New {RuNO} polyoxometalate $[PW_{11}O_{39}Ru^{II}(NO)]^{4-}$: synthesis and reactivity

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A Q-TOF premier mass spectrometer with an orthogonal Z-spray electrospray source (Waters, Manchester, UK) was used. The temperature of the source block was set to 100 ºC and the desolvation temperature to 120 ºC. A capillary voltage of 3.3 kV was used in the negative scan mode and the cone voltage was set to 5 V to control the extent of fragmentation of the identified species. TOF mass spectra were acquired in the W-mode operating at a resolution of ca. 15000 (FWHM). Mass calibration was performed using a solution of sodium iodide in isopropanol:water (50:50) from m/z 50 to 3000. Sample solutions were infused via syringe pump directly connected to the ESI source at a flow rate of 10 μL/min. The observed isotopic pattern of each compound perfectly matched the theoretical isotope pattern calculated from their elemental composition using the MassLynx 4.1 program. For ESI tandem MS/MS experiments, the anions of interest were mass-selected using the first quadrupole (Q1) and interacted with argon in the T-wave collision cell at variable collision energies (CE = 0–20 eV). The ionic products of fragmentation were analyzed with the time-of-flight analyzer. The isolation width was reduced to mass-select a single isotopomer in the first quadrupole analyser.

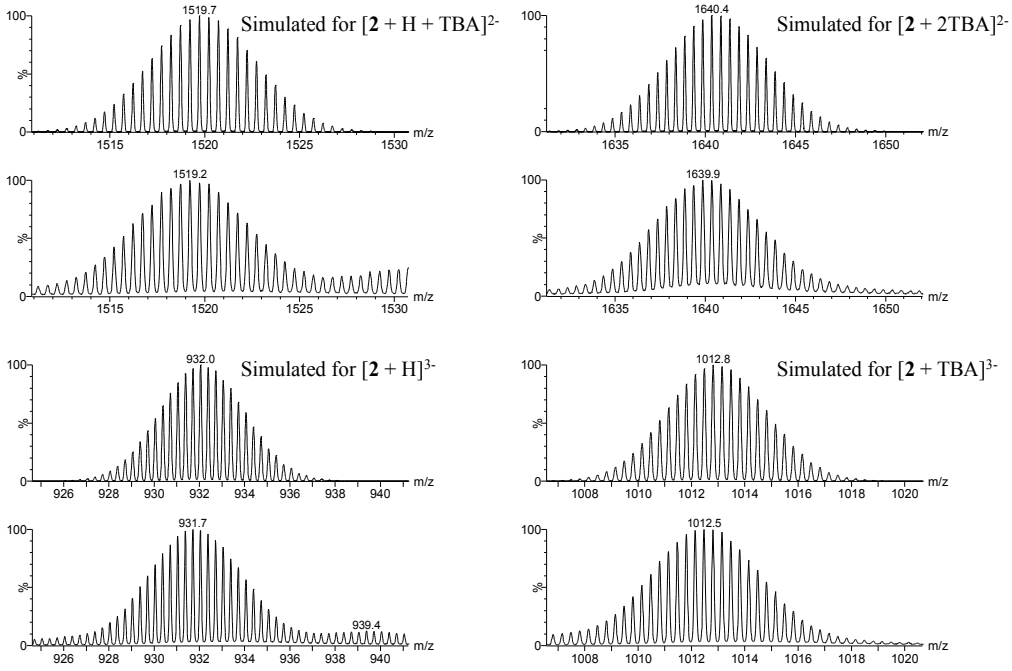

Figure S1. Simulated and experimental peaks for the triply-charged [**2** + H]$^{3-}$ and [**2** + TBA]$^{3-}$ (bottom) and doubly-charged [**2** + H + TBA]$^{2-}$ and [**2** + 2TBA]$^{2-}$ (top) anions.

