR (Wavemetrics, Lake Oswego, OR) running on a Macintosh computer.[9]

Crystallography. Crystals of the potassium salt of **2** were obtained by the following procedure. A solution of the potassium salt of **1-Cl** obtained by the above hydrothermal procedure was diluted with an equal volume of a 1.0 M sodium acetate buffer solution and electrolytically reduced to generate a dark red solution of **2** as described above. One milliliter of this solution was mixed with 1 mL of N_2-purged water, followed by about 200 mg of KCl. The solution was repurged with N_2 and carefully layered with 2 mL of deoxygenated ethanol in a screw-top vial. After the headspace had been flushed with N_2, the vial was closed. Very small, dark red crystals appeared after approximately 1 week.

All crystallographic measurements were performed at −100 °C on a Siemens SMART-CCD system with Mo Kα radiation. As the crystals rapidly decompose via solvent loss, a small (0.20 × 0.06 × 0.02 mm) red platelike needle was mounted directly from the mother liquor on a glass fiber using epoxy cement and quickly placed in the cold stream on the goniometer. The initial unit cell was determined using a least-squares analysis of a set of random reflections obtained from three short (20 data frame) series of 0.3°-wide ω-scans which were well distributed in space. The intensity data were then collected using ω-scans (0.3° wide) with a crystal-to-detector distance of 5.0 cm to yield 39 301 data (19 186 unique, $R_{int} = 0.3715$) with a maximum resolution of 0.75 Å ($2\theta_{max} = 56.62$). The final unit cell was calculated using a least-squares refinement of 4688 reflections culled from the entire data set. The data were corrected for Lorentz and polarization effects and for absorption using equivalent reflection data by employing the empirical routines included in the SHELXTL-PC software.[10] Due to its overall poor quality, the data set was truncated on the basis of intensity statistics at a resolution of 0.90 Å ($2\theta_{max} = 46.26°$) to yield the final data set of 21 117 reflections (11 842 unique, $R_{int} = 0.2532$). The space group was chosen as $P\bar{1}$ on the basis of intensity statistics. This choice was eventually shown to be correct by the successful solution of the structure. The structure was solved using direct methods and refined against F^2 using the routines included in the SHELXTL-PC software suite. The initial solution located all of the rhodium and tungsten atoms. They were refined anisotropically; however, their displacement parameters had to be restrained via an ISOR command to prevent many of them from becoming nonpositive definite. The phosphorus atoms and the oxygen atoms were located in the difference map through successive refinement cycles. The phosphorus atoms were refined isotropically, while the oxygen atoms (both anion and water oxygens) were refined with a common isotropic displacement parameter. The difference maps also revealed 10 cation positions, with one occurring on an inversion center; these potassium cations were refined isotropically. The refinement converged with final residuals of $wR_2 = 0.5251$ (F^2, all data) and $R_1 = 0.1831$ (F, $I > 2\sigma(I)$). The essential crystallographic parameters are provided in Table 1. All crystallographic data (excluding structure factors) are available as Supporting Information.

Table 1. Crystal Data

formula	$K_{10}[(PW_{11}O_{39}Rh)_2]\cdot 10H_2O$	
formula weight	6131.6	
crystal system	triclinic	
space group	$P\bar{1}$	
crystal size/color	0.2 × 0.06 × 0.02 mm³/red	
unit cell dimensions	$a = 12.703(6)$ Å	$\alpha = 96.56(2)°$
	$b = 17.868(8)$ Å	$\beta = 97.12(2)°$
	$c = 19.131(9)$ Å	$\gamma = 91.318(13)°$
Z	2	
$R1$ [$I > 2\sigma(I)$]	0.1831	
GOF on F^2	1.168	

Table 2. Phosphorus-31 Chemical Shifts of $[PW_{11}O_{39}RhL]^{4,5-}$ and Related Complexes

terminal ligand, L	$\delta^{31}P$	
	solvent = H_2O	solvent = MeCN[a]
H_2O	−9.4	
CH_3COO^-	−9.6	
Cl^-	−10.0	
Br^-	−10.6	−7.1
I^-	−11.7	−8.2
CN^-		−9.1
pyridine		−7.3
dmso	−11.4	−9.5[b]
anion **2**	−12.0	−8.1 (−8.8[b])
$\{Rh_2(OAc)_2\}$[c]	−12.6	

[a] Except where noted. [b] Solvent = DMSO. [c] $[PW_{11}O_{39}\{Rh_2(OAc)_2(H_2O)_2\}]^{5-}$: Wei, X.; Dickman, M. H.; Pope, M. T. *Inorg. Chem.* **1997**, *36*, 130.

