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Trilacunary Heteropolytungstates Functionalized by Organometallic Ruthenium(II), $[(RuC_6H_6)_2XW_9O_{34}]^{6-}$ (X = Si, Ge)

Li-Hua Bi,[†] Ulrich Kortz,*[,†] Michael H. Dickman,[†] B. Keita,[‡] and L. Nadjo*[,‡]

International University Bremen, School of Engineering and Science, P.O. Box 750 561, 28725 Bremen, Germany, and Laboratoire de Chimie Physique, UMR 8000, CNRS, Equipe d'Electrochimie et Photoélectrochimie, Université Paris-Sud, Bâtiment 420, 91405 Orsay Cedex, France

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The benzene–Ru(II)-supported trilacunary heteropolytungstates $[(RuC_6H_6)_2XW_9O_{34}]^{6-}$ (X = Si, **1**; Ge, **2**) have been synthesized and characterized by multinuclear solution NMR (^{183}W, ^{13}C, ^{1}H, ^{29}Si), UV–vis and IR spectroscopy, electrochemistry, and elemental analysis. Single-crystal X-ray analysis was carried out on $Rb_2Na_4[(RuC_6H_6)_2SiW_9O_{34}]\cdot 21H_2O$ (**RbNa-1**), which crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 11.9415(2)$ Å, $b = 13.3123(2)$ Å, $c = 19.4927(4)$ Å, $\alpha = 96.6460(10)°$, $\beta = 95.1570(10)°$, $\gamma = 98.2560(10)°$, and $Z = 2$ and on $Cs_2Na_4[(RuC_6H_6)_2GeW_9O_{34}]\cdot 19.5H_2O$ (**CsNa-2**), which crystallizes also in the triclinic system, space group $P\bar{1}$, with $a = 11.930(4)$ Å, $b = 13.353(4)$ Å, $c = 19.586(6)$ Å, $\alpha = 95.982(5)°$, $\beta = 95.414(6)°$, $\gamma = 98.142(5)°$, and $Z = 2$. The novel polyanion structure consists of two (RuC_6H_6) units linked to a trilacunary (XW_9O_{34}) Keggin fragment via Ru–O(W) and Ru–O(X) bonds resulting in an assembly with C_s symmetry. Polyanions **1** and **2** were synthesized by reaction of $[RuC_6H_6Cl_2]_2$ with $[A\text{-}\alpha\text{-}XW_9O_{34}]^{10-}$ in aqueous buffer medium (pH 6.0). Both **1** and **2** are stable in solution as indicated by the expected 5-line pattern (2:1:2:2:2) in the ^{183}W NMR and the expected ^{13}C, ^{1}H, and ^{29}Si spectra. Descriptions of the respective electrochemical behaviors of the W centers and the Ru centers in **1** and **2** are given in media where these processes are clearly defined. In a pH = 3 acetate medium, the cyclic voltammetry of the W centers shows the known fingerprint of the trilacunary $\alpha\text{-}[XW_9O_{34}]^{n-}$ (X = Ge, Si) moieties. The presence of the (RuC_6H_6) substituents imparts a good stability to these fragments in solution. Stepwise oxidation of the Ru centers was suspected in pH = 5 acetate medium, but only the first step was well-separated from a large current composite wave. The stepwise oxidation was finally observed clearly in a DMF–water (90/10 v/v) mixture and shows two well-behaved Ru oxidation processes. A short comparison is made with DMSO-bearing Ru polyoxometalates.

Introduction

Polyoxometalates (POMs) are a unique class of inorganic metal−oxygen clusters. This family of compounds has been known for more than 200 years, and numerous new structural types with fascinating topological beauty and the associated multitude of properties are still being discovered.[1−3] There have been increasing efforts toward the decoration of polyoxoanions with various organic and/or transition metal complex moieties.[4−6] The motivation for this work lies in the synthesis of potentially new types of catalyst systems as well as interesting functional materials with optical, electronic, and magnetic properties. Of interest is also the exploration of possible atomic level structural models for the determination of the mechanisms of oxide-supported

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* To whom correspondence should be addressed. E-mail: u.kortz@iu-bremen.de (U.K.). Fax: +49-421-200 3229 (U.K.).

[†] International University Bremen.

[‡] Université Paris-Sud.

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catalysts. This work has led to a large number of transition metal containing POM derivatives including 3d- and f-block metals. However, there are very few reports on POMs incorporating 4d or 5d transition metal ions.[7−9] Therefore, the rational design, synthesis, and characterization of new types of such polyanions remain an important research objective.

Synthesis of POMs containing ruthenium is of great industrial interest owing to the unique redox and catalytic properties of this element.[10] Discovery of the mono-Ru(III)-substituted silicotungstate $[SiW_{11}Ru(H_2O)O_{39}]^{5-}$ and its high reactivity and selectivity in the catalytic oxidation of a variety of organic substrates by O_2 and H_2O_2 has motivated research groups worldwide to engage in the synthesis of ruthenium POMs.[11] To date, $RuCl_3 \cdot nH_2O$, $[Ru(H_2O)_6][C_7H_7SO_3]_2$, $Ru(acac)_3$, and *cis*-$Ru(DMSO)_4Cl_2$ have been used as Ru precursors to synthesize Ru-decorated POMs.[12−14] However, the number of structurally characterized, Ru-containing polyoxotungstates has been extremely small until recently. Only two species had been known, namely Finke's $[O\{Ru^{IV}Cl(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{16-}$ and Neumann's $[WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2]$.[11−15,16] The difficulty of making pure Ru-containing polyoxometalates and the nonreproducibility of some reported Ru-containing polyanions has been discussed by Nomiya et al.[14b]

Very recently our group reported on the structures of three types of $Ru^{II}(DMSO)_3$-supported polyoxotungstates, $[HW_9O_{33}Ru_2(DMSO)_6]^{7-}$, $[Ru(DMSO)_3(H_2O)XW_{11}O_{39}]^{6-}$ (X = Ge, Si), and $[HXW_7O_{28}Ru(DMSO)_3]^{6-}$ (X = P, As).[17] These polyanions were fully characterized in solution and in the solid state by single-crystal XRD, elemental analysis, IR, UV−vis, and ^{183}W, ^{1}H, and ^{13}C NMR spectroscopy.

