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Communications to the Editor

Rhodium−Carbon Bond Formation in Aqueous Solution. Synthesis, Structure, and Reactivity of the Functionalized Heteropolytungstates, $[XW_{11}O_{39}RhCH_2COOH]^{5,6-}$ (X = P, Si)

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Although applications in catalysis drive much of the current interest in polyoxometalate chemistry,[1] there are also many other areas in which the unusual and often unique combinations of properties of these species can provide valuable and important contributions.[2] Derivatization of polyoxometalate surfaces is an important research goal, since this can lead to the design and synthesis of new polymeric species and materials, to the immobilization of catalytically active polyanions, and to localization of electron-dense imaging agents,[3] among other possibilities. We report here new functionalized tungstorhodates with Rh−C bonds that are formed in good yield in aqueous solution from acetate, rhodium(III), and heteropolytungstate, a process that, to our knowledge, has no precedent in rhodium chemistry.

The complexes $[PW_{11}O_{39}RhCH_2COOH]^{5-}$ (**1**) and $[SiW_{11}O_{39}RhCH_2COOH]^{6-}$ (**2**) are obtained by the hydrothermal reaction of an equimolar mixture of rhodium(III) chloride and $K_7PW_{11}O_{39}$ or $K_8SiW_{11}O_{39}$ in an acetate buffer at 120 °C.[4] Yields of the tetramethylammonium salt of **1** and the cesium salt of **2** were 93% and 60%, respectively. The cesium salt of α_2-$[P_2W_{17}O_{61}RhCH_2COOH]^{8-}$ (**3**) was isolated in 20% yield from an analogous nonoptimized reaction using the corresponding lacunary anion. The above formulas for **1** and **2** are confirmed by elemental analysis and multinuclear NMR spectroscopy.[5]

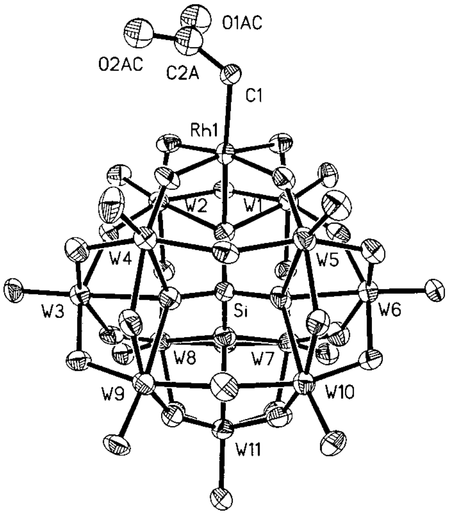

Figure 1. Structure of anion **2**, showing atoms with 50% thermal ellipsoids. The carboxyl group is shown in one of the two disordered positions; the second position corresponds to a slight rotation about the Rh−C bond. Selected interatomic distances (Å): Rh−O(Si), 2.248(12); Rh−C, 1.98(2); Rh−O(W), 1.987(13)−2.036(13); Si−O(Rh), 1.645(12); Si−O(W), 1.636(13); C−C, 1.43(5); C−O, 1.31(6), 1.36(5).

Crystals of $Cs_6[SiW_{11}O_{39}RhCH_2COOH]\cdot 6H_2O$ were obtained from a solution of the product of the hydrothermal synthesis of **2** that had been purified by electrolysis.[6] Structural analysis[7] revealed the anion depicted in Figure 1. Remarkably, the Keggin moiety is not disordered, and the Rh−C linkage (1.98(2) Å) is clearly identified.

The mechanism of formation of **1** (and its analogues) is unclear at present. Although the synthesis from the lacunary anion and rhodium chloride in 0.5 M acetate buffer is almost quantitative, the new species can be detected in smaller amounts in hydrothermal reactions of $[PW_{11}O_{39}RhX]^{5-}$ (X = Cl, Br, I, OAc).[8,9] In

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[1] Kozhevnikov, I. V. *Chem. Rev.* **1998**, *98*, 171. Okuhara, T.; Mizuno, N.; Misono, M. *Adv. Catal.* **1996**, *41*, 113. Hill, C. L.; Prosser-McCartha, C. M. *Coord. Chem. Rev.* **1995**, *143*, 407.

[2] Pope, M. T.; Müller, A. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34.