Results and Discussion

Syntheses and Characterization of 1 and 2. Preliminary attempts to synthesize these complexes using procedures analogous to those described by Zonnevijlle et al. led, in our hands, to mixtures of phosphorus-containing products, among which were $[PW_{12}O_{40}]^{3-}$ and species later identified as **1-Cl** and **1-aq.** These could be separated by chromatography on a Sephadex G-50 column,[11] but the yields of rhodium-containing species were poor (ca. 25%). The more efficient hydrothermal synthesis of the chloro derivative succeeds in an unbuffered LiCl medium. The Li^+ cation stabilizes the lacunary tungstophosphate anion[12] sufficiently at the high temperatures required for reaction with substitution-inert Rh^{III}. Although **1-Br** can be prepared by an analogous procedure in 1 M NaBr, other derivatives, $[PW_{11}O_{39}RhX]^{n-}$ (**1-X**), are more conveniently generated via the dimeric reduced species, **2** (see below).

Full characterization of **1-Cl** is provided by the six-line (2:2:2:1:2:2) W NMR spectrum, by solution molecular weight

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(7) Johnson, M. L.; Correia, J. J.; Yphantis, D. A.; Halvoson, H. R. *Biophys. J.* **1981**, *36*, 575.

(8) Johnson, M. L.; Fraser, S. G. *Methods Enzymol.* **1985**, *117*, 301.

(9) Brooks, I. S.; Soneson, K. K.; Hensley, P. *Biophys. J.* **1993**, *64*, A244.

(10) SHELXTL-PC Version 5.03 1994; Bruker Analytical X-ray Services, Madison, WI.

(11) On Sephadex columns, the heteropolyanions were eluted in the order of charge: 5− (**1-Cl**) before 4− (**1-aq**). Zonnevijlle et al.[4] report a pK_a of 3. 5 for **1-aq**. Although the solute species present in solutions of higher pH might be more appropriately designated "**1-OH**" (or even **"1-O"**), we have chosen to use the abbreviation based on the formula of the tetrakis tetramethylammonium salt isolated and analyzed.

(12) (a) Canny, J.; Tézé, A.; Thouvenot, R.; Hervé, G. *Inorg. Chem.* **1986**, *25*, 2114. (b) Brévard, C.; Schimpf, R.; Tourné, G. F.; Tourné, C. M. *J. Am. Chem. Soc.* **1983**, *105*, 7059.

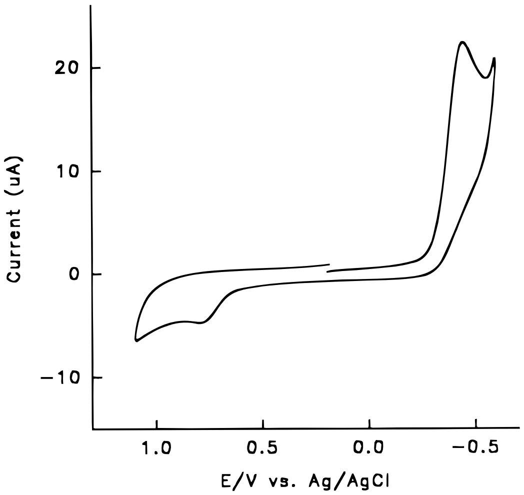

Figure 2. Cyclic voltammogram of 3.0 mM solution of **1-Cl** in 0.1 M acetate buffer, pH 4.2. Glassy carbon electrode.

determination (see below), and by a preliminary crystallographic investigation of the tetramethylammonium salt which revealed a disordered Keggin anion. To date, the only fully assigned W NMR spectrum of a metal-substituted Keggin anion is that of $[PW_{11}O_{39}Zn(H_2O)]$.[5−13] Guided by the spectra of a series of $[PW_{11}O_{39}Ru^{II}(L)]^{5-}$ complexes, and in view of the fact that Rh(III) is isoelectronic with Ru(II),[14] the resonances at 112.4 and −52.1 ppm are attributed to the four W atoms which are adjacent to the Rh atom. Further assignment of these two types of W atoms might be possible via 2D-NMR, although no W−Rh coupling was detected in our spectra. The infrared spectra of **1-Cl** and other complexes are shown in Figure 1.