In the last years organometallic ruthenium precursors have also been used for the synthesis of ruthenium-containing POMs. The groups of Attanasio, Finke, and Klemperer, respectively, reported on $[(p\text{-cymene})Ru(Nb_2W_4O_{19})]^{2-}$, $[(C_6H_6)Ru \cdot P_2W_{15}Nb_3O_{62}]^{7-}$, $[(C_6H_6)Ru(Cp^*TiW_5O_{18})]^{-}$, and $[(Cp^*TiW_5O_{18})_2Ru_2(CO)_4]^{4-}$, all of which were characterized by elemental analysis, IR, and multinuclear NMR.[18−20] Subsequently, Süss-Fink and co-workers and Proust and co-workers described the formation of organometallic oxides by self-condensation of simple molybdates or tungstates with $\{Ru^{II}(arene)\}^{2+}$ units (arene = benzene, toluene, *p*-cymene, mesitylene, durene, or hexamethylbenzene).[21,22] In 2003,

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Proust and co-workers reported on the structure of the carbene−Ru−heteropolytungstate $[(PW_9O_{34})_2(cis\text{-}WO_2)(cis\text{-}RuL^{Me}_2)]^{13-}$ (L^{Me} = 1,3-dimethylimidazolidine-2-ylidene).[23] Very recently, the same group reported on the $\{Ru(arene)\}^{2+}$ derivatives $[PW_{11}O_{39}\{Ru(arene)(H_2O)\}]^{5-}$ and $[\{PW_{11}O_{39}\{Ru(arene)\}\}_2\{WO_2\}]^{8-}$ (arene = benzene, toluene, *p*-cymene, hexamethylbenzene).[24]

The trilacunary tungstosilicate and germanate $[\alpha\text{-}XW_9O_{34}]^{10-}$ (X = Si, Ge) have been routinely used as precursors for the synthesis of polyanions containing first-row transition metals or lanthanides. To date, monomeric trimetallo Keggin derivatives (e.g., $[Co_3(H_2O)_3SiW_9O_{37}]^{10-}$),[25] Keggin dimers (e.g., $[Fe_6(OH)_3(A\text{-}\alpha\text{-}GeW_9O_{34}(OH)_3)_2]^{11-}$),[26] Keggin tetramers (e.g., $Na_{19}K_4\{[(SiW_9O_{34})(SiW_9O_{33}(OH))(Cu(OH))_6Cu]_2Br\}^{23-}$),[27] and Keggin-based sandwich complexes (e.g., $[Mn_4(H_2O)_2(GeW_9O_{34})_2]^{12-}$)[28] have been reported. On the other hand, examples of discrete molecular species with organometallic groups grafted on trilacunary tungstosilicates/germanates are much more rare, e.g., $[(CpTi)_3XW_9O_{37}]^{7-}$ (X = Si, Ge),[29] $[CpRh\cdot SiW_9Nb_3O_{40}]^{5-}$, and $[(CpTi)(\beta\text{-}1,2,3\text{-}SiW_9V_3O_{40})]^{4-}$ (Cp = C_5H_5).[30] In fact, for none of these polyanions has a single-crystal X-ray structure been reported.

We are particularly interested in the synthesis, structure, and oxidation catalysis properties of Ru-containing polyoxometalates. However, we noticed that the $Ru^{II}(DMSO)_3$-supported polyanions are probably not very useful for homogeneous applications, as the bound DMSO ligands are very inert. Therefore, we searched for other cationic, water soluble, organo-Ru precursors with more labile ligands. Here we report on the interaction of $[RuC_6H_6Cl_2]_2$ with the trilacunary Keggin precursors $[\alpha\text{-}SiW_9O_{34}]^{10-}$ and $[\alpha\text{-}GeW_9O_{34}]^{10-}$, respectively.

Experimental Section

Synthesis. The polyanion precursors $Na_{10}[\alpha\text{-}SiW_9O_{34}]\cdot 18H_2O$ and $Na_{10}[\alpha\text{-}GeW_9O_{34}]\cdot 18H_2O$ were synthesized according to published procedures, and purity was confirmed by infrared spectroscopy.[31] All other reagents were used as purchased without further purification.

$Rb_2Na_4[(RuC_6H_6)_2SiW_9O_{34}]\cdot 21H_2O$ (RbNa-1). A 0.09 g (0.18 mmol) sample of $[RuC_6H_6Cl_2]_2$ was dissolved in 20 mL of sodium acetate buffer (0.5 M, pH 6.0) followed by addition of 0.5 g (0.18 mmol) of $Na_{10}[\alpha\text{-}SiW_9O_{34}]\cdot 18H_2O$. This solution was heated to 80 °C for 1 h and then cooled to room temperature. The solution was filtered, and then 1.0 mL of 1.0 M RbCl was added. This solution was allowed to evaporate in an open beaker at room temperature. A yellow crystalline product started to appear after 2 weeks. Evaporation was continued until the solvent approached the solid product (yield 0.23 g, 40%). IR of **RbNa-1**: 1434(m), 1146(w), 1000(m), 968(w), 951(sh), 928(m), 865(s), 837(sh), 743(w), 689(m), 658(sh), 621(w), 554(w), 522(w), 437(w) cm^{-1}. Anal. Calcd (Found) for **RbNa-1**: Rb, 5.3 (5.0); Na, 2.9 (3.0); W, 51.3 (52.1); Ru, 6.3 (6.0); Si, 0.9 (1.1); C, 4.5 (4.2); H, 1.7 (2.0). NMR of **RbNa-1** in D_2O at 293 K: ^{183}W δ 24.4, −98.2, −109.9, −173.0, −188.9 ppm (all singlets with intensities 2:1:2:2:2); ^1H δ 5.7, 6.0 ppm (all singlets with equal intensities); ^{13}C δ 81.1, 81.7 ppm (all singlets with equal intensities); ^{29}Si δ −81.8 ppm. UV−vis (H_2O) [λ_{max} (ϵ)]: 410 (7.6×10^2 $L\cdot mol^{-1}\cdot cm^{-1}$), 318 nm ($3.6 \times 10^3$ $L\cdot mol^{-1}\cdot cm^{-1}$).

$Cs_2Na_4[(RuC_6H_6)_2GeW_9O_{34}]\cdot 19.5H_2O$ (CsNa-2). A 0.09 g (0.18 mmol) sample of $[RuC_6H_6Cl_2]_2$ was dissolved in 20 mL of sodium acetate buffer (0.5 M, pH 6.0) followed by addition of 0.5 g (0.17 mmol) of $Na_{10}[\alpha\text{-}GeW_9O_{34}]\cdot 18H_2O$. This solution was heated to 80 °C for 1 h and then cooled to room temperature. The solution was filtered, and then 1.0 mL of 1.0 M CsCl was added. This solution was allowed to evaporate in an open beaker at room temperature. A yellow crystalline product started to appear after 2 weeks. Evaporation was continued until the solvent approached the solid product (yield 0.24 g, 42%). IR of **CsNa-2**: 1432(m), 1145(w), 972(w), 927(m), 843(s), 764(m), 669(w), 620(w), 558(w), 535(w), 504(w) cm^{-1}. Anal. Calcd (Found) for **CsNa-2**: Cs, 8.0 (7.7); Na, 2.8 (2.9); W, 49.6 (50.1); Ru, 6.1 (6.0); Ge, 2.2 (2.0); C, 4.3 (4.5); H, 1.5 (1.7). NMR of **CsNa-2** in D_2O at 293 K: ^{183}W δ 52.9, −101.4, −106.6, −139.8, −157.9 ppm (all singlets with intensities 2:1:2:2:2); ^1H δ 5.7, 6.0 ppm (all singlets with equal intensities); ^{13}C δ 80.8, 81.5 ppm (all singlets with equal intensities). UV−vis (H_2O) [λ_{max} (ϵ)]: 416 (7.0×10^2 $L\cdot mol^{-1}\cdot cm^{-1}$), 315 nm ($3.6 \times 10^3$ $L\cdot mol^{-1}\cdot cm^{-1}$).

