New Routes for Multiple Derivatization of Polyoxometalates. Bis(acetato)dirhodium-11-tungstophosphate, $[(PO_4)W_{11}O_{35}\{Rh_2(OAc)_2\}]^{5-}$

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Current interest in polyoxometalates is driven by the potential applications of these complexes in areas as diverse as catalysis, medicine, and materials science.[1] The great variety of structures and the possibilities of modifying these for specific purposes ensures continued emphasis on synthesis, characterization, and reactivity studies. We report the high-yield rational synthesis of examples of a potentially large class of hydrolytically-stable polyoxometalate derivatives of metal−metal-bonded dimers which offer several possibilities for further derivatization, molecular engineering, and catalysis.

The so-called lacunary polyoxometalate anions such as $[(SiO_4)W_{11}O_{35}]^{8-}$ and $[\alpha_2\text{-}(PO_4)_2W_{17}O_{53}]^{10-}$ have structures derived from the well-known Keggin ($[(SiO_4)W_{12}O_{36}]^{4-}$) and Dawson ($[(PO_4)_2W_{18}O_{54}]^{6-}$) species by removal of a single metal atom and its terminal oxo ligand.[1] The lacunary structures can incorporate a variety of metal cations into the surface vacancy, and the resulting substituted species have widespread applicability as robust oxidation catalysts,[2] e.g. $[(SiO_4)W_{11}O_{35}Co(H_2O)]^{6-}$, and as selective electron microscopy imaging agents,[3] e.g. $[(PO_4)_2W_{17}O_{53}Ti(\eta^5\text{-}C_5H_4R)]^{7-}$. In these transition-metal-substituted species, the lacunary anions generally function as pentadentate or tetradentate ligands towards a single metal cation.

We report here examples of a coordination mode involving dimetal substitution into lacunary anions which offers routes to new types of polyoxometalate derivatives with new applications. Although precedents for this type of coordination have been noted in non-metal chemistry,[4a] the first example of this type of coordination involving transition metal atoms with potentially replaceable ligands was reported by Randall, Weakley, and Finke in $[O\{Ru^{IV}Cl(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{16-}$, which was obtained adventitiously from reaction of $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ with $RuCl_3{\cdot}xH_2O$. No direct rational synthesis from, e.g. $[Cl_5RuORuCl_5]^{4-}$, appeared to be possible.[4b]

The title anion (**1**) was synthesized by hydrothermal reaction of rhodium(II) acetate dimer with lithium 11-tungstophosphate, prepared *in situ*, at pH 3.[5] The resulting solution showed a single ^{31}P NMR line at −12.6 ppm. Addition of CsCl yielded a brown precipitate which was filtered off and washed with 2:1 (v:v) water−ethanol. Yield: 85%. Proton and ^{183}W NMR data are consistent with a monosubstituted Keggin anion of C_s symmetry in which the Rh−Rh bond is perpendicular to the mirror plane. This structure is confirmed in the guanidinium salt of the dimethyl sulfoxide derivative, the anion of which is illustrated in Figure 1.[6] Compared to the structure of $Rh_2(OAc)_4(dmso)_2$,[7] the Rh-Rh bond in **1** is stretched by 0.119 Å, apparently to accommodate the size of the lacunary Keggin anion vacancy. Additionally, the S−Rh−Rh−S bonds are not colinear, with values of 171.6(2) and 168.2(2)° for the angles at Rh(1) and Rh(2), respectively. This results, presumably, from steric crowding by the polyoxometalate ligand. Curiously, the

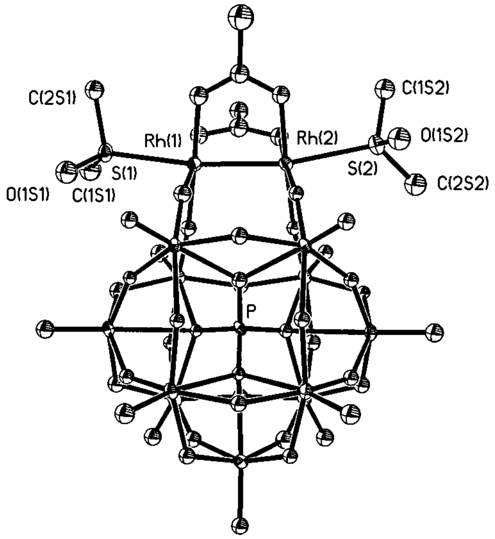

Figure 1. Structure of $[(PO_4)W_{11}O_{35}\{Rh_2(OAc)_2(dmso)_2\}]^{5-}$ in crystals of the guanidinium salt, showing 50% probability ellipsoids. Hydrogen atoms are not shown. Selected bond lengths (Å) and angles (deg): Rh(1)−Rh(2), 2.525(2); Rh(1)−S(1), 2.465(6); Rh(2)−S(2), 2.535(6); S(1)−Rh(1)−Rh(2), 171.6(2); S(2)−Rh(2)−Rh(1), 168.2(2).

