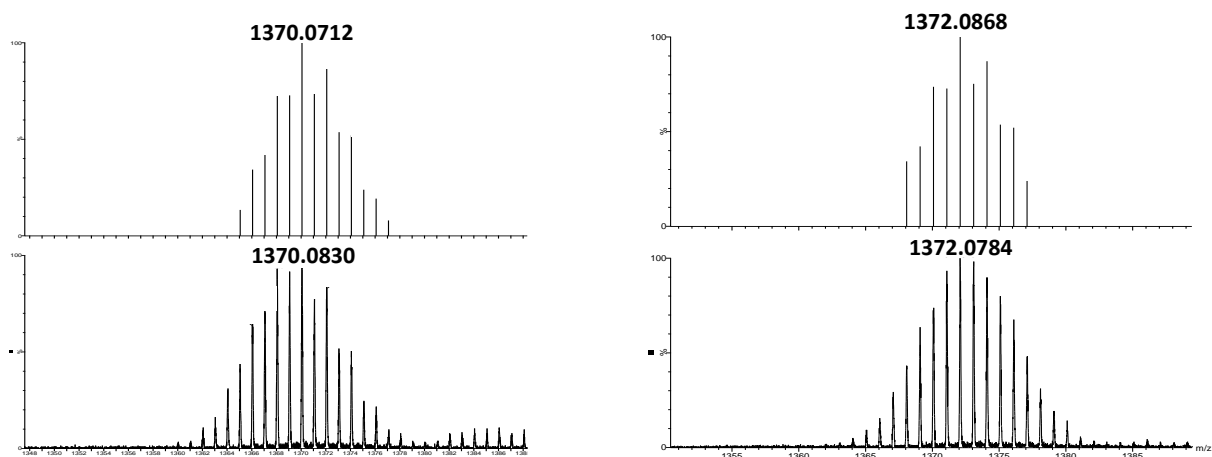


## Contents

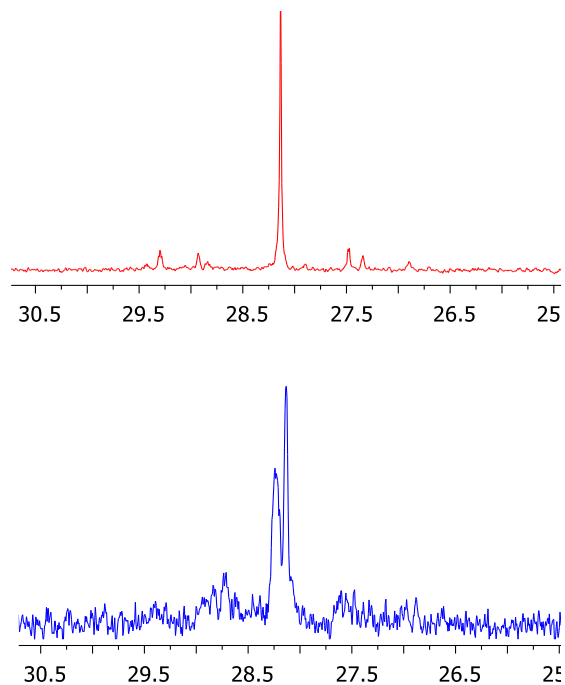
1. MS spectra of  $[W_3S_4H_3(edpp)_3]^+$  and  $[W_3S_4D_2H(edpp)_3]^+$  clusters.
2.  $^{31}P\{^1H\}$  NMR spectra of  $[W_3S_4H_3(edpp)_3]^+$  and  $[W_3S_4D_2H(edpp)_3]^+$  species.
3. FT-IR spectra of  $[W_3S_4H_3(edpp)_3]^+$  and  $[W_3S_4D_2H(edpp)_3]^+$  compounds.
4. Spatial position of the hydridic and protonic H atoms in the trimetallic cluster.
5. Calculated UV-vis spectra for further species formed upon addition of HCl/HBr.

## 1. MS spectra of the $[W_3S_4H_3(edpp)_3]^+$ and $[W_3S_4D_2H(edpp)_3]^+$ clusters



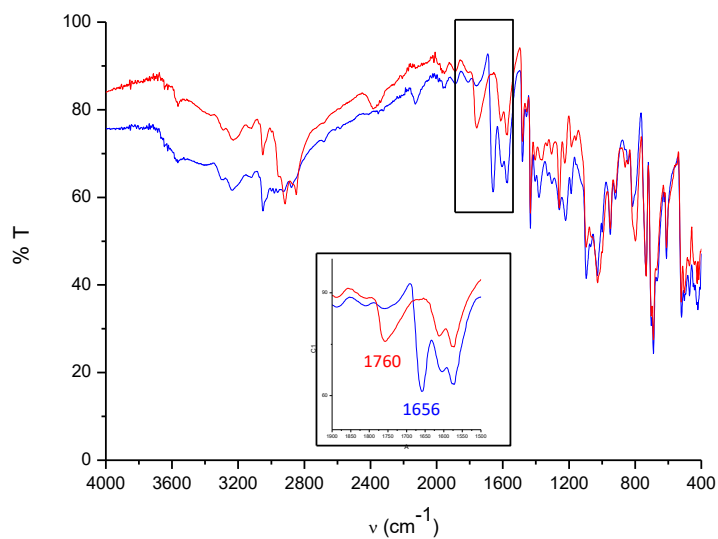
**Figure S1.** MS-Q-TOF experimental (bottom) and calculated (top) spectra of the  $[W_3S_4H_3(edpp)_3]^+$  (left) and  $[W_3S_4D_2H(edpp)_3]^