Elemental analyses were performed by Kanti Labs Ltd., Mississauga, Canada. Infrared spectra were recorded on KBr pellets using a Nicolet Avatar spectrophotometer. UV−vis spectra were recorded on a Cary 100 Bio UV−vis spectrophotometer on 3.5×10^{-4} M solutions of the relevant polyanions. Matched 1.000 cm optical path quartz cuvettes were used. TGA experiments were performed on a Thermal Analysis Q 600 instrument from $T = 20-250$ °C using a N_2 atmosphere.

NMR. All NMR spectra were recorded on a 400 MHz JEOL ECX instrument at room temperature using D_2O as solvent. The chemical shifts are reported with respect to the standard references TMS (^1H, ^{13}C, ^{29}Si) and 1M Na_2WO_4 (^{183}W). ^{183}W NMR: 16.65 MHz, resolution 1.27 Hz, sweep width 16.66 MHz, pulse width (45°) 35 μs, acquisition time 0.79 s, relaxation delay 0.5 s, number of scans, 110 220 for **1** and 63 546 for **2**. $^{13}C\{^1H\}$ NMR: 100.53 MHz, resolution 0.96 Hz, sweep width 31.45 kHz, pulse width (45°) 4.75 μs, acquisition time 1.04 s, relaxation delay 1 s, Waltz-type proton decoupling at 14 dB, number of scans, 342 for **1** and 2258 for **2**. ^1H NMR: 399.78 MHz, resolution 0.23 Hz, sweep width

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Table 1. Crystal Data and Structure Refinement for $Rb_2Na_4[(RuC_6H_6)_2SiW_9O_{34}]\cdot 21H_2O$ (**RbNa-1**) and $Cs_2Na_4[(RuC_6H_6)_2GeW_9O_{34}]\cdot 19.5H_2O$ (**CsNa-2**)

	RbNa-1	CsNa-2
emp formula	$C_{12}H_{54}Na_4O_{55}Rb_2Ru_2SiW_9$	$C_{12}Cs_2GeH_{51}Na_4O_{53.5}Ru_2W_9$
fw	3226.5	3338.9
space group (No.)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
a (Å)	11.9415(2)	11.930(4)
b (Å)	13.3123(2)	13.353(4)
c (Å)	19.4927(4)	19.586(6)
α (deg)	96.6460(10)	95.982(5)
β (deg)	95.1570(10)	95.414(6)
γ (deg)	98.2560(10)	98.142(5)
vol (Å^3)	3028.08(9)	3052.9(16)
Z	2	2
temp (°C)	−100	−120
wavelength (Å)	0.710 73	0.710 73
d_{calcd} (mg m^{-3})	3.42	3.50
abs coeff (mm^{-1})	18.659	18.855
R [$I > 2\sigma(I)$]^a	0.038	0.061
R_w (all data)^b	0.098	0.112

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

7.50 kHz, pulse width (45°) 6.05 μs, acquisition time 4.37 s, relaxation delay 2 s, number of scans, 16 for **1** and **2**. ^{29}Si NMR: 79.43 MHz, resolution 1.53 Hz, sweep width 50 kHz, pulse width (30°) 4.17 μs, acquisition time 0.66 s, relaxation delay 4 s, number of scans, 12 294 for **1**.

X-ray Crystallography. A single crystal of compound **RbNa-1** was mounted on a Hampton cryoloop for indexing and intensity data collection at 173 K on a Bruker Kappa APEX2 single-crystal diffractometer (at International University Bremen) using Mo Kα radiation ($\lambda = 0.71073$ Å). On the other hand, a single crystal of compound **CsNa-2** was mounted on a glass fiber for indexing and intensity data collection at 153 K on a Bruker D8 SMART APEX CCD single-crystal diffractometer (at Hamburg University) using Mo Kα radiation ($\lambda = 0.71073$ Å). In both cases direct methods were used to solve the structures and to locate the heavy atoms (SHELXS97). Then the remaining atoms were found from successive difference maps (SHELXL97). The final cycle of refinement for **RbNa-1**, including the atomic coordinates, anisotropic thermal parameters (W, Ru, and Rb atoms), and isotropic thermal parameters (Na, Si, O, and C atoms) converged at $R = 0.038$ and $R_w = 0.098$ ($I > 2\sigma(I)$). In the final difference map, the deepest hole was −2.818 eÅ^{-3} and the highest peak was 4.173 eÅ^{-3}. On the other hand, the final cycle of refinement for **CsNa-2**, including the atomic coordinates, anisotropic thermal parameters (W, Ru, Ge, and Cs atoms), and isotropic thermal parameters (Na, O, and C atoms) converged at $R = 0.061$ and $R_w = 0.112$ ($I > 2\sigma(I)$). In the final difference map, the deepest hole was −2.652 eÅ^{-3} and the highest peak was 3.280 eÅ^{-3}. For both structures, benzene hydrogens were added in calculated positions and were allowed to ride on the carbon atoms they are connected to during refinement with a fixed temperature factor. Routine Lorentz and polarization corrections were applied, and an absorption correction was performed using the SADABS program.[32] Several of the water molecules of hydration in **RbNa-1** and **CsNa-2** were disordered, as is usually observed in polyoxometalate crystallography. This was accounted for by assigning partial occupancies (e.g., 0.5). The crystal water content of **RbNa-1** and **CsNa-2** was also verified by thermogravimetric analysis (see the Supporting Information, Figure S1). Crystallographic data are summarized in Table 1.

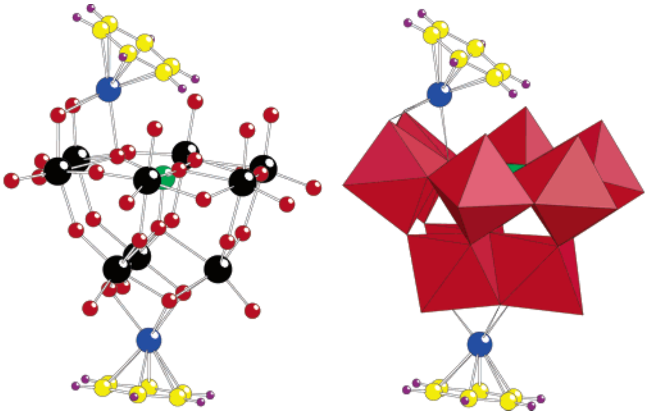

Figure 1. Ball and stick (left) and polyhedral (right) representations of $[(RuC_6H_6)_2XW_9O_{34}]^{6-}$ (X = Si, **1**; Ge, **2**). The balls represent tungsten (black), germanium/silicon (green), ruthenium (blue), oxygen (red), carbon (yellow), and hydrogen (violet). Hydrogens were added in calculated positions.