[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] For **1**, a solution of 0.35 g (1.32 mmol) of $RhCl_3\cdot xH_2O$ in 12 mL of water was added dropwise to 40 mL of 0.5 M acetate buffer (pH 4.0) containing 4.0 g (1.22 mmol) of $K_7PW_{11}O_{39}\cdot 13H_2O$. The solution was then heated in a Parr acid digestion bomb at 120 °C for 17 h. The ^{31}P NMR spectrum of the resulting dark red solution showed a single peak at −11.47 ppm (cf. −10.2 ppm for $K_7PW_{11}O_{39}$). Solid KCl (2 g) was added into the solution, which was then refrigerated for 1 h. A green precipitate (dirhodium acetate complexes, ca. 0.1 g) was filtered out. To the remaining dark red filtrate was added 1 g of tetramethylammonium chloride. The resulting orange precipitate was collected and washed with H_2O/EtOH (2:1 v/v). Yield: 3.74 g (93%). Elemental analysis, found (calcd for $[(CH_3)_4N]_5[PW_{11}O_{39}RhCH_2CO_2H]$): P, 0.82 (0.92); W, 59.85 (59.97); Rh, 2.68 (3.05); N, 2.09 (2.08); C, 8.63 (7.84). The lithium salt of **1** was obtained through ion-exchange (Dowex-50). Elemental analysis, found (calcd for $Li_{4.5}H_{0.5}PW_{11}O_{39}RhCH_2CO_2H\cdot 27H_2O$): P, 0.84 (0.92); W, 60.06 (60.24); Rh, 3.09 (3.06); C, 0.68 (0.72); Li, 0.93 (0.93). The cesium salt of **2** was prepared analogously. Elemental analysis, found (calcd for $Cs_{5.5}H_{0.5}[SiW_{11}O_{39}RhCH_2CO_2H]\cdot 10H_2O$): Cs, 19.51 (19.50); Si, 1.85 (0.75); W, 53.94 (53.96); Rh, 2.65 (2.75). Anion **3**: To a solution of 1 g of α_2-$Li_{10}[P_2W_{17}O_{61}]$ dissolved in 9 mL of 0.5 M acetate buffer (pH 4.0) was added a solution of 0.06 g of $RhCl_3\cdot H_2O$ dissolved in 2 mL of H_2O. The mixture was heated in a Parr bomb at 150 °C for 5 h. The ^{31}P NMR spectrum of the resulting solution indicated that $[P_2W_{18}O_{62}]^{6-}$ (−12.4 ppm) was the dominant product. The desired product was separated by chromatography on Sephadex G50, and the first dark red band was isolated as a Cs salt. Yield based on $Li_{10}P_2W_{17}O_{61}$: 20%.

[5] NMR data are as follows. **1**: ^{31}P, −11.5; ^{183}W, −4.0 (2W), −54.8 (2W), −96.3 (2W), −104.1 (1W), −127.3 (2W), −142.4 (2W); ^1H, 4.0 (d, 2H, $^2J_{H-Rh}$ = 3.5 Hz, CH_2); ^{13}C, 9.74 (d, $^1J_{C-Rh}$ = 27.8 Hz, CH_2), 190 (s, COOH). **2**: ^{29}Si, −85.2; ^{183}W, −133.2 (2W), −71.4 (2W), −95.3 (2W), −112.5 (1W), −142.3, −143.8 (4W); ^1H, 3.92 (d, 2H, $^2J_{H-Rh}$ = 3.5 Hz, CH_2); ^{13}C, 9.5 (d, $^1J_{C-Rh}$ = 26.4 Hz, CH_2), 191.7 (s, COOH). **3**: ^{31}P, −8.5, −13.3; ^1H, 3.86 (d, $^2J_{H-Rh}$ = 3.5 Hz).

[6] The cyclic voltammogram (HMDE; acetate buffer, pH 4.5; 0.05 V s^{-1}) of the cesium salt of **2** revealed, in addition to a pair of reversible tungsten reductions at E_{pc} = −0.68 and −0.87 V, an irreversible feature at −0.38 V. Controlled potential reduction at −0.45 V on a mercury pool cathode led to a slightly turbid solution and the loss of the irreversible feature. Addition of extra CsCl to the electrolyzed solution yielded a precipitate of $Cs_8[SiW_{11}O_{39}]\cdot nH_2O$, which was filtered off. The filtrate yielded red crystals after 1−5 days. Elemental analysis, found (calcd for $Cs_6[SiW_{11}O_{39}RhCH_2COOH]\cdot 6H_2O$): Cs, 19.86 (21.31); Si, 0.98 (0.75); W, 53.98 (54.05); Rh, 2.76 (2.75); C, 0.65 (0.64). NMR: ^1H, 3.9 (d, 2H, $^2J_{H-Rh}$ = 3.0 Hz); ^{13}C, 9.3 (d, $^1J_{C-Rh}$ = 26.4 Hz), 191.5 (s).