The cyclic voltammogram of **1-Cl** (Figure 2) shows an irreversible reduction feature at −0.45 V. Controlled potential reduction resulted in the consumption of one electron per anion. The resulting dark red solution was ESR-silent and yielded narrow-line ^{31}P and ^{183}W NMR spectra consistent with the C_s symmetry of a diamagnetic monosubstituted Keggin anion. When the electrolysis was monitored by ^{31}P NMR, only the peaks corresponding to **1-Cl** and the product **2** were observed. Addition of CsCl to the red solution yielded a microcrystalline solid as described above. Solution molecular weights of **1-Cl** and **2** were determined by equilibrium ultracentrifugation in 0.1 M NaCl. The results confirmed that both solutions were monodisperse with effective solute molecular weights of 2744 ± 63 (**1-Cl**) and 5821 ± 186 (**2**). Calculated anionic weights are 2816 and 5561, respectively.

After several attempts, only very small crystals of a potassium salt of **2** could be obtained, and these proved to be only marginally satisfactory for structural analysis. As a result, the structure is of poor quality, although it is sufficient to reveal the anticipated dimer. As shown in Figure 3, the notable features of this structure are the unsupported Rh−Rh bond of length 2.52(2) Å and a gauche disposition of the two Keggin moieties. Ten potassium cation positions, accounting for 9.5 cations (one position resides on an inversion center), were located crystallographically. The most likely explanation for the deficiency of half of a univalent cation is that it is disordered over several sites. This is frequently a problem with the crystallography of large polyoxometalates; indeed, it is often not possible to locate all the hydrate water molecules in structures of these complexes. Although the quantity of crystals was inadequate for elemental analysis, there is no doubt about the total anion charge based on the diamagnetism revealed by the narrow-line NMR spectra and the unambiguous oxidation states of the constituents. Three of the cations (K2, K3, K9) occupy "bridging" sites between the Keggin units. The metal−metal bond length is not exceptional for Rh_2 species,[15] but the staggered conformation of the O_4RhRhO_4 moiety is not supportive of the $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ configuration anticipated for such bonds. This reflects the weakness of the bonding interaction, which is also revealed by the chemical instability of **2** in solution. The potassium cations that bridge the Keggin moieties probably contribute to the stability of the dimer in the crystal. The six-line W NMR spectrum in solution demonstrates that rotation about the Rh−Rh bond is rapid on the NMR time scale.

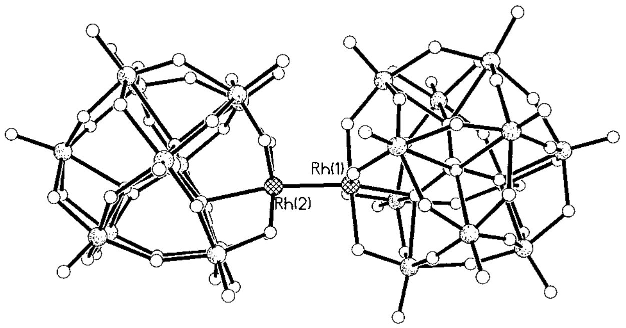

Figure 3. Ball-and-stick representation of the structure of anion **2**.

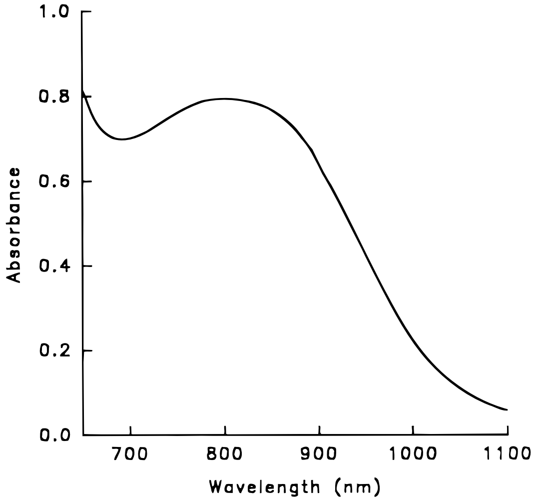

Figure 4. Electronic absorption spectrum of anion **2** in 0.1 M acetate buffer, pH 4.0. Molar absorptivity at 792 nm, 370 M^{-1} cm^{-1}.