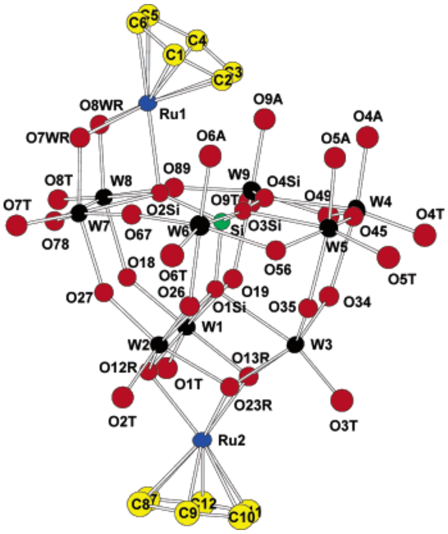

Figure 2. Ball and stick representation of $[(RuC_6H_6)_2SiW_9O_{34}]^{6-}$ (**1**) showing thermal ellipsoids (50%) and the labeling scheme. The Ru−O bond lengths are as follows: Ru1−O7WR 2.074(5), Ru1−O8WR 2.078(5), Ru1−O2SI 2.184(5), Ru2−O12R 2.088(5), Ru2−O23R 2.108(5), and Ru2−O13R 2.111(5) Å.

Electrochemistry

General Methods and Materials. Pure water was used throughout. It was obtained by passing through an RiOs 8 unit followed by a Millipore-Q Academic purification set. The compositions of the various media were as follows: for pH 3, 0.4 M $CH_3COONa + CH_2ClCOOH$; for pH 5, 0.4 M $CH_3COONa + CH_3COOH$; for the mixed solvent, DMF (Fluka)−Millipore water (90/10 v/v) + 0.1 M Bu_4NPF_6 (Fluka) or $LiClO_4$ (Aldrich).

Electrochemical Experiments. The polyanion concentration was 2×10^{-4} M, unless otherwise indicated. The solutions were deaerated thoroughly for at least 30 min with pure argon and kept under a positive pressure of this gas during the experiments. The source, mounting, and polishing of the glassy carbon electrodes (GC, Tokai, Japan) has been described.[33] The glassy carbon samples had a diameter of 3 mm. The electrochemical setup was an EG & G 273 A driven by a PC with the M270 software. Potentials are quoted against a saturated calomel electrode (SCE). The counter

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(32) Sheldrick, G. M. *SADABS*; University of Göttingen: Göttingen, Germany, 1996.

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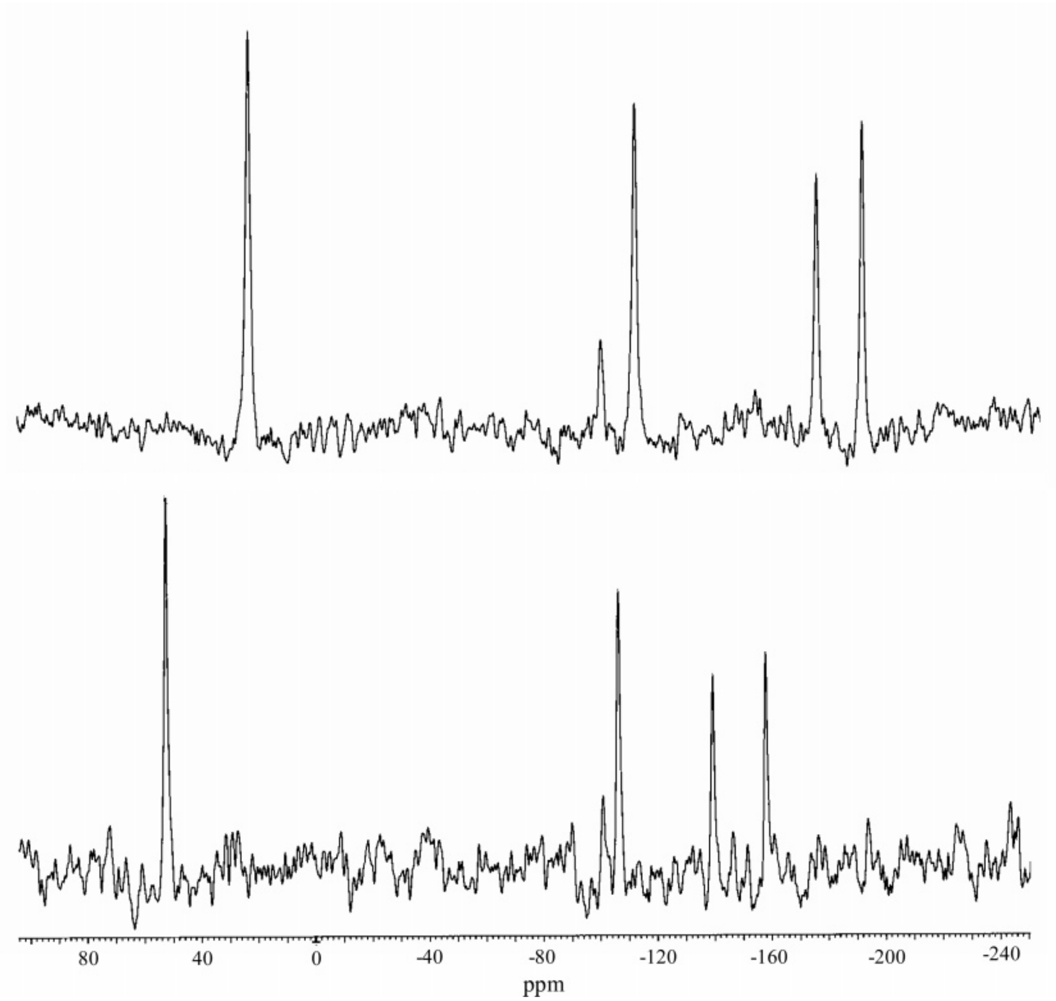

Figure 3. Tungsten-183 NMR spectra of $[(RuC_6H_6)_2XW_9O_{34}]^{6-}$ (X = Si, **1,** top; Ge, **2,** bottom) at 293 K.

electrode was a platinum gauze of large surface area. All experiments were performed at room temperature.

