Electronic Supplementary Material (ESI) for Chemical Communications

Synthesis and characterization of $[PW_{11}O_{39}Ir(H_2O)]^{4-}$ - first successful complete incorporation of Ir into polyoxometalate framework and study of the substitutional lability at the Ir Site

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Electrospray Ionization mass spectrometry

Experimental details for the substitutional lability screening

Figure S1. Negative ESI mass spectrum (U_c = 5 V) of CH_2Cl_2:CH_3CN solutions of compound **1a** in the m/z 400 to 5500 range.

Figure S2. Negative ESI mass spectrum (U_c = 5 V) of acetone:acetonitrile (9:1) solutions of **1a** in the presence of methanol after 1 day. In this case, H_2O to CH_3OH replacement was manifested as a broadening of the peak centered at m/z =1565.0 due to the partial overlapping of $[W_{11}O_{39}P(IrH_2O) + H + TBA]^{2-}$ (m/z = 1565.0) and $[W_{11}O_{39}P(IrCH_3OH) + H + TBA]^{2-}$ (m/z = 1572.0); however, ESI tandem MS/MS provide definitive proof that H_2O to CH_3OH replacement has occurred since mass-selection of m/z = 1572 resulted in the release of one CH_3OH molecule (see figure S3 below).

Figure S3. ESI tandem MS/MS mass spectrum of mass selected m/z = 1572 (U_c = 5 V; $E_{laboratory}$ 10 eV) corresponding to a mixture of partially overlapped species $[W_{11}O_{39}P(IrH_2O) + H + TBA]^{2-}$ and $[W_{11}O_{39}P(IrCH_3OH) + H + TBA]^{2-}$.

Figure S4. Negative ESI mass spectrum (U_c = 5 V) of acetone:acetonitrile (9:1) solutions of **1a** in the presence of dimethylsulfoxide after 1 day.

Figure S5. Negative ESI mass spectrum (U_c = 5 V) of acetone:acetonitrile (9:1) solutions of **1a** in the presence of dimethylformamide after 2 days.

Figure S6. Negative ESI mass spectrum (U_c = 5 V) of acetone:acetonitrile (9:1) solutions of **1a** in the presence of 2-butenol after 2 days.

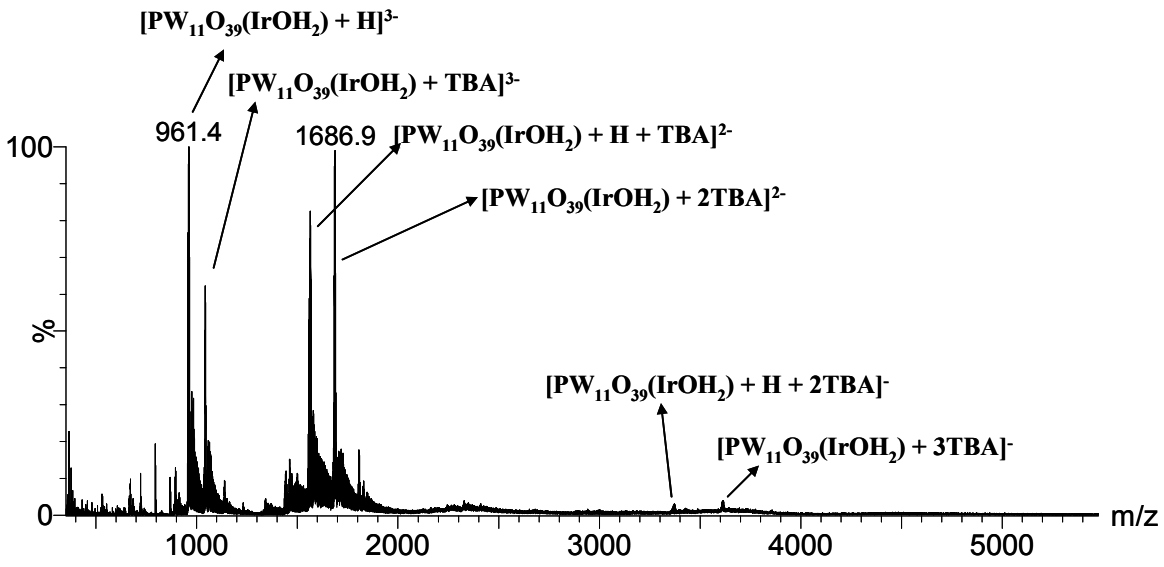
Figure S7. Negative ESI mass spectrum (U_c = 5 V) of acetone:acetonitrile (9:1) solutions of **1a** in the presence of methylpropiolate after 2 days.

Electrospray Ionization mass spectrometry

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 200 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 V-mode operating at a resolution of ca. 10000 (FWHM). Tandem ESI-MS/MS were recorded using argon as collision gas, an isolation width of ca. 0.5 Da and a collision energy ($E_{laboratory}$) in the 2 to 15 eV range. 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.