The electronic spectrum of a fresh solution of **2** (Figure 4) shows a broad absorption at 792 nm (ϵ, 370 M^{-1} cm^{-1}) that we tentatively attribute to the $\pi^* \rightarrow \sigma^*$ transition. This is comparable to that observed for the hexafluoroacetonyl acetate complex, $[Rh_2(hfacac)_4(H_2O)_2]$, at 725 nm (130 M^{-1} cm^{-1}), which also has an unsupported Rh−Rh bond surrounded by oxygen donor atoms.[16] The energy of this transition is solvent-dependent, based on measurements of fresh solutions of the tetrabutylammonium salt in DMSO (820 nm), MeCN and DMF (both 740 nm), and acetone (710 nm), and is markedly lower than corresponding transitions in $[Rh_2(OAc)_4(H_2O)_2]$ (585 nm),[17] $[PW_{11}O_{39}\{Rh(OAc)\}_2(H_2O)_2]^{5-}$ (644 nm),[18] and $[Rh_2$-

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[13] Jorris, T. L.; Kozik, M.; Casan-Pastor, N.; Domaille, P. J.; Finke, R. G.; Miller, W. K.; Baker, L. C. W. *J. Am. Chem. Soc.* **1987**, *109*, 7402.

[14] Rong, C.; Pope, M. T. *J. Am. Chem. Soc.* **1992**, *114*, 2922.

[15] Cotton, F. A.; Walton, R. H. *Multiple Bonds Between Metal Atoms*, 2nd ed.; Oxford University Press: New York, 1993.

[16] Dikareva, L. M.; Andrianov, V. I.; Zhilyaev, A. N.; Baranovskii, I. B. *Russ. J. Inorg. Chem.* **1989**, *34*, 219.

[17] Felthouse, T. R. *Prog. Inorg. Chem.* **1982**, *29*, 73.

[18] Wei, X.; Dickman, M. H.; Pope, M. T. *Inorg. Chem.* **1997**, *36*, 130.

$(H_2O)_{10}]^{4+}$ (649 nm).[19] Solutions of **2,** monitored by P NMR, are unstable and decompose to a mixture of products at rates that roughly correlate with the energy of the visible absorption band, slowest for acetone, fastest for DMSO. For this reason, spectra were recorded and the ultracentrifugation measurements made on freshly prepared solutions of **2**.

Reactions of 2. (a) Chemical Oxidation. Aqueous solutions of **2** are aerobically oxidized to **1-aq** (see Experimental Section), δ^{31}P, −9.4 ppm. The mechanism of this reaction is not clear. Oxidation of the octaethylporphyrin analogue of **2**, [(OEP)Rh]$_2$, by dioxygen leads first (at −80 °C) to paramagnetic [(OEP)-Rh(O_2)], described as a superoxo-Rh^{III} species. Upon warm-up, a bridged peroxo dimer is formed.[20] When a similar experiment was attempted on a solution of the tetrabutylammonium salt of **2** in acetone at −80 °C, no ESR-active species could be detected. In the porphyrin case, O_2 can attack open axial positions trans to the Rh−Rh bond; such positions are inaccessible in the heteropolyanion.

Reaction of **2** with H_2O_2 leads to a mixture of unidentified products according to P NMR, but Br_2 and aqueous hypochlorite yield **1-Br** and **1-Cl**, respectively, in clean, rapid reactions. A solution of the TBA salt of **2** in dimethyl sulfoxide yielded a yellow solution of the dmso derivative, $[PW_{11}O_{39}Rh(Me_2SO)]^{4-}$ (**1-dmso**) within a few hours at ambient temperature. During this process, the ^{31}P resonance of **2** at −8.8 ppm was replaced by a new one at −9.5 ppm. W NMR of **1-dmso** (DMSO solution): 90.1 (2W), −66.1 (2W), −80.3 (2W), −82.9 (1W), −110.5 (2W), −123.9 (2W). A water-soluble tetramethylammonium salt was prepared by warming a solution of the TMA salt of **2** in DMSO and isolating the product by addition of water. NMR: ^{31}P, −11.4; ^{1}H, 3.52 (s, 6H, C*H*$_3$). The proton chemical shift is indicative of an S-bonded dmso ligand (characteristic range 3.2−3.8 ppm), and this conclusion is supported by observation of ν_{S-O} at 1172 cm^{-1}.[21]