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(1) Pope, M. T., *Heteropoly and Isopoly Oxometalates*; Springer Verlag: New York, 1983. *Polyoxometalates*: *From Platonic Solids to Anti-Retroviral Activity*; Pope, M. T., Müller, A., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1994.

(2) Hill, C. L.; Prosser-McCartha, X. *Coord.Chem.Rev.*, **1995**, *143*, 407.

(3) Keana, J. F. W.; Ogan, M. D.; Lu, Y.; Beer, M.; Varkey, J. *J. Am. Chem. Soc.* **1985**, *107*, 6714. Keana, J. F. W.; Ogan, M. D. *J. Am. Chem. Soc.* **1986**, *108*, 7951. Keana, J. F. W.; Ogan, M. D.; Lu, Y.; Beer, M.; Varkey, J. *J. Am. Chem. Soc.* **1986**, *108*, 7957.

(4) (a) Knoth, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 759, 2211. Kim, G.-S.; Hagen, K. S.; Hill, C. L., *Inorg. Chem.* **1992**, *31*, 5316. (b) Randall, W. J.; Weakley, T. J. R.; Finke, R. G., *Inorg. Chem.* **1993**, *32*, 1068.

(5) A solution of $H_3[PW_{12}O_{40}]$ (0.325g, 0.11 mmol) was dissolved in 10 mL of water and the pH adjusted to 4.8 by the addition of solid Li_2CO_3 in small portions. The pH of the solution was adjusted to 3.0 by the addition of 1 M HCl, $Rh_2(OAc)_4$ (0.05 g, 0.11 mmol) was added, and the mixture was placed in a Teflon-lined Parr acid digestion bomb at 120 °C for 16 h. Proton NMR of the resulting homogeneous solution showed lines for **1**, unreacted rhodium acetate, and free acetate released in the reaction. Yield of isolated cesium salt: 85%. Anal. Calcd (found) for $Cs_5PW_{11}O_{39}Rh_2(OOCCH_3)_2$: Cs, 18.91 (18.13); P, 0.65 (0.85); W, 54.85 (55.17); Rh, 5.10 (5.62); C, 1.35 (1.31); H, 0.34 (0.16). NMR spectroscopy: ^{183}W, 2.6 (2W), −41.6 (2W), −107.7 (2W), −123.2, −124.5 (3W), −155.6 (2W); ^1H, 2.01 (s, CH_3), 2.15 (s, CH_3). Long relaxation times of the two low-field W resonances sometimes resulted in low integrated intensities for these two lines.

(6) Crystals of $(CN_3H_6)_5[(PO_4)W_{11}O_{35}\{Rh_2(OAc)_2(dmso)_2\}]{\cdot}4H_2O$ were obtained adventitiously by addition of a few drops of dimethyl sulfoxide to a dilute mixture of guanidinium chloride and the potassium salt of **1** in water. X-ray data were collected on a crystal with dimensions 0.06 × 0.08 × 0.40 mm using a Siemens P4 rotating anode diffractometer and Mo Kα radiation, at 173 K. Crystal data: monoclinic, space group *Cc*; $a = 22.451(3)$ Å, $b = 11.8408(14)$ Å, $c = 25.698(3)$ Å, $\beta = 110.833(8)°$, $Z = 4$, $D_x = 3.614$ Mg m^{-3}. Of 10 598 data collected ($2\theta_{max} = 60°$), 9728 were independent ($R_{int} = 3.06\%$) and 8999 were observed ($2\sigma(I)$). An empirical absorption correction from ψ-scans was applied ($\mu = 20.429$ mm^{-1}). Tungsten, rhodium, sulfur, and phosphorus atoms were refined anisotropically; all others were refined isotropically. Hydrogen atoms were not included. $R_1(F)_{obs} = 4.68\%$, $R_w(F^2)_{all} = 11.46\%$, and absolute structure parameter = 1.7(13)% for 458 parameters and two restraints.

(7) Cotton, F. A., Felthouse, T. R. *Inorg. Chem.* **1980**, *19*, 323. Felthouse, T. R. *Prog. Inorg. Chem.* **1982**, *29*, 73. Cotton, F. A.; Walton, R. H. *Multiple Bonds between Metal Atoms*, 2nd. ed.; Oxford University Press: New York, 1993.

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anion adopts a chiral conformation in the crystal as a result of noneclipsed DMSO ligands.

The structure provides a rare, nondisordered, view of the effects of removing a WO^{4+} unit from the Keggin anion to produce the lacunary $[(PO_4)W_{11}O_{35}]^{7-}$ moiety. Since the rhodium dimer is not coordinated by the phosphate oxygen in the vacant site (O(1P)), this oxygen bridges only two metal atoms (W1 and W2) rather than three as do the other phosphate oxygens. As a consequence the oxygen−tungsten distances for O(1P) are shortened by about 0.1 Å, to 2.35(2) Å. This has the effect of pulling a stereochemically-rigid PO_4^{3-} tetrahedron *toward* W(1) and W(2) and *away* from the tungsten atoms on the opposite side of the anion, W(10) and W(11), for which the phosphate oxygen−tungsten distances are lengthened by about 0.1 Å, to 2.53(1) Å. The other phosphate oxygen−tungsten distances range from 2.41(2) to 2.48(1) Å with a mean of 2.43 Å. (See Supporting Information.)