Experimental details for the substitutional lability screening

Stock 1 x 10^{-3} M solutions of **1a** were prepared in acetone with minimum amounts of CH_3CN (ca. 9:1) to ensure complete dissolution and to minimize competition with the target substrate (nevertheless, species corresponding to water to CH_3CN substitution were incidentally observed). To this solution an excess (x 500) of substrate L (where L = CH_3CN, DMSO, CH_3OH, DMF, 2-butenol or methylpropiolate) was added and the resulting solution was allowed to react at room temperature for several days. ESI-MS monitoring was performed at 2 hours intervals at which a drop of the solution was extracted, diluted with CH_3CN to a 1 x 10^{-4} M solution (based on **1a**) and directly introduced into the mass spectrometer. The substitutional lability order was determined assuming that water to L replacement in **1a** did not affect the inherent ionization factor of each species, so that the abundances observed in the ESI mass spectra directly reflect their abundances in solution. On the basis of the relative abundance of the new formed [M – H_2O + L] species to [M] (where M denotes the initial POM of formula $PW_{11}O_{39}(IrOH_2)$), the following order was determined DMSO > CH_3CN > DMF > MeOH ≈ 2-butenol > methylpropiolate.



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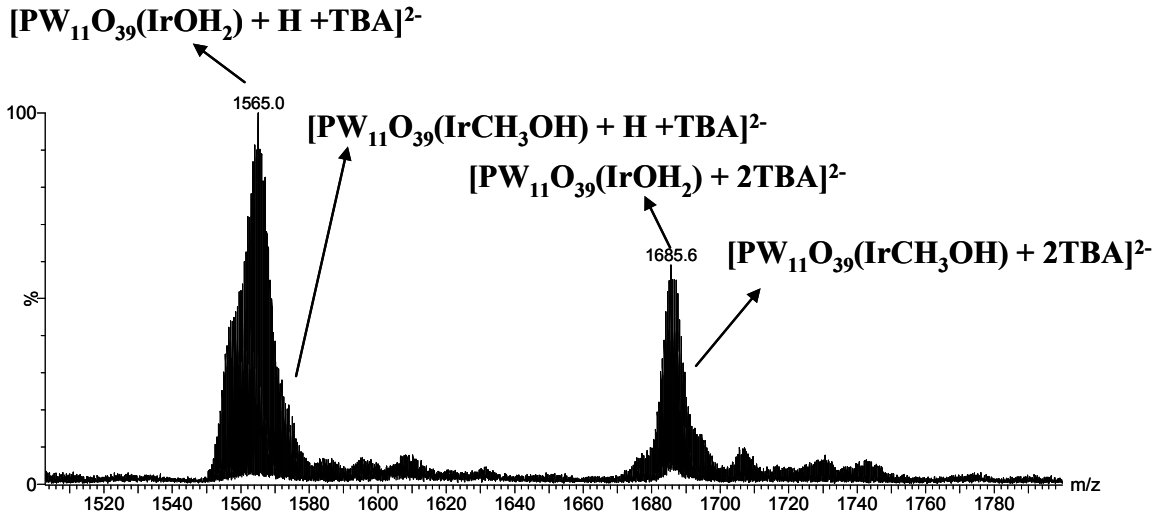


Figure S2. Negative ESI mass spectrum (U_c = 5 V) of acetone:acetonitrile (9:1) solutions of **1a** in the presence of methanol after 1 day. In this case, H_2O to CH_3OH replacement was manifested as a broadening of the peak centered at m/z =1565.0 due to the partial overlapping of $[W_{11}O_{39}P(IrH_2O) + H + TBA]^{2-}$ (m/z = 1565.0) and $[W_{11}O_{39}P(IrCH_3OH) + H + TBA]^{2-}$ (m/z = 1572.0); however, ESI tandem MS/MS provide definitive proof that H_2O to CH_3OH replacement has occurred since mass-selection of m/z = 1572 resulted in the release of one CH_3OH molecule (see figure S3 below).