[7] $Cs_6[SiW_{11}O_{39}RhCH_2COOH]\cdot 6H_2O$, monoclinic; $P2_1/n$; red blocks with a = 11.2577(2), b = 22.9293(5), and c = 17.6274(4) Å; β = 94.4080(10)°; V = 4536.7(2) Å^3; Z = 4. Final R indices $[I > 2\sigma(I)]$, $R1$ = 0.0667, $wR2$ = 0.1612; GOF = 1.11. The COOH group is disordered over two positions which were just resolvable and refined with occupancy factors of 0.5 for each. Further details of the structure determination are given in the Supporting Information.

[8] Wei, X.; Bachman, R. E.; Pope, M. T. *J. Am. Chem. Soc.* **1998**, *120*, 10248.

[9] The reactions were carried out in 0.5 M buffer at 150 °C for 16 h. Yields of **1** varied from ca. 10% to 30%. Other major products were $[PW_{11}O_{39}]^{7-}$ and $[PW_{11}O_{39}Rh_2(OAc)_2]^{5-}$.

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the absence of heteropolyanions, hydrothermal reaction of $RhCl_3$ in acetate buffer leads to the well-known rhodium(II) acetate dimer. In more dilute (0.1 M) buffer, the yield of **1** decreases, and $[PW_{11}O_{39}RhCl]^{5-}$ (δP −10.0 ppm)[8] is also formed. Reactions in formate and propionate buffers lead to reduction (and no new heteropolyanion) and to ca. 10% formation of $[PW_{11}O_{39}\{Rh_2(O_2CC_2H_5)_2\}]^{5-}$,[10] respectively.

The new heteropolyanions carry a terminal functional group which can be further derivatized. The amide $[PW_{11}O_{39}RhCH_2CONHPh]^{5-}$ (**4**) was synthesized in 60−70% yield by a standard procedure.[11] Remarkably, **4** is sufficiently hydrolytically stable in aqueous solution to permit its isolation as a cesium salt and to record NMR spectra.[12] The short linker between the heavy quasi-spherical polyoxometalate and the reactive carboxyl group is particularly advantageous for structural analysis (by derivatization for multiple isomorphous replacement) of very large biomolecules and molecular assemblies. Such approaches are currently in progress for the structural investigation of the large ribosomal subunit of *Haloarcula marismortui* in the laboratory of Professor Ada Yonath.[13]

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, interatomic distances and angles, and anisotropic thermal parameters for **2** (19 pages, print/PDF). X-ray crystallographic files, in CIF format, for **2** are available on the Internet only. See any current masthead page for ordering information and Web access instructions.

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(10) Wei, X.; Dickman, M. H.; Pope, M. T. *Inorg. Chem.* **1997**, *36*, 130.

(11) Komiotis, D.; Wencel-Drake, J. D. *Biochem. Pharmacol.* **1996**, *52*, 763. An aqueous solution containing 0.25 g (0.07 mmol) of $Li_5[PW_{11}O_{39}RhCH_2COOH]$ was stirred with a dichloromethane solution containing a 5−10-fold excess of tetra-*n*-heptylammonium bromide [Katsoulis, D. E.; Pope, M. T. *J. Am. Chem. Soc.* **1984**, *106*, 2737]. After the red heteropolyanion had been completely extracted into the organic phase, the latter was separated, dried with $MgSO_4$, and evaporated to a volume of ca. 3 mL. Under nitrogen, 9.5 mL (0.08 mol) of 1-methylpiperidine was added, the solution was immediately cooled in an acetone−dry ice bath (−78 °C), and 11 mL (0.08 mol) of isobutyl chloroformate was added. After 45 min, the solution was transferred to an ethanol−dry ice bath (−25 °C) and stirred for 35 min, and 250 μL (2.7 mmol) of aniline was added. The final solution was stirred for 40 min, allowed to warm to room temperature, and washed successively with 1 M HCl and water. The heteropolyanion products were extracted back into water by stirring with aqueous 0.2 M $NaClO_4$. The separated aqueous phase was treated with KCl to precipitate excess perchlorate as $KClO_4$. Addition of CsCl to the filtrate precipitated the heteropolyanions. The solid was washed with 2:1 v/v water−ethanol and allowed to dry in the air. Based on P NMR of a solution of the cesium salt in D_2O, about 5% of unreacted **1** was present in the product.

(12) NMR: ^{31}P, −11.4; ^{1}H, 4.27 (d, 2H, $^{2}J_{H-Rh} = 2.64$ Hz), 7.13 (t), 7.31 (t), 7.55 (d), $^{2}J = 7.02$ Hz; ^{13}C, 15.2 (d, $^{1}J_{C-Rh} = 27.6$ Hz), 124.9, 127.7, 131.8, 140.7, 185.7.

(13) Weinstein, S., Weizmann Institute, Rehovot, Israel, private communication.