The electronic absorption spectrum of **1** exhibits a broad maximum at 644 nm (ϵ 140 M^{-1} cm^{-1}) which is assigned to the Rh_2-based $\pi^* \rightarrow \sigma^*$ transition (cf. 585 nm[7] for $Rh_2(OAc)_4$). A cyclic voltammogram of **1** (glassy carbon electrode, sweep rate 100 mV s^{-1}, 1.0 M acetate buffer, pH 4.7) reveals a quasi-reversible ($E_{pa} - E_{pc} = 82$ mV) redox feature at +1.00 V *vs* Ag/AgCl, similar to that observed for $Rh_2(OAc)_4$. Electrolytic oxidation at +1.20 V consumed one equivalent of electrons per mol and yielded a dark brown solution of the $Rh^{II}Rh^{III}$ derivative. The oxidized solution was characterized by $\lambda_{max} =$ 730 nm and $\delta(^{31}P) = -28.4$ ppm ($\Delta\nu_{1/2} = 163$ Hz). Upon exposure to air the solution slowly decomposes to unidentified products.

Rhodium(II) acetate dimer is an efficient catalyst for cyclopropanation reactions.[8] Anion **1** appears, from preliminary experimetns, to be less effective than $Rh_2(OAc)_4$ for cyclopropanation of styrene with ethyl diazoacetate. Under similar conditions the yields of ethyl 2-phenylcyclopropanecarboxylate are 6.9% (cis) and 9.6% (trans) vs 38% (cis) and 60% (trans).[9] This may be the result of steric crowding by the Keggin fragment and/or eventual blocking of the axial coordination sites.[9] Addition of pyridine to **1** yields a stable red adduct, which, after isolation, shows the characteristic proton NMR of Rh-bound pyridine and an irreversible oxidation wave at +0.74 V in the cyclic voltammogram. The pyridine adduct is totally inactive for cyclopropanation. Further investigation of this system is in progress.

The simple direct synthesis of **1** from $Rh_2(OAc)_4$ suggests that analogous complexes can be derived from other lacunary polyanions and from other dimetal precursors, and we are exploring several possibilities.[10] As a distinct class of polyoxometalate derivatives these complexes offer sites for ligand binding and opportunities for molecular engineering through the remaining carboxylate ligands that could result in numerous applications in catalysis and elsewhere.

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Supporting Information Available: Tables 1−4 (crystal and structure refinement data, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, and anisotropic displacement parameters, respectively) and Figure 2, showing the arrangement of tungsten atoms surrounding the PO_4 tetrahedron (9 pages). Ordering information is given on any current masthead page.

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[8] Doyle, M. P.; Dorow, R. L.; Buhro, W. E.; Griffin, J. H.; Tamblyn, W. H.; Trudell, M. L. *Organometallics* **1984**, *3*, 44

[9] A solution of 0.5 mmol of ethyl diazoacetate in 3 mL of dichloromethane was added over 7 h by means of a syringe pump to 5 mmol of styrene and 0.005 mmol of catalyst (the tetra-*n*-butylammonium salt of **1** in 3 mL of dichloromethane). During the addition the catalyst dissolved, and the final solution was stirred for an additional hour before analysis. Gas chromatographic analyses were carried out with a Hewlett-Packard 5890 gas chromatograph equipped with a hydrogen flame ionization detector and a Hewlett-Packard Model 3396 II integrator. A cross-linked methylsilicone-coated capillary column (25 m; i.d. 0.32 mm, purchased from Hewlett-Packard) was used. Products were analyzed and identified by comparing their retention times with those of authentic samples and by GC-MS. Ethyl 2-phenylcyclopropanecarboxylate is the main product. Both *cis*- and *trans*- isomers are observed in all cases. The two byproducts are diethyl fumarate (DEF) and diethyl maleate (DEM) which result from the dimerization of the putative intermediate carbene. No other products were observed. Distribution of products (yield in terms of ethyldiazoacetate added): without catalyst, cis 1.0%, trans 1.5%, DEM 0.1%, DEF 0.1%; with $Rh_2(OAc)_4$, cis 38%, trans 60.4%, DEM 0.3%, DEF 0.3%; with $[(n\text{-}C_4H_9)_4N]_4HPW_{11}O_{39}Rh_2(OAc)_2$, cis 6.9%, trans 9.6%, DEM 1.2%, DEF 1.4%.

[10] $[\alpha\text{-}(SiO_4)W_{11}O_{35}[Rh_2(OAc)_2\}]^{6-}$ and $[\alpha_2\text{-}P_2W_{17}O_{61}Rh_2(OAc)_2]^{8-}$ were also synthesized by hydrothermal reaction under appropriate pH conditions. Both compounds display physical and chemical properties similar to those of **1**.