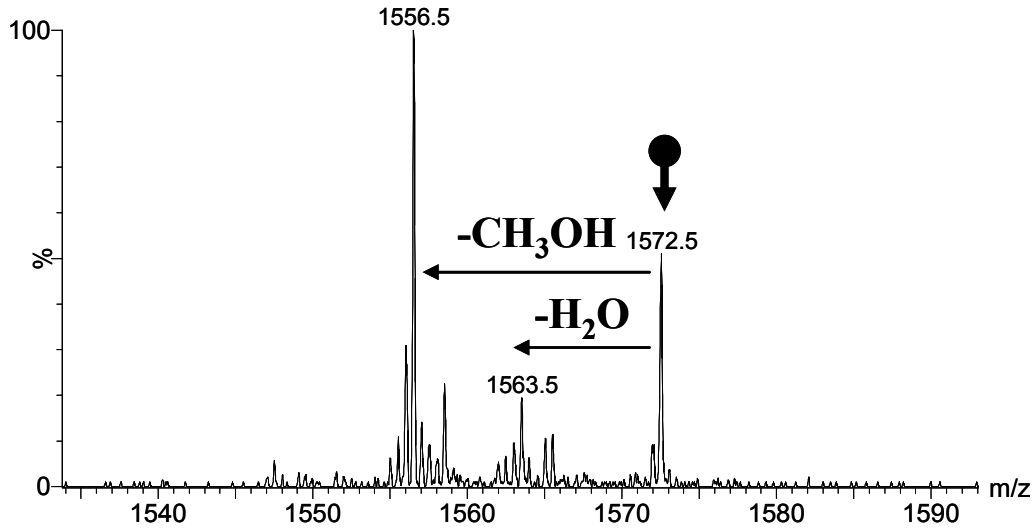
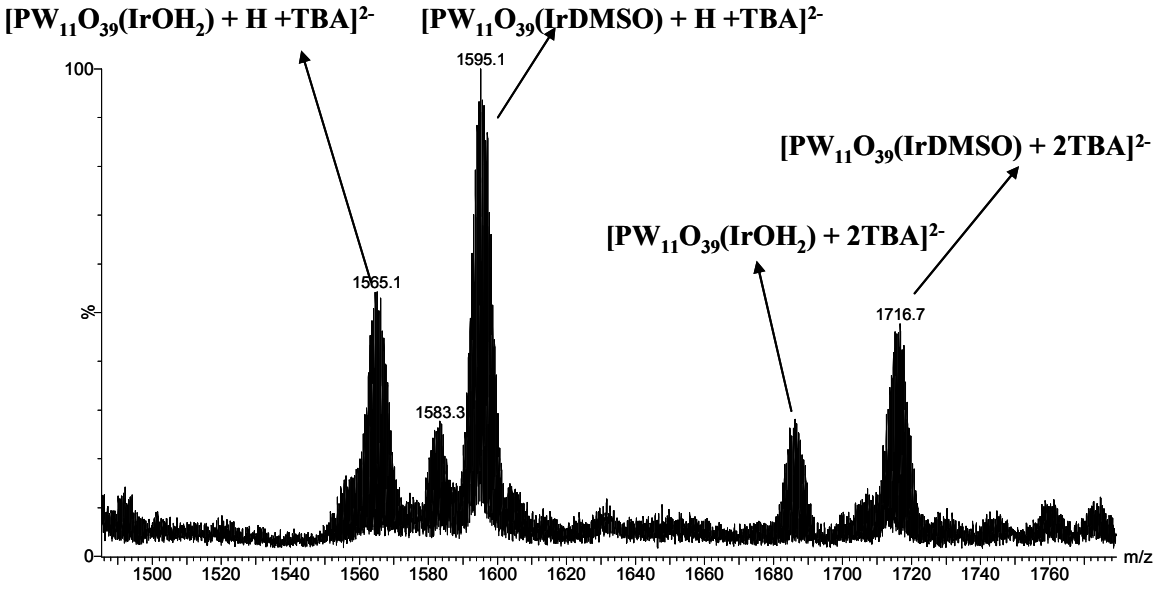


Figure S3. ESI MS/MS mass spectrum of mass selected m/z = 1572 (U_c = 5 V; $E_{laboratory}$ 10 eV, isolation width ca. 0.5 Da) corresponding to a mixture of partially overlapped species $[W_{11}O_{39}P(IrH_2O) + H + TBA]^{2-}$ and $[W_{11}O_{39}P(IrCH_3OH) + H + TBA]^{2-}$.