The pyridine derivative, **1-py**, could be obtained by refluxing 0.2 g of the tetrabutylammonium salt of **2** in 30 mL of pyridine for 1 h. Pyridine was stripped from the resulting orange solution by rotary evaporation, leaving an orange solid which was washed three times with ethanol and allowed to dry. NMR (MeCN-*d*$_3$): ^{31}P, −7.3; ^{1}H, 7.59, 8.01, 8.36 (cf. free pyridine, 7.31. 7.72. 8.58). The cyano derivative, **1-CN**, was prepared by refluxing a solution of 0.2 g of the tetrabutylammonium salt of **2** and 0.3 g of NaCN in dimethylformamide for 1 h. The solvent was stripped by rotary evaporation, and the resulting orange residue was washed three times with water to remove excess NaCN. P NMR: −9.1. IR (in addition to the normal pattern for substituted Keggin anions, see Figure 1): ν(C−N) was observed at 2125 cm^{-1} (cf. 2163 cm^{-1} for $[Rh(CN)_6]^{3-}$ [22]).

(b) Electrochemical Oxidation. The cyclic voltammogram of a solution of **2** in 0.2 M acetate buffer shows an irreversible oxidation feature at +0.85 V. Controlled potential electrolytic oxidation at +1.0 V resulted in the consumption of 2 equiv/mol and yielded a single phosphorus-containing product, identified as **1-aq** by P NMR (−9.4 ppm). When the electrolytic oxidation was carried out in a more concentrated buffer (0.5 M), two heteropoly products, δP −9.4 (**1-aq**) and −9.6 ppm, were generated. These were isolated by precipitation as tetramethylammonium salts and separated by chromatography on Sephadex G-50. The first species to be eluted (δP −9.6 ppm, yield about 20%) was subsequently identified as the acetato derivative $[PW_{11}O_{39}RhOAc)]^{5-}$ (**1-OAc**). The same complex could be prepared more efficiently by hydrothermal treatment of a solution of 0.2 g of **1-aq** (TMA salt) in 10 mL of 0.5 M acetate buffer, pH 4.6, at 120 °C for 16 h. Following chromatography on Sephadex, the yield was 70%. NMR: ^{31}P, −9.6; ^{1}H, 2.1 (s, 3H, C*H*$_3$); ^{13}C, 25.7 (q, *C*H$_3$, $^1J_{C-H}$ = 143 Hz), 187.2 (d, *C*OO, $^2J_{C-Rh}$ = 6.5 Hz).

Electrolytic oxidations carried out in 0.5 M buffer and in the presence of chloride yielded a mixture of **1-aq**, **1-Cl,** and **1-OAc**, which were separated by elution (in that order) from a Sephadex column. Addition of a few drops of DMSO to the buffer solution before electrolysis resulted in a mixture of **1-aq** and **1-dmso** after oxidation.

(c) Photochemical Oxidation. Rhodium porphyrin dimers, [(Por)Rh]$_2$, have been shown to react with a variety of organic molecules, presumably through homolytic Rh−Rh bond cleavage followed by Rh−C or Rh−H bond formation.[23] Correspondingly simple thermal reactions of **2** do not always seem to occur. For example, the octaethylporphyrin complex [(OEP)-Rh]$_2$ reacts with $PhCH_2Br$ within several minutes to yield (OEP)RhBr and (OEP)RhCH$_2$Ph,[24] but a mixture of $PhCH_2Br$ and the TBA salt of **2** in acetone remained unchanged after stirring overnight at ambient temperature. After an 8-h reflux under nitrogen, the resulting red solution showed P NMR resonances corresponding to **1-Br** (−7.1) and smaller amounts of three other unidentified species (−6.9, −7.8, and −9.8 ppm). The difference in reactivity may be attributable to the ca. 1-V difference in oxidation potential between the heteropolyanion and the metalloporphyrin. However, **2** can be photochemically activated. A mixture of a solution of 0.25 g of the TBA salt of **2** in acetone and 1.5 mL of benzyl bromide was photolyzed for 5 h at ambient temperature. The resulting light brown solution was separated from a small quantity of light brown solid and the acetone allowed to evaporate. The residue consisted of a light brown solid and ca. 1 mL of clear supernatant. The ^{1}H NMR spectrum of the supernatant in MeCN-*d*$_3$ showed that it was mainly the excess $PhCH_2Br$, but a singlet at 2.91 ppm demonstrated the presence of dibenzyl, $PhCH_2CH_2Ph$, confirmed by measurement of an authentic sample. The solid was washed three times with ethanol and gave a P NMR spectrum (in MeCN) with a single line at −7.1 ppm (**1-Br**). The same (and only) heteropolyanion product was obtained from photolysis of a solution of **2** with $BrCH_2COOH$, but the reaction carried out with $PhCH_2Cl$ yielded two unidentified heteropoly species with δP −6.3 and −6.6 ppm (MeCN). Neither **1-Cl** nor dibenzyl was observed in this case.