Results and Discussion

Synthesis and Structure. The benzene−Ru(II)-supported heteropolytungstates $[(RuC_6H_6)_2SiW_9O_{34}]^{6-}$ (**1**) and $[(RuC_6H_6)_2GeW_9O_{34}]^{6-}$ (**2**) were synthesized in aqueous medium (pH 6.0) using a one-pot reaction of $[RuC_6H_6Cl_2]_2$ with the trilacunary polyanion precursors $[A\text{-}\alpha\text{-}XW_9O_{34}]^{10-}$ (X = Si, Ge). Polyanions **1** and **2** consist of a Keggin fragment (α-XW_9O_{34}) to which two (RuC_6H_6) groups are coordinated resulting in an unprecedented polyanion structure with C_s symmetry (see Figures 1 and 2). Interestingly, the two (RuC_6H_6) groups are bound at different sites and via different bonding modes to the lacunary polyanion fragment. One (RuC_6H_6) unit is coordinated at the lacuna of the polyanion via two Ru−O(W) bonds and one Ru−O(X) bond, whereas the other (RuC_6H_6) unit is bound at the other end of the structure to three bridging oxygen atoms of a W_3O_{13} triad. This indicates that the vacant site of the polyanion does not allow binding of more than one (RuC_6H_6) group, most likely due to steric effects. Therefore, the second organo-Ru group attaches to the cap of the Keggin fragment involving all three W−O−W bridging oxygens of the W_3O_{13} triad.

Bond-valence sum calculations[34] for **1** and **2** indicate that there are no protonation sites, and therefore the charge of the polyanions must be −6. In the solid state the negative charges of **1** and **2** are balanced by two rubidium and four sodium ions and by two cesium and four sodium ions, respectively. For **1** only 1.25 of the 2 rubidium ions and 3.9 of the 4 sodium ions and for **2** only 1.5 of the 2 cesium ions could actually be detected by single crystal XRD, probably due to disorder. However, the complete chemical composition was obtained by elemental analysis.

Polyanions **1** and **2** are stable in the pH 3−7 range as determined by monitoring their UV−vis spectra as a function of pH over a period of at least 1 month. In this pH range, all spectra were reproducible with respect to absorbances and wavelengths. We also decided to perform a multinuclear solution NMR study on the diamagnetic polyanions **1** and **2** at room temperature, and for this purpose we redissolved solid **RbNa-1** and **CsNa-2** in D_2O. The ^{183}W NMR spectra for **1** and **2** exhibit the expected 5-line pattern with relative intensities 2:1:2:2:2, confirming the C_s symmetry of the polyanions (see Figure 3). The ^1H- and $^{13}C\{^1H\}$ NMR spectra of **1** and **2** display two signals each of equal intensity (see Figures 4 and 5), indicative of two magnetically inequivalent

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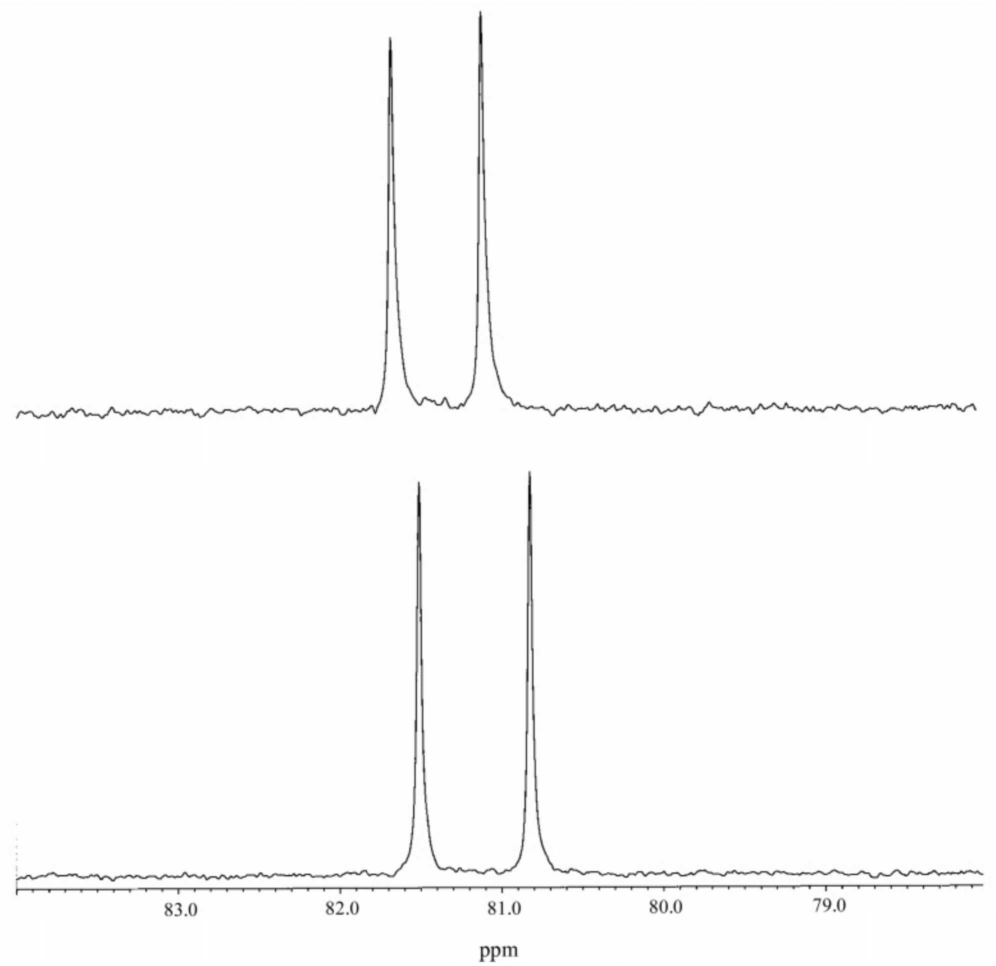

Figure 4. Carbon-13 NMR spectra of $[(RuC_6H_6)_2XW_9O_{34}]^{6-}$ (X = Si, **1,** top; Ge, **2,** bottom) at 293 K.

(RuC_6H_6) groups. These results indicate that the carbon and hydrogen atoms of each benzene ring appear magnetically equivalent on the NMR time scale. The only possible explanation for this phenomenon is fast rotation of the benzene unit around the Ru$-$(η^6-C_6H_6) bond axis, and this is in complete agreement with the observations of Artero et al.[24] Finally, the ^{29}Si NMR spectrum of **1** shows a singlet (see Figure 6). All of the above is in agreement with the solid-state structures of **1** and **2**.

In recent years some other organo-ruthenium(II)-substituted polyoxometalates have been reported, predominantly by Proust and co-workers. They described synthesis and structural characterization of the Ru^{II}(arene)-containing tungstophosphates $[PW_{11}O_{39}\{Ru(p\text{-cymene})(H_2O)\}]^{5-}$, $[\{PW_{11}O_{39}\{Ru(arene)\}\}_2\{WO_2\}]^{8-}$ (arene = benzene, toluene), and $[(PW_9O_{34})_2(cis\text{-}WO_2)(cis\text{-}RuL^{Me}{}_2)]^{13-}$ (L^{Me} = 1,3-dimethylimidazolidine-2-ylidene).[23,24] In addition, they reported on some Ru^{II}(arene)-containing tungsten and molybdenum oxides, e.g., $[\{Ru(\eta^6\text{-}p\text{-}MeC_6H_4iPr)\}_4W_4O_{16}]$, $[\{Ru(\eta^6\text{-}p\text{-}MeC_6H_4iPr)\}_4W_2O_{10}]$, $[\{Ru(\eta^6\text{-}p\text{-}MeC_6H_4iPr)\}_2(\mu\text{-}OH)_3]_2\text{-}[\{Ru(\eta^6\text{-}p\text{-}MeC_6H_4iPr)\}_2\text{-}W_8O_{28}(OH)_2\{Ru(\eta^6\text{-}p\text{-}MeC_6H_4iPr)(H_2O)\}_2]$, and $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2Mo_5O_{18}\{Ru(\eta^6\text{-}C_6Me_6)(H_2O)\}]$.[22b]