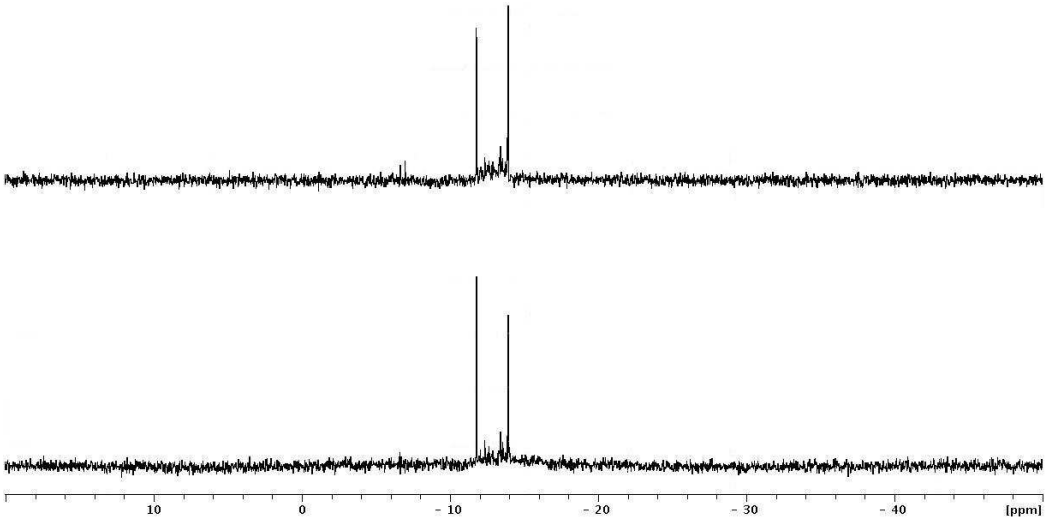

Figure S2. ^{31}P NMR spectra of reaction solution ($[PW_{11}O_{39}]^{7-}$ + $K_2[Ru(NO)Cl_5]$, reflux) after 16 (bottom) and 31 (top) h. Left peak –starting POM, right peak – product.

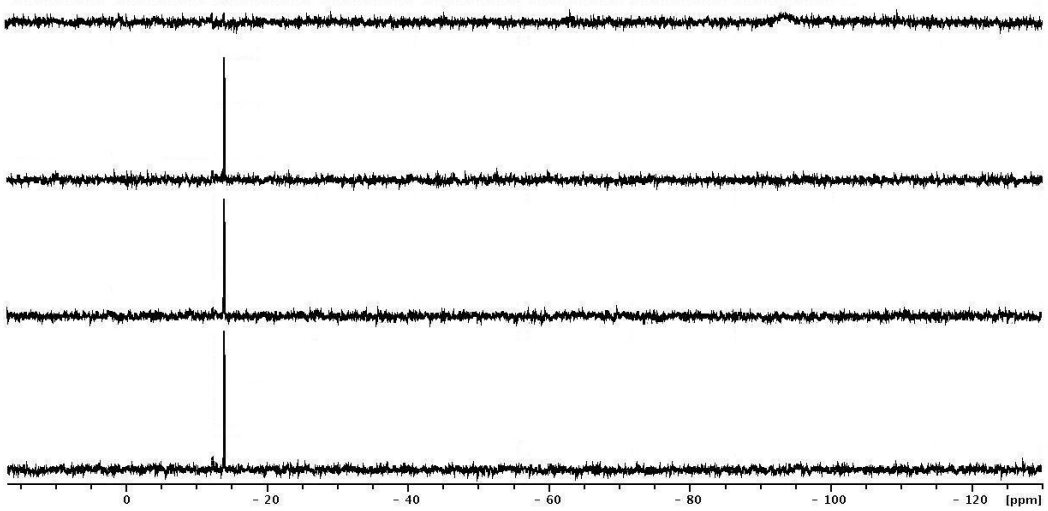

Figure S3. ^{31}P NMR monitoring of reaction between $[PW_{11}O_{39}Ru(NO)]^{4-}$ and $N_2H_4{\cdot}H_2SO_4$ at RT (after 5 min, 50 min, 70 min and 96 h, respectively)