Irradiation of **2** with CH_3I for 9 h yielded a green precipitate and red-brown supernatant. After removal of the solvent, the residue was washed successively with acetone (to remove unreacted **2**) and ethanol. The final green solid showed a P NMR resonance at −8.2 ppm (in MeCN). This is attributed to $[PW_{11}O_{39}RhI]^{5-}$ (**1-I**). A separate sample of this complex was

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(19) (a) Maspero, F.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 7361. (b) Wilson, C. R.; Taube, H. *Inorg. Chem.* **1975**, *14*, 405.

(20) Wayland, B. B.; Newman, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 6472.

(21) (a) Kagan, H. B.; Ronan, B. *Rev. Heteroatom Chem.* **1992**, *7*, 92. (b) Goggin, P. L. *Comprehensive Coordination Chemistry: Synthesis, Reactions, Properties and Applications of Coordination Compounds*; Oxford University Press: UK, Oxford, 1987; Vol. 2, p 489.

(22) Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*; John Wiley & Sons: New York, 1963.

(23) (a) Wayland, B. B.; Woods, B. A.; Pierce, R. *J. Am. Chem. Soc.* **1982**, *104*, 302. (b) Paonessa, R. S.; Thomas, N. C.; Halpern J. *J. Am. Chem. Soc.* **1985**, *107*, 4333. (c) Wayland, B. B.; Van Voorhees, S. L.; Wilker, C. *Inorg. Chem.* **1986**, *25*, 4039. (d) Wayland, B. B.; Woods, B. A.; Coffin, V. L. *Organometallics* **1986**, *5*, 1059. (e) Poszmik, G.; Carroll, P. J.; Wayland, B. B. *Organometallics* **1993**, *12*, 3410. (f) Ni, Y.; Fitzgerald, J. P.; Carroll, P.; Wayland, B. B. *Inorg. Chem.* **1994**, *33*, 2029. (g) Del Rossi, K. J.; Zhang, X.; Wayland, B. B. *J. Organomet. Chem.* **1995**, *504*, 47.

(24) Ogoshi, H.; Setsune, J.; Yoshida, Z. *J. Am. Chem. Soc.* **1977**, *99*, 3869.

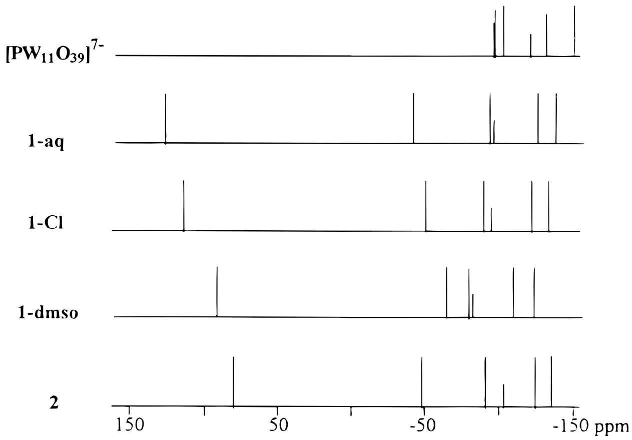

Figure 5. Stick representation of W NMR spectra of lacunary $[PW_{11}O_{39}]^{7-}$ and four of the rhodium derivatives. The two lowest-field lines in the spectra of the Rh-containing anions are assigned to the two pairs of tungstens that are adjacent to the rhodium atoms.

prepared by photolyzing an aqueous solution of 0.2 g of the cesium salt of **2** and 0.4 g of NaI in 25 mL of 0.1 M acetate buffer. After 4 h, a green-brown solution (P NMR, −11.7 ppm) and traces of a black precipitate (I_2?) were formed. Addition of Bu_4NBr (0.2 g) to the solution gave a green solid that was filtered off and washed with ethanol. Elemental analysis, found (calcd for $[(C_4H_9)_4N]_4H[PW_{11}O_{39}RhI]$): I, 3.08 (3.28). ^{31}P NMR (MeCN-d_3): −8.3 ($\Delta\nu_{1/2} = 48$ Hz).[25] The UV−visible absorption spectrum of an aqueous solution of **1-I** showed a maximum at 650 nm which is attributed to a d−d transition of Rh^{III} ($^1A_{1g} \rightarrow {}^1T_{1g}$). The corresponding transitions of **1-Br** and **1-Cl**, which should appear at higher energies, are obscured by the O→W charge-transfer absorption.