However, **1** and **2** represent the first examples of tungstosilicates and tungstogermanates to which Ru(arene) groups have been grafted. Furthermore, they are the first examples of trilacunary and monomeric heteropolyanions decorated by Ru(arene) units. Polyanions **1** and **2** can be considered as ”semilacunary” species, as four of the six belt tungsten centers are not involved in bonding to the (RuC_6H_6) group in the lacuna at all. This could be of major interest for catalytic applications of this compound (substrate binding, etc.), especially if it were possible to remove the benzene ligand from this Ru center (”active site”) and keep the overall polyanion structure intact. In summary, polyanions **1** and **2** exhibit unprecedented and highly interesting features in the area of organo-ruthenium-containing polyoxometalates.

Synthesis of **1** and **2** was accomplished by reaction of $[\alpha\text{-}XW_9O_{34}]^{10-}$ (X = Si, Ge) and $[RuC_6H_6Cl_2]_2$ in equimolar ratio in aqueous medium (pH 6.0) at 80 °C. This indicates that the dimeric Ru precursor is hydrolyzed at such conditions, providing the reactive mononuclear electrophile in situ. We also performed reactions between $[RuC_6H_6Cl_2]_2$ and $[\alpha\text{-}XW_9O_{34}]^{10-}$ (X = Si, Ge) in ratios larger than 1:1 (e.g., 3:1), but we always observed formation of **1** and **2** only. These observations suggest that for steric and electronic reasons not more than two (RuC_6H_6) groups can be attached to the trilacunary Keggin core.

The synthetic conditions for **1** and **2** are very similar to our recently reported $[Ru(DMSO)_3(H_2O)XW_{11}O_{39}]^{6-}$ (X =

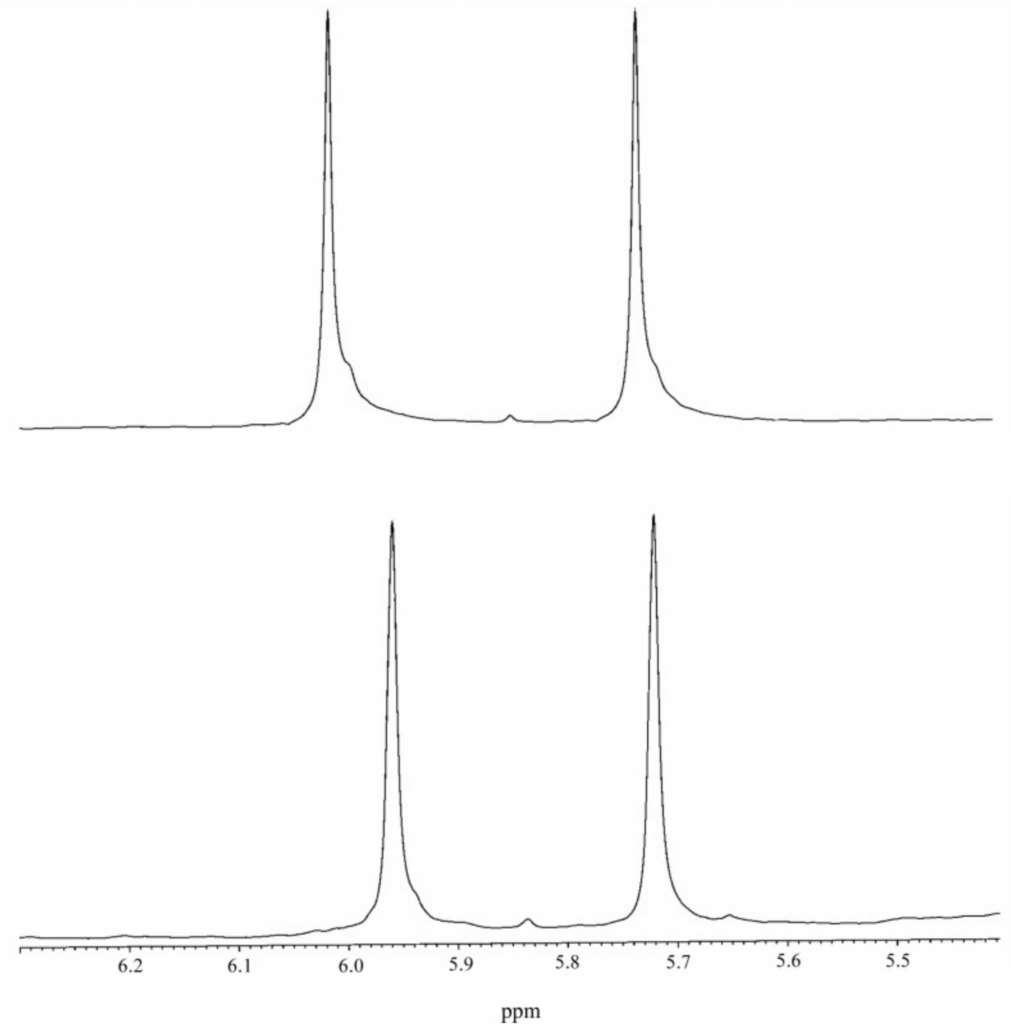

Figure 5. Proton-1 NMR spectra of $[(RuC_6H_6)_2XW_9O_{34}]^{6-}$ (X = Si, **1,** top; Ge, **2,** bottom) at 293 K.

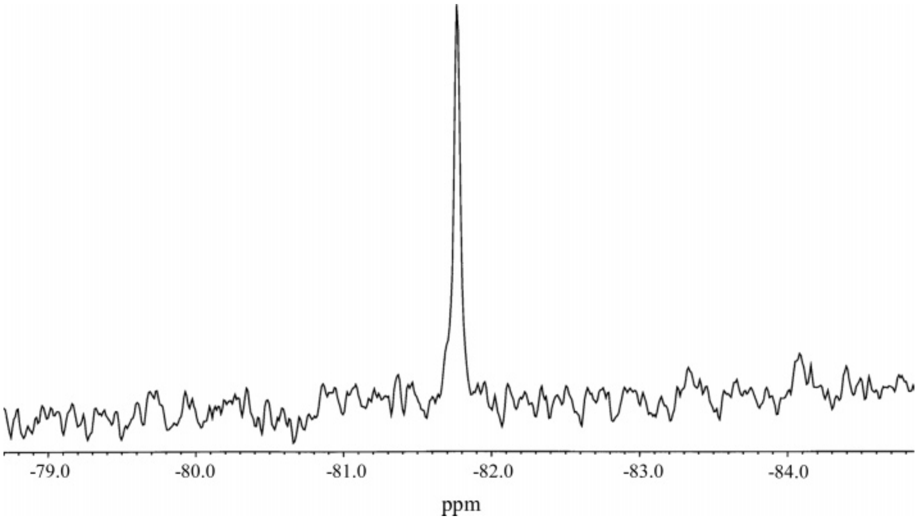

Figure 6. Silicon-29 NMR spectrum of $[(RuC_6H_6)_2SiW_9O_{34}]^{6-}$ at 293 K.