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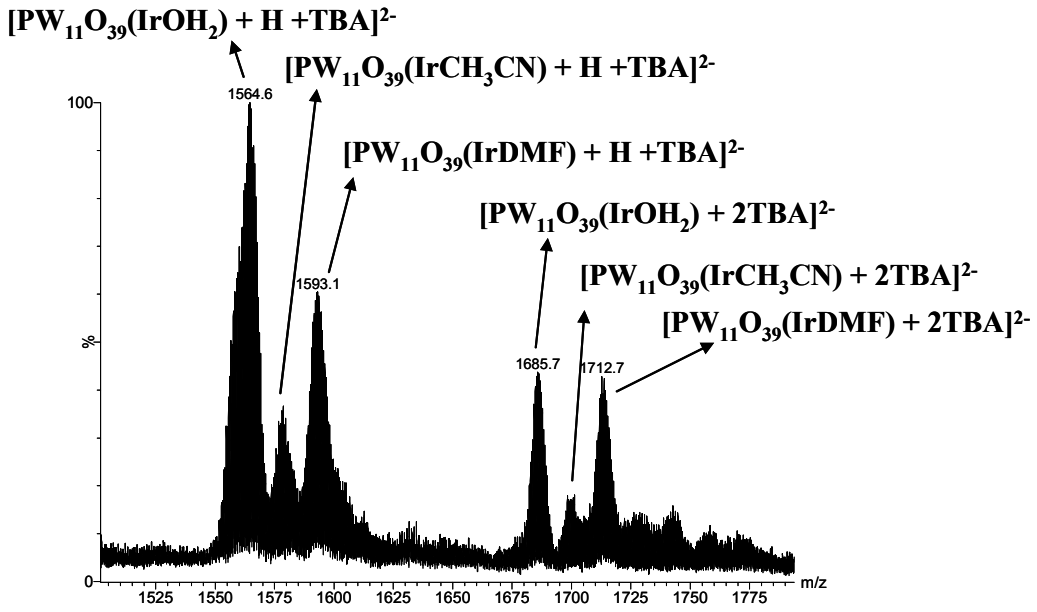


Figure S5. Negative ESI mass spectrum (U_c = 5 V) of acetone:acetonitrile (9:1) solutions of **1a** in the presence of dimethylformamide after 1 days.

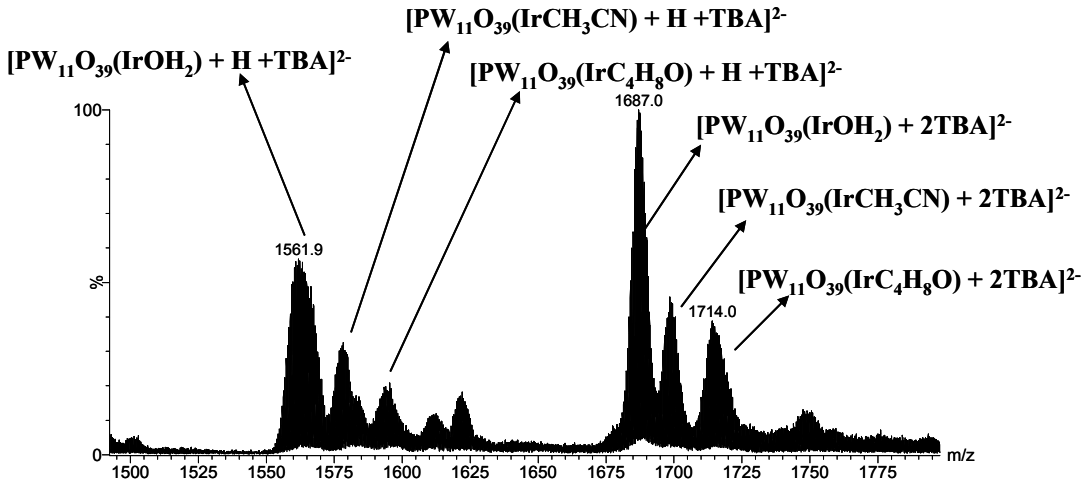


Figure S6. Negative ESI mass spectrum (U_c = 5 V) of acetone:acetonitrile (9:1) solutions of **1a** in the presence of 2-butenol after 2 days.

