Supporting Information

Hydrothermal and Solid-state Transformation of Ruthenium-supported Keggin-type Heteropolytungstates $[\text{XW}_{11}\text{O}_{39}\{\text{Ru(II)(benzene)(H}_2\text{O)}\}]_n^{1n}$ ($X = \text{P (n = 5)}, \text{Si (n = 6), Ge (n = 6)}$) to Ruthenium-substituted Keggin-type Heteropolytungstates.

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Figure S1. Cyclic voltammograms of reaction solutions obtained by reaction of $\text{K}_7[\text{PW}_{11}\text{O}_{39}]$ and $[\text{Ru}(\text{benzene})\text{Cl}_2)_2$ at (red line) 215 °C, (black line) 170 °C, (blue line) 150 °C and (solid line with open circles) 100 °C for 5 hours. The reaction mixture (0.1 ml) was dissolved in 0.526 M $\text{KH}_2\text{PO}_4$ (1.9 ml) (pH ca. 4.3).
Figure S2. Cyclic voltammograms of reaction solutions obtained by reaction of K₈[SiW₁₁O₃₉] and [Ru(benzene)Cl₂]₂ at (red line) 215 °C, (black line) 170 °C, (blue line) 150 °C and (solid line with open circles) 100 °C for 5 hours. The reaction mixture (0.1 ml) was dissolved in 0.526 M KH₂PO₄ (1.9 ml) (pH ca. 4.3). Green line is cyclic voltammogram of [{SiW₁₁O₃₉Ru(IV/II)O}₂]₁₁⁻ (3b) (0.45 mM) in 0.5 M KH₂PO₄ (pH 4.3). Arrows indicate peaks corresponding to redox peaks of 3b.
Figure S3. Cyclic voltammograms of reaction solutions obtained by reaction of K₈[GeW₁₁O₃₉] and [Ru(benzene)Cl₂]₂ at (red line) 215 °C, (black line) 170 °C and (blue line) 150 °C for 5 hours. The reaction mixture (0.1 ml) was dissolved in 0.526 M KH₂PO₄ (1.9 ml) (pH ca. 4.3). Green line is cyclic voltammogram of [[GeW₁₁O₃₉Ru(IV/III)]₂O]¹¹⁻ (3c) (0.45 mM) in 0.5 M KH₂PO₄ (pH 4.3). Arrows indicate peaks corresponding to redox peaks of 3c.
Figure S4. pH dependence on redox potentials $E_{1/2}$ (Pourbaix diagram) for (black) $1a$, (red) $1b$ and (blue) $1c$. Squares, triangles and circles indicate redox potentials of Ru(V/IV), Ru(IV/III) and Ru(III/II), respectively.
Chemical shift / ppm