Si, Ge), which are composed of a monolacunary ($XW_{11}O_{39}$) Keggin fragment with a $\{Ru(DMSO)_3(H_2O)\}$ group attached via two Ru−O(W) bonds to the lacunary site.[17b] Interestingly, these polyanions were also prepared from the trilacunary Keggin precursors $[\alpha\text{-}XW_9O_{34}]^{10-}$ (X = Si, Ge), indicating in situ isomerization to the more stable monolacunary derivatives. Our results on **1** and **2** indicate that in this case the highly reactive trilacunary Keggin species $[\alpha\text{-}XW_9O_{34}]^{10-}$ (X = Si, Ge) are stabilized by coordination of two (RuC_6H_6) fragments so that isomerization to the monolacunary

$[\alpha\text{-}XW_{11}O_{39}]^{8-}$ is inhibited. Therefore, we have shown that the Ru(II) precursors $[RuC_6H_6Cl_2]_2$ and *cis*-$Ru(DMSO)_4Cl_2$ react very differently with trilacunary tungstosilicates and germanates.

Electrochemistry. We also decided to study the respective electrochemical behaviors of the W centers and the Ru centers in **1** and **2**, using media in which these processes are clearly defined. As a consequence, the Keggin core and the (RuC_6H_6) substituents of **1** and **2** will be described separately.

Figure 7A shows in superposition the patterns obtained for **1** and **2**, respectively, in a pH = 3 acetate medium. The voltammograms feature a fingerprint analogous to that known for $\alpha\text{-}[PW_9O_{34}]^{n-}$ fragments.[35,36] As also observed previously for $[Ru(DMSO)_3(H_2O)XW_{11}O_{39}]^{6-}$ (X = Ge, Si), the W waves in the Ge derivative are located at slightly less negative potentials than those of the Si derivative.[17b] With restriction to the potential domain explored in Figure 7A, the shown pattern remains reproducible from run to run, which underscores the remarkable stabilization of the $\alpha\text{-}[XW_9O_{34}]^{n-}$ (X = Si or Ge) fragment by the presence of the two (RuC_6H_6) groups. It is worth noting that, in the same pH = 3 acetate medium, a strong stabilization by the presence of Ni^{2+} ions was not observed. To the contrary, in this case we observed gradual transformation of $\alpha\text{-}[SiW_9O_{34}]^{10-}$ to $\alpha\text{-}[SiW_{11}O_{39}]$.[8-37] It was found that **1** and **2** are not very stable in 1 M NaCl, pH = 3 medium. At pH = 5, the W waves are very close to the solvent limit. Extension of the potential domain toward more negative values than those used previously results in deposition, on the electrode surface, of a film (not shown) which grows fast with every additional run and renders the voltammogram featureless. This film is associated with a reoxidation surface wave peaking roughly around + 0.94 V vs SCE depending on the film thickness. The study of this process was not pursued further.

In the pH = 3 acetate medium, exploration of the potential domain up to 1.3 V vs SCE shows only a very high intensity featureless current that might represent both possible oxidation of the $Ru(C_6H_6)$ centers and oxidation of the electrolyte. In contrast, increasing the pH up to pH = 5, acetate medium, favors observation of the Ru centers. Figure 7B shows, in superposition, the first Ru waves obtained in a pH = 5 acetate medium. As expected, the wave related to the Si derivative **1** is slightly less positive than that corresponding to the Ge derivative **2**. In contrast to previous observation with $[Ru(DMSO)_3(H_2O)XW_{11}O_{39}]^{6-}$ (X = Ge, Si)[17b] for which only a partial oxidation of the Ru center could be achieved, a well-developed wave appears in Figure 7B. The chemical reversibility of this process is poor, even though a small but persistent reduction wave exists. At more positive potential, a second, chemically irreversible wave is observed (not shown), the large intensity current and the composite nature of which suggest that it might represent a combination of an additional $Ru(C_6H_6)$ wave and the oxidation of a solution component. Such a possibility would comply with previous results of Rong and Pope[38] who detected one or two oxidation steps for the Ru center in $[PW_{11}O_{39}Ru^{III}(H_2O)]^{4-}$ depending on the pH of the electrolyte. These authors substituted the