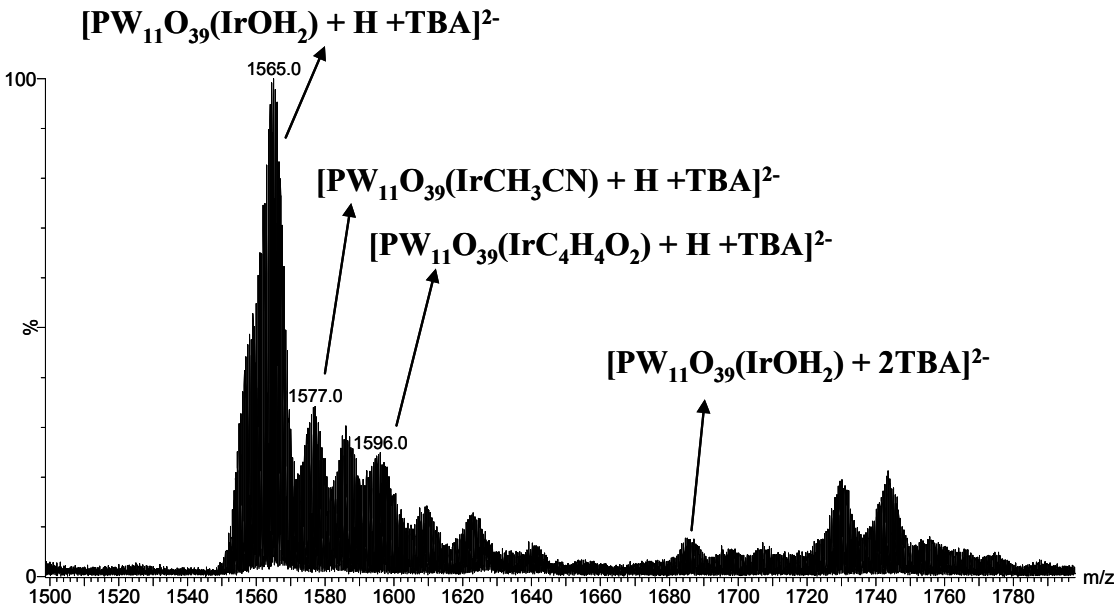


Figure S7. Negative ESI mass spectrum (U_c = 5 V) of acetone:acetonitrile (9:1) solutions of **1a** in the presence of methylpropiolate after 2 days.

NMR Measurements.

NMR data were obtained at room temperature on a Bruker Avance 500 spectrometer. A vertical 10 mm broadband observe probe with the standard lower-frequency limit corresponding to the 109Ag resonance (23.260 MHz) was used. Nevertheless, this probe allowed us to record the 183W NMR spectra at 20.805 MHz (π/2 pulse ≈ 67 μs). 31P and 183W NMR spectra were obtained for 0.1M solution of **1** in CD3CN and referenced to external 85% H3P04 and 2M Na2WO4 in D2O, respectively. Owing to extreme low concentration, that solution required four-day acquisition time to obtain a satisfactory 183W NMR spectrum (ca 370,000 scans).

This spectrum (Fig. 1) consists of a six-line pattern (75.6 (2 W), -82.4 (2 W), -90.0 (2 W), -99.5 (1 W), - 118.4 (2 W) and -136.4 (2 W) ppm) consistent with the expected *C*s symmetry and is indicative of a mono-substituted Keggin system rather than [PW11O39]7- anion with the vacant W site [1-3]. Doublets expected with J(183W-31P) ≈ 1 Hz in 183W NMR spectra could not be resolved due to large value of SW (1200 ppm) parameter used during the acquisition in order to decrease the repetition time for single scan. Also, for the same purpose Cr(acac)3 was added in the solution as a paramagnetic relaxation enhancement probe. The labeled solution displays a 31P NMR resonance at –7.17 ppm (Fig.2) coinciding with the resonance position in the absence of paramagnetic probe that indirectly testifies nonappearance of notable paramagnetic shift in 183W spectra.

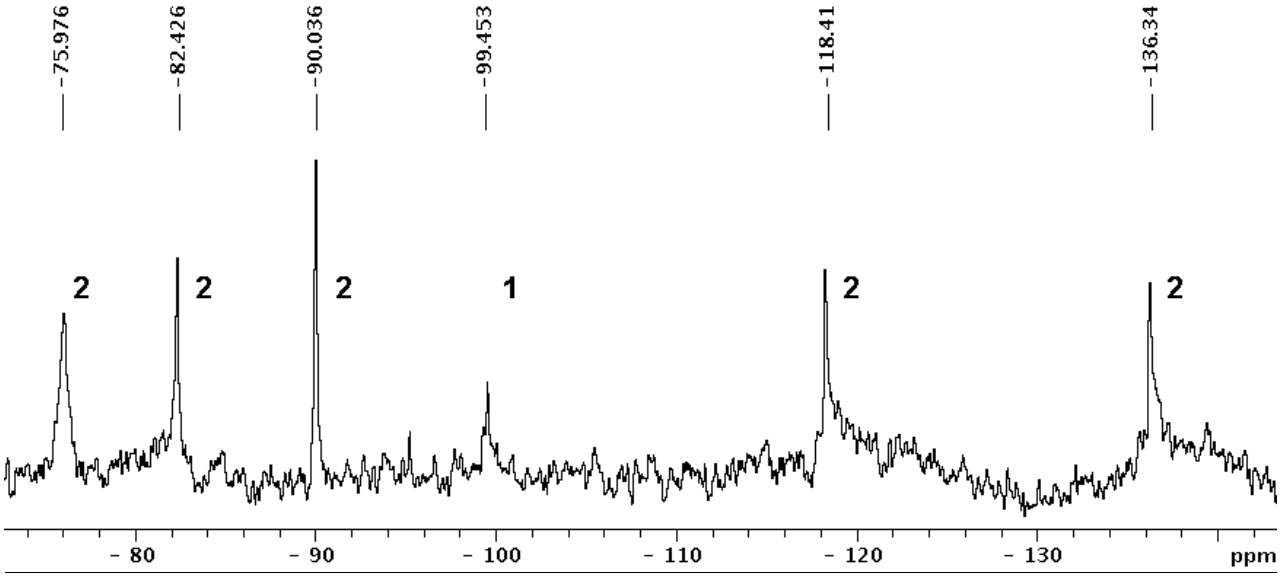


Fig. 1. ^{183}W NMR (CD_3CN, 20.805 MHz) spectrum displays six signals with approximate 2 : 2 : 2 : 1 : 2 : 2 relative intensities at –75.6, -82.4, -90.0, -99.5, - 118.4 and -136.4 ppm.