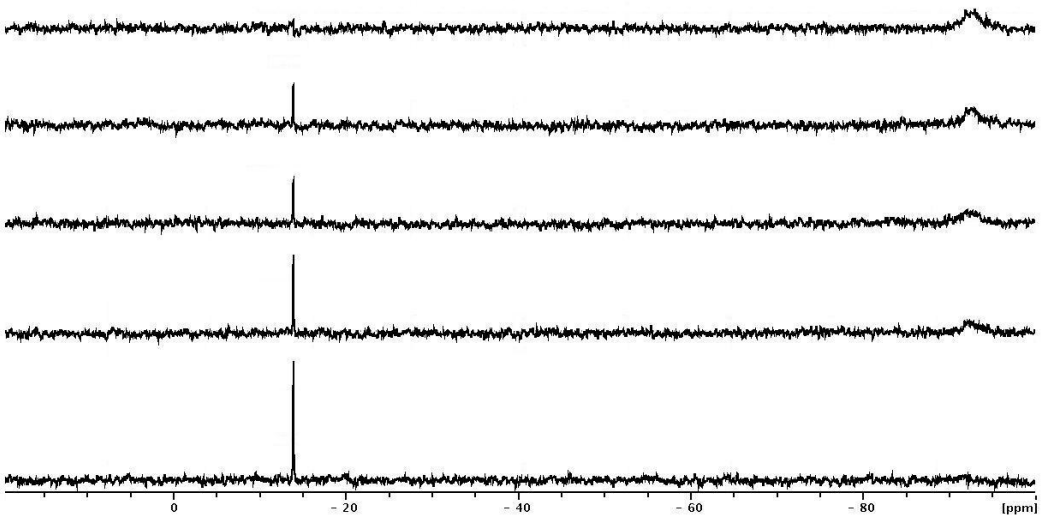

Figure S4. ^{31}P NMR monitoring of reaction between $[PW_{11}O_{39}Ru(NO)]^{4-}$ and $N_2H_4 \cdot H_2SO_4$ at 60ºC (after 2.5 h, 5 h, 6.5 h and 24 h)

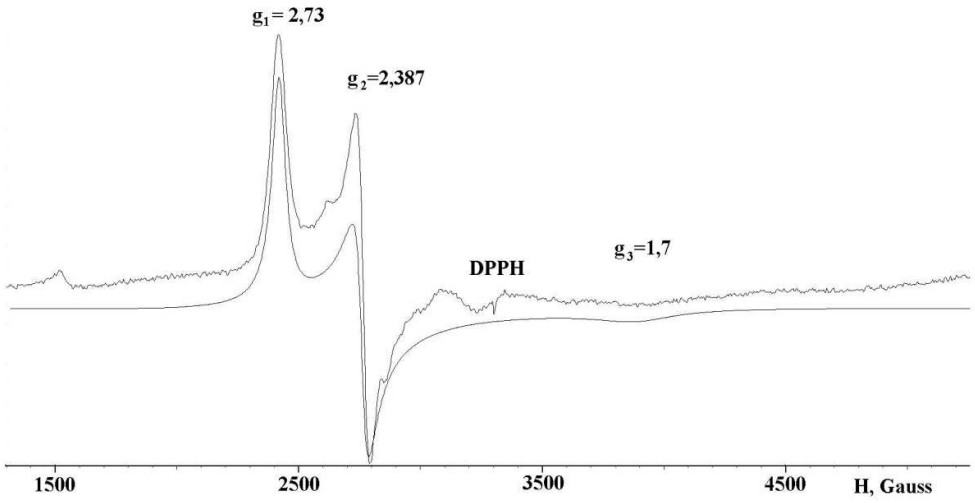

Figure S5. EPR spectrum of $(Bu_4N)_4[PW_{11}O_{39}Ru^{III}(NH_3)]$

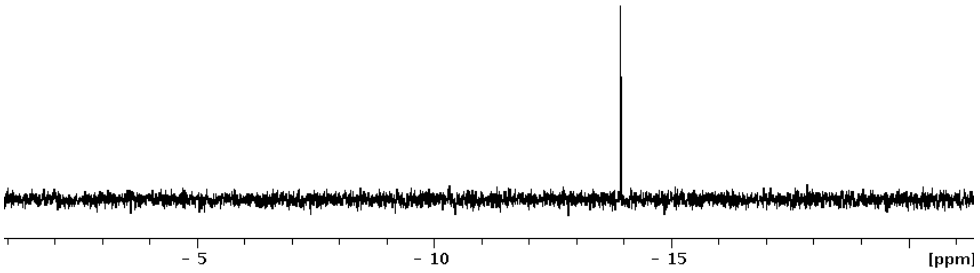

Figure S7. ^{31}P NMR spectra of $[PW_{11}O_{39}Ru(NO)]^{4-}$ (solution after hydrothermal reaction between $[PW_{11}O_{39}]^{7-}$ and $K_2[Ru(NO)Cl_5]$, $H_2O + D_2O$)