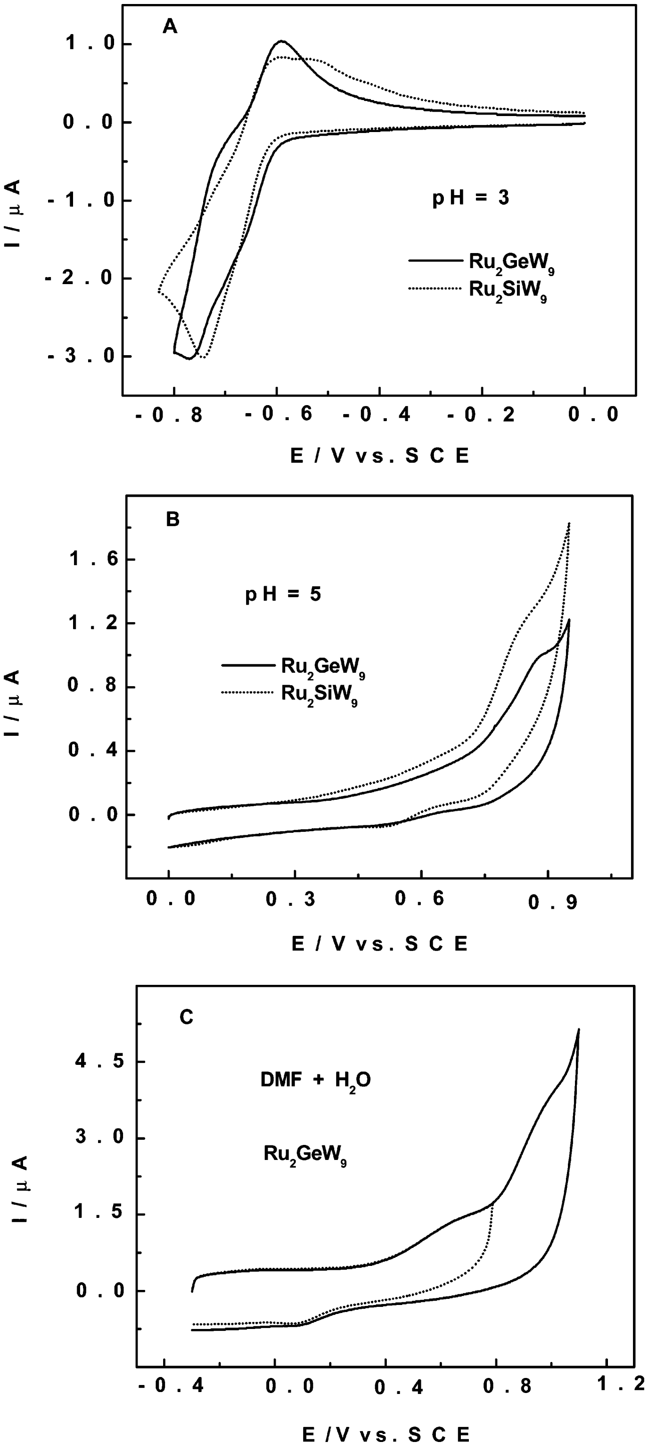

Figure 7. Cyclic voltammograms of $[(RuC_6H_6)_2XW_9O_{34}]^{6-}$ (X = Si, **1**; Ge, **2**) in various media. The working electrode was glassy carbon, and the reference electrode was SCE. (A) The voltammetric pattern is restricted to the W redox processes in a pH 3 medium (0.4 M CH_3COONa + $CH_2ClCOOH$). Polyanion concentration: 2×10^{-4} M. The scan rate was 10 $mV{\cdot}s^{-1}$. (B) The voltammetric pattern is restricted to the first Ru-centered process in a pH 5 medium (0.4 M CH_3COONa + CH_3COOH). Polyanion concentration: 2×10^{-4} M. The scan rate was 10 $mV{\cdot}s^{-1}$. (C) The voltammetric pattern is extended to the two Ru-centered processes in a mixed dimethylformamide−water solvent (90/10 v/v) + 0.1 M Bu_4NPF_6. Polyanion concentration: $\sim 1.5 \times 10^{-4}$ M. The scan rate was 100 $mV{\cdot}s^{-1}$.

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(37) Contant, R.; Hervé, G. *Rev. Inorg. Chem.* **2002**, *22*, 63.

terminal water ligand on Ru by sulfoxides, dialkyl sulfides, pyridine, and active alkenes. Then they showed by cyclic voltammetry a reversible Ru^{III}/Ru^{II} couple, but no further ruthenium oxidations. With the present arene-substituted Ru centers in **1** and **2**, the observation of a large current intensity composite wave in water following the first Ru oxidation step called for further experimentation. The goal was achieved in a mixed dimethylformamide−water solvent (90/10 v/v) as appears in Figure 7C. Water was necessary to enhance the solubility of **1** and **2** which proved sparingly soluble in DMF + 0.1 M Bu_4NPF_6 or $LiClO_4$. A second wave is clearly seen, close to the large discharge process. The intensity of this second wave is slightly larger than that of the first one, but its current ratio decreases and gradually approaches one as the scan rate increases. These observations are fully consistent with all the assumptions made previously. The partial chemical reversibility of the first wave is highlighted. Interestingly, only a one-step oxidation was observed for $[Ru(DMSO)_3(H_2O)GeW_{11}O_{39}]^{6-}$ both in water[17b] and in a DMF−water mixture. In short, the presence of DMSO or C_6H_6 as ligands on Ru(II) results in distinctly different redox behavior of the Ru centers when bound to a polyanion fragment.

Conclusions

We have synthesized and structurally characterized two novel organometallic Ru^{II}-supported heteropolytungstates. The monomeric polyanions $[(RuC_6H_6)_2XW_9O_{34}]^{6-}$ (X = Si, **1**; Ge, **2**) consist of two (RuC_6H_6) units linked to a trilacunary (XW_9O_{34}) Keggin fragment at different sites resulting in an assembly with C_s symmetry. One of the (RuC_6H_6) groups is bound at the vacant polyanion site via two Ru−O(W) bonds and one Ru−O(X) bond, whereas the second (RuC_6H_6) group is coordinated to the Keggin cap via three equivalent Ru−O(W) bonds. Polyanions **1** and **2** represent the first structurally characterized, organometallic Ru-containing silicotungstate and germanotungstate, respectively. Both species were characterized by FT-IR, UV−vis, and multinuclear solution NMR spectroscopy (^{183}W, ^{13}C, ^{1}H, ^{29}Si), electrochemistry, single-crystal X-ray diffraction, and complete elemental analysis. Our NMR results indicate that the solid-state polyanion structures of **1** and **2** are preserved in solution.

We have shown that the trilacunary Keggin-type heteropolyanions $[\alpha\text{-}XW_9O_{34}]^{10-}$ (X = Si, Ge) are strong nucleophiles, which react instantaneously with the in situ formed, formally dicationic (RuC_6H_6) fragment. This reactivity is not limited to the vacant polyanion site but includes also the three μ_2-oxo ligands of the complete W_3O_{13} triad on the other end of the Keggin fragment.

Comparison of synthesis and structure of **1** and **2** with our recently reported $Ru(DMSO)_3$-supported polyanions $[Ru(DMSO)_3(H_2O)XW_{11}O_{39}]^{6-}$ (X = Si, Ge) deserves emphasis, because the latter were also synthesized from $[\alpha\text{-}XW_9O_{34}]^{10-}$ (X = Si, Ge) at almost identical conditions as those for **1** and **2**. Transformation from the trilacunary $(\alpha\text{-}XW_9O_{34})$ to the monolacunary $(\alpha\text{-}XW_{11}O_{39})$ Keggin fragment in the case of *cis*-$Ru(DMSO)_4Cl_2$ clearly indicates that this Ru species acts as a weaker electrophile than $[RuC_6H_6Cl_2]_2$ in aqueous acidic medium. In other words, the (RuC_6H_6) group allows for stabilization of labile polyanion fragments better than the $Ru(DMSO)_3$ group, which is an important guideline for our future work.

Electrochemistry studies of **1** and **2** also demonstrated a stabilization of the $\alpha\text{-}[XW_9O_{34}]^{n-}$ (X = Ge, Si) fragments by the (RuC_6H_6) substituents. To our knowledge, this is the second example, following that described by Rong and Pope,[38] in which stepwise oxidation of Ru centers could be demonstrated.

Currently, we are investigating if other trilacunary Keggin-type polyanions (e.g., $PW_9O_{34}^{9-}$) form analogues of **1** and **2**. In principle, it should be possible to graft the (RuC_6H_6) group to a large variety of lacunary and perhaps also nonlacunary heteropolyanions. We will also study the reactivity of the *p*-cymene analogue of $[RuC_6H_6Cl_2]_2$ with lacunary heteropolytungstates. Furthermore, we are interested in the oxidation catalysis and photochemical properties of **1** and **2**.

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Supporting Information Available: One figure showing thermogravimetric analysis for **RbNa-1** and **CsNa-2** from *T* = 20−250 °C. Complete X-ray crystallographic data for **RbNa-1** and **CsNa-2** (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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