The formation of dibenzyl is consistent with a mechanism in which the tungstorhodium(II) radical anion is produced, i.e.:

$$[(PW_{11}O_{39}Rh)_2]^{10-} + h\nu \rightarrow 2\,[(PW_{11}O_{39}Rh^{\bullet}]^{5-} \qquad (1)$$

$$[(PW_{11}O_{39}Rh^{\bullet}]^{5-} + PhCH_2Br \rightarrow [PW_{11}O_{39}RhBr]^{5-} + PhCH_2^{\bullet} \qquad (2)$$

$$PhCH_2^{\bullet} + PhCH_2Br \rightarrow PhCH_2CH_2Ph + Br^{\bullet} \qquad (3a)$$

$$2PhCH_2^{\bullet} \rightarrow PhCH_2CH_2Ph \qquad (3b)$$

The relative importance of steps 3a and 3b and the fate of any Br atoms produced must await further investigation of the stoichiometry of the overall reaction. What is clear is that no organometallic Rh heteropolyanion is detected, indicating a strong preference of the rhodium center for the halogen atom in step 2. A similar process presumably occurs with the methyl iodide reaction, but with benzyl chloride the stronger C−Cl bond forces a different sequence of events, leading to multiple, so far unidentified, tungstophosphates.

Conclusions

Eight tungstophosphates, $[PW_{11}O_{39}RhL]^{n-}$, that differ in the identity of the terminal ligand L have been isolated thanks to the substitution inertness of octahedral Rh^{III} complexes. These complexes can often be separated by chromatography on Sephadex G-50, and they are easily identified by ^{31}P NMR, the chemical shift of which is remarkably sensitive to the nature of a ligand three bonds distant from the phosphorus atom see (Table 1). A rough correlation between δ and the “softness” of L may be detected. The only other observation of such chemical shift sensitivity has been recently made by Radkov et al., who reported δP for $[PW_{11}O_{39}NbS]^{4-}$ and $[PW_{11}O_{39}NbSe]^{4-}$ as −13.6 and −13.8 ppm, respectively.[25a]

In an earlier investigation of $[PW_{11}O_{39}RuL]^{n-}$ complexes, we had interpreted changes in W NMR chemical shifts in terms of the “π-acceptor” property of the lacunary tungstophosphate ligand.[14] Since rhodium(III) is isoelectronic with ruthenium(II), it is not unexpected that a similar pattern of chemical shifts would be observed. Figure 5 compares the W NMR spectra of **1-aq**, **1-Cl**, **1-dmso**, and **2** with that of the lacunary ligand $[PW_{11}O_{39}]^{7-}$. The two lowest-field lines in each of these spectra are attributed to the tungstens that are adjacent to the rhodium atom in the Keggin anion, since they are the most affected by the addition of Rh to the lacunary anion. These lines, particularly the one with the most positive chemical shift, are especially sensitive to the “softness” of the terminal ligand on Rh, or to the extent of covalent character in the Rh−L bond, $OH_2 < Cl^- < OSMe_2 <$ Rh.

The reductive coupling of the rhodium centers, while precedented in rhodium chemistry, is a new development for heteropolyanions. Anion **2** is the first example of polyoxometalate anions directly linked by metal−metal bonds. Parallels to the metalloporphyrins are striking, and the photochemical homolysis of the Rh−Rh bond in **2**, and other potential analogues, offers opportunities for new pathways of reactivity in polyoxometalate chemistry.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, and equivalent isotropic displacement parameters for **2** (4 pages, print/PDF). X-ray crystallographic files, in CIF format, for $K_{10}[(PW_{11}O_{39}Rh)_2]\cdot 10H_2O$, are available on the Internet only. See any current masthead page for ordering information and Web access instructions.

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[25] (a) Radkov, E.; Lu, Y.-J.; Beer, R. H. *Inorg. Chem.* **1996**, *35*, 551. (b) Cadot, E.; Bereau, V.; Secheresse, F. *Inorg. Chim. Acta* **1995**, *239*, 39.