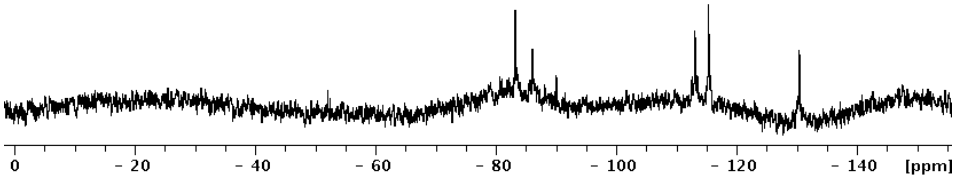

Figure S8. ^{183}W NMR spectra of $(Bu_4N)_4[PW_{11}O_{39}Ru(NO)]$ (CD_3CN)

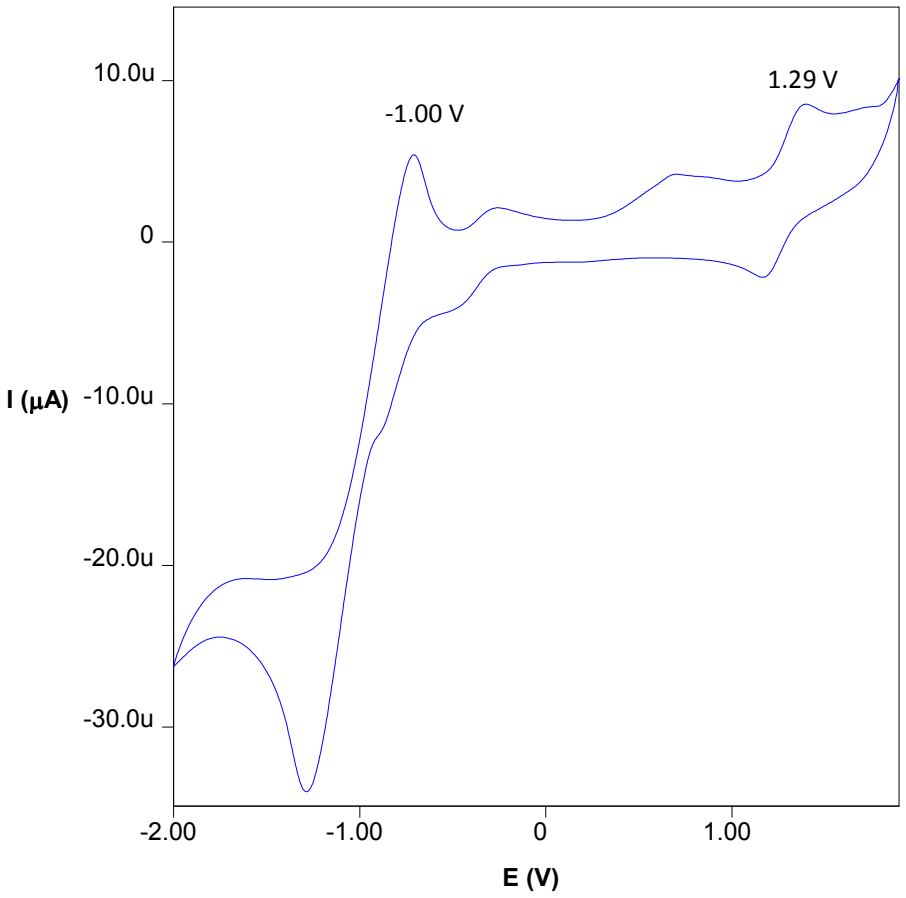

Figure S9. The cyclic voltammogram of **1** in CH_3CN in the potential route of -2 ↔ 1.8 V (scan rate of 0.1 V/s).