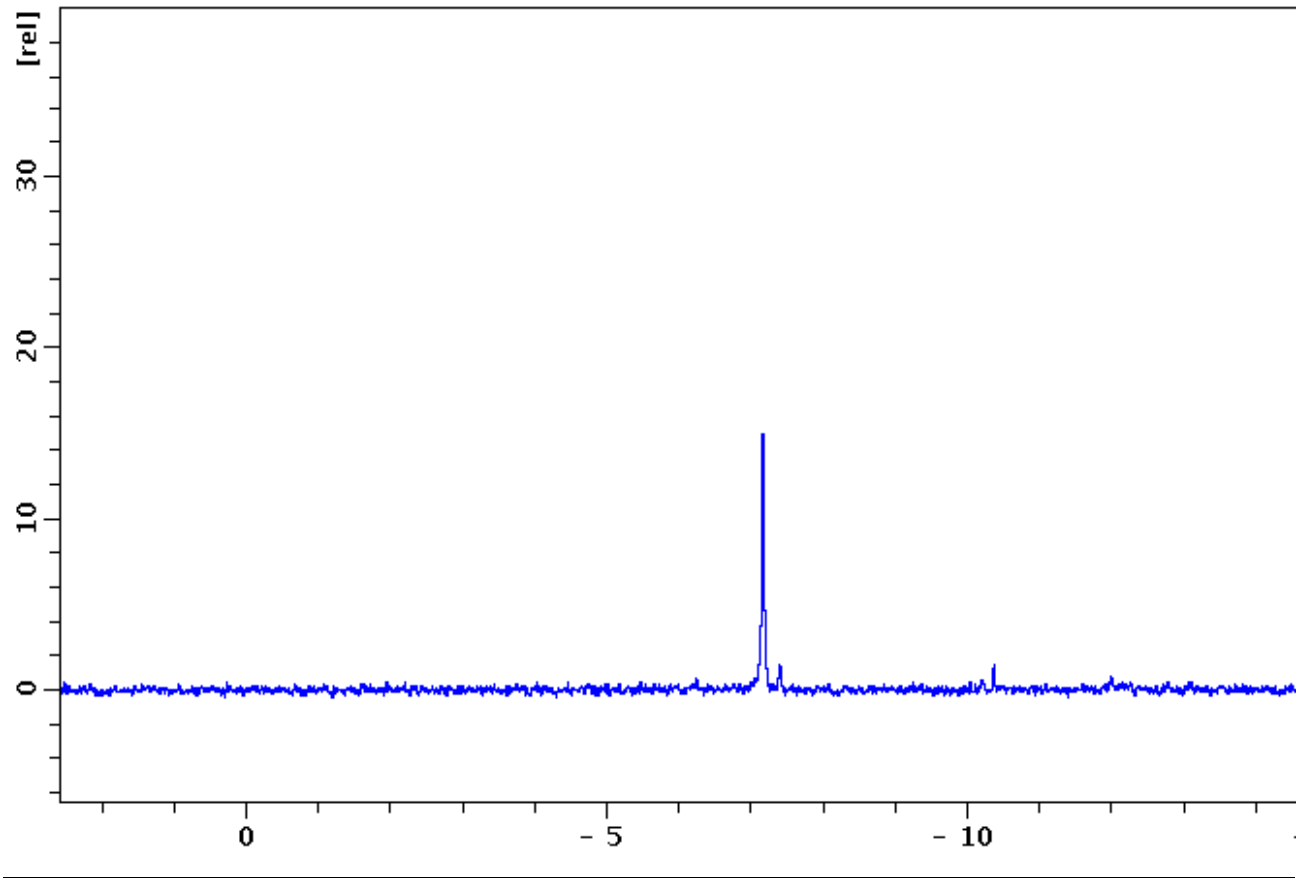


Fig. 2. ^{31}P NMR (CD_3CN, 202.404 MHz) spectrum with the dominating resonance at –7.17 ppm.

X-ray powder diffractometry.