(a) -12.180 ppm
-10.464 ppm
-12.943 ppm

(b) -12.170 ppm

(c) 5.968 ppm
HOD 4.654 ppm
6.042 ppm

(d) 5.982 ppm
HOD 4.654 ppm

(e) 5.983 ppm

(f) 5.975 ppm

(g) 80.403 ppm

(h) 80.189 ppm
Figure S5. (a) $^{31}$P-NMR and (c) $^1$H-NMR of yellow solid obtained by a reaction of [PW$_{11}$O$_{39}$]$^{7-}$ and [Ru(benzene)Cl$_2$]$_2$ at 100 ºC for 5 hours. The solid was isolated by adding CsCl. (b) $^{31}$P-NMR and (d) $^1$H-NMR of [PW$_{11}$O$_{39}${Ru(benzene)(H$_2$O)}]$^{5+}$ (2a) prepared at room temperature (Proust’s group method, V. Artero, V. Lahootun, R. Villanneau, R. Thouvenot, P. Herson and A. Proust, *Inorg. Chem.*, 2005, **44**, 2826-2835.). $^1$H-NMR of (e) [SiW$_{11}$O$_{39}${Ru(benzene)(H$_2$O)}]$^{6+}$ (2b) and (f) [GeW$_{11}$O$_{39}${Ru(benzene)(H$_2$O)}]$^{6+}$ (2c) prepared at room temperature. $^{13}$C-NMR of (g) 2a, (h) 2b and (i) 2c prepared at room temperature.
Figure S6. UV-Vis spectra of reaction solution obtained by reaction of (blue) K₈[SiW₁₁O₃₉] or (black) K₈[GeW₁₁O₃₉] with [Ru(benzene)Cl₂]₂ at 215 ºC for 5 hours. The reaction mixture (0.1 ml) was dissolved in 0.526 M KH₂PO₄ (1.9 ml) (pH ca. 4.3). Concentration of Ru is ca. 0.85 mM. Red line is UV-Vis spectrum of [[SiW₁₁O₃₉Ru(IV/III)]₂O]¹⁻ (3b) (0.18 mM) in 0.5 M KH₂PO₄.
Figure S7. IR spectra of Ru-substituted heteropolytungstates produced by reactions of (black) $[\text{PW}_{11}\text{O}_{39}]^{7-}$, (red) $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ or (blue) $[\text{GeW}_{11}\text{O}_{39}]^{8-}$ with (a) $[\text{Ru(benzene)}\text{Cl}_{2}]_{2}$ or (b) $\text{Ru(acac)}_{3}$ as a Ru source. Reaction temperature was 170 °C and reaction time was 5 hours or 20 hours for reactions with $[\text{Ru(benzene)}\text{Cl}_{2}]_{2}$ or $\text{Ru(acac)}_{3}$, respectively. The solid was isolated by adding CsCl. Arrows in (b) indicate peaks corresponding to CO of $[\text{PW}_{11}\text{O}_{39}\text{Ru(II)(CO)}]^{5-}$, $[\text{SiW}_{11}\text{O}_{39}\text{Ru(II)(CO)}]^{6-}$ or $[\text{GeW}_{11}\text{O}_{39}\text{Ru(II)(CO)}]^{6-}$. 
Figure S8. Cyclic voltammograms of the complex 2b after calcination at (blue) 100 °C, (green) 200 °C, (pink) 400 °C, (red) 450 °C, (purple) 500 °C and (black) 600 °C. The sample was heated with a ramp of 5 °C/min. CV was measured in 0.5 M KH$_2$PO$_4$ (pH 4.3).
Figure S9. IR of the complex 2b after calcination at (blue) 100 °C, (green) 200 °C, (pink) 400 °C, (red) 450 °C, (purple) 500 °C and (black) 600 °C. The sample was heated with a ramp of 5 °C/min. The black arrow indicates the peak corresponding to benzene and the white arrow indicates the peak corresponding to CO coordinating to Ru(II).
Figure S10. Cyclic voltammograms of sample obtained (black) after calcination of 2b at 450 °C and (red) after recrystallization of the calcined 2b (450 °C) from water.
Figure S11. TG-DTA profile of 2a.
Figure S12. Cyclic voltammograms of the complex 2a after calcination at (green) 200 °C, (brown) 300 °C, (pink) 400 °C and (purple) 500 °C. The sample was heated with a ramp of 5 °C/min. CV was measured in 0.5 M KH₂PO₄ (pH 4.3).
Figure S13. IR of the complex 2a after calcination at (green) 200 °C, (brown) 300 °C, (pink) 400 °C and (purple) 500 °C. The sample was heated with a ramp of 5 °C/min. The black arrow indicates the peak corresponding to benzene and the white arrow indicates the peak corresponding to CO coordinating to Ru(II).
Figure S14. TG-DTA profile of 2c.
Figure S15. Cyclic voltammograms of the complex 2c after calcination at (green) 200 °C, (pink) 400 °C, (red) 450 °C and (purple) 500 °C. The sample was heated with a ramp of 5 °C/min. CV was measured in 0.5 M KH₂PO₄ (pH 4.3).
Figure S16. IR of the complex 2c after calcination at (green) 200 °C, (pink) 400 °C, (red) 450 °C and (purple) 500 °C. The sample was heated with a ramp of 5 °C/min. The black arrow indicates the peak corresponding to benzene and the white arrow indicates the peak corresponding to CO coordinating to Ru(II).