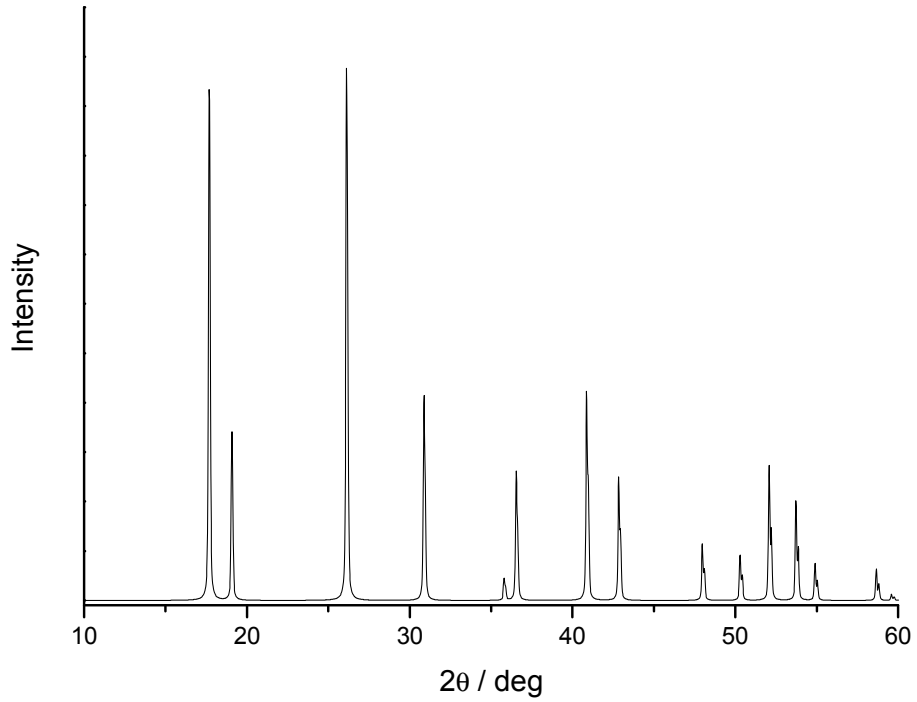
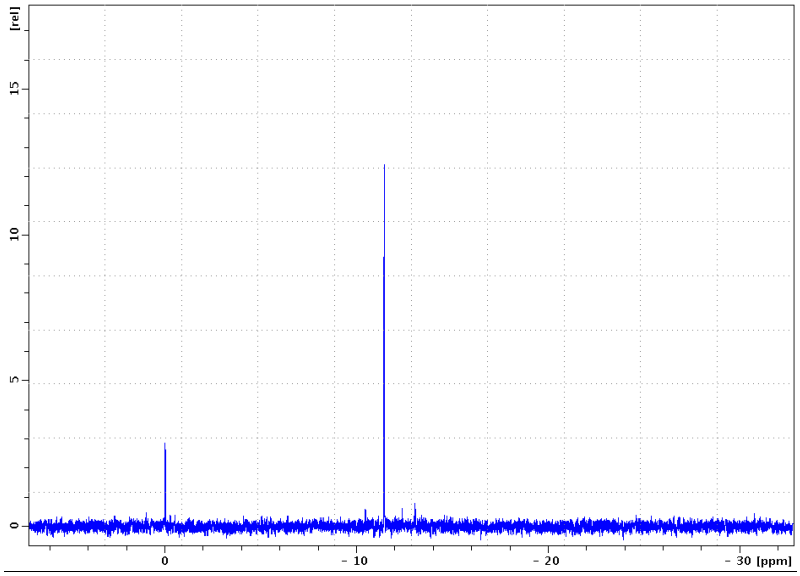


Fig.D1. X-ray powder diffraction of K_2IrF_6.

Additional experiments

1. 60 mg of K_2IrF_6 was dissolved in 10 ml of H_2O, then $LiNO_3$ was added until the 2M concentration was reached. The solution was heated hydrothermally in Teflon bomb (120ºC, 48h). The resulting solution is colorless and contains only the trace amounts of iridium, whereas there is a copious deposit of the dark hydrated iridium oxide on the bottom.

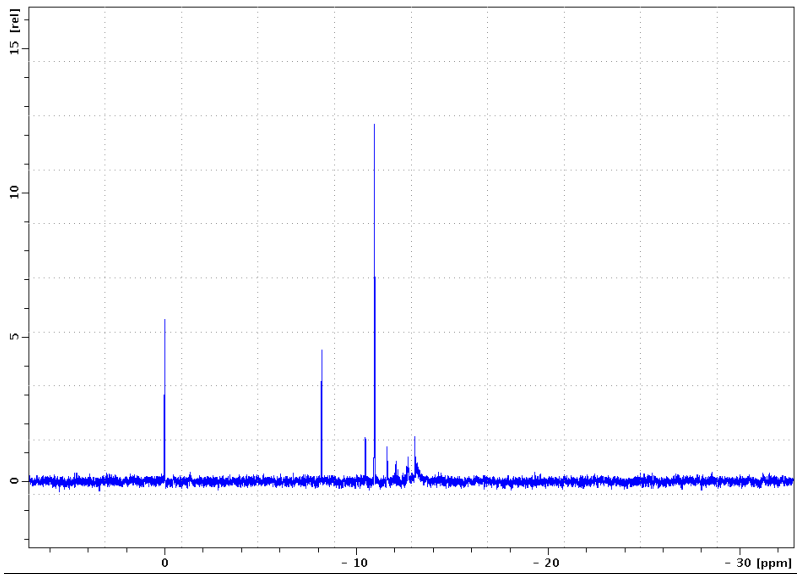
1a. To the hydrated Ir oxide stochiometric amount of the sodium salt of $[PW_{11}O_{39}]^{7-}$ was added; the suspension was heated hydrothermally in a Teflon bomb (120ºC, 48h). The solution was colorless and ^{31}P spectrum is shown below. Ir hydroxide remained unchanged.



^{31}P NMR spectrum of 1a (H_2O + D_2O) after reaction.

There are no Ir-POM species there, *quod erat demonstrandum*. Only signals from phosphate and $PW_{11}O_{39}$ are seen.

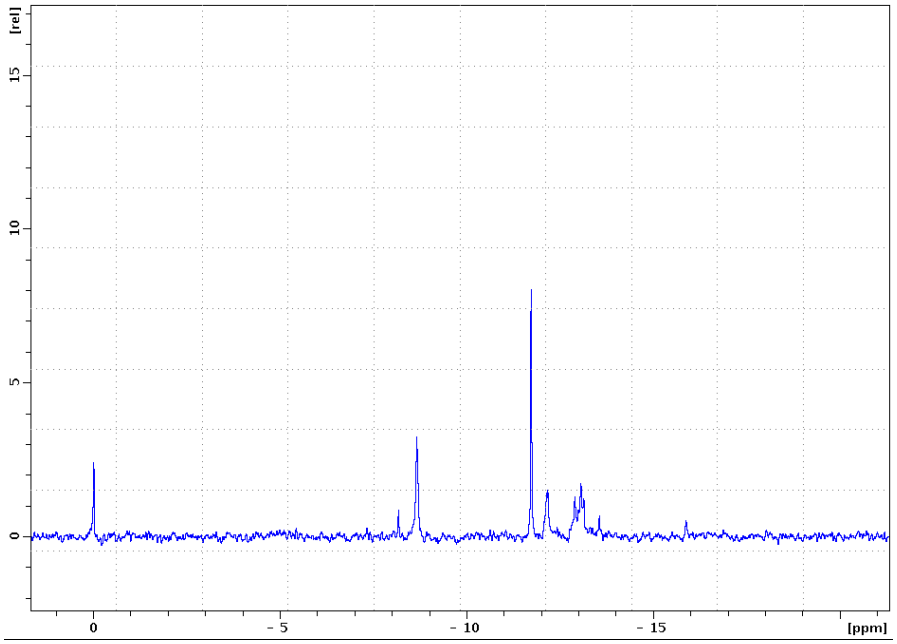
2. 500 mg of $H_3PW_{12}O_{40}\cdot H_2O$ was dissolved in 10 ml of H_2O. pH was adjusted to 4.5 with K_2CO_3 under vigorous stirring to generate PW_{11} species *in situ*, the solution was placed into a Teflon bomb and stoichiometric amount of solid K_2IrF_6 was added. The bomb was heated (120ºC, 48h). The resulting solution was brownish green; ^{31}P spectrum is shown below.



^{31}P NMR spectrum of sample 2 (H_2O + D_2O).

As can be seen, a mixture of different POMs in this case is produced; i.a. the Ir-Keggin polyoxoanion (-8.18 ppm) as one of the products. There are also signals from the PW_{11} and species. This experiment confirms that the presence of Li^+ ion is essential for preparation of pure $\{PW_{11}Ir\}$.

3. 500 mg of $H_3PW_{12}O_{40}\cdot H_2O$ was dissolved in 15 ml of H_2O. pH was adjusted to 4.5 with Li_2CO_3 under vigorous stirring, then $LiNO_3$ was added $[Li^+]$ = 2M, then the stoichiometric amount of K_2IrCl_6 was added. The solution was placed into a Teflon bomb and was heated (120ºC, 48h). The resulting solution was brownish green; ^{31}P spectrum is shown below.



^{31}P NMR spectrum of sample 3 (H_2O + D_2O).

As can be seen, we have a mixture of different POMs in this case; i.a. the same Ir(H_2O)-Keggin polyoxoanion (-8.18 ppm); the next signal (-8.68 ppm) probably belongs to the $[PW_{11}O_{39}IrCl]^{5-}$ form. There is signal from PW_{11} (cation-dependent). This experiment confirms that the presence of Li^+ ion has some positive effect, but still cannot help in obtaining the pure Ir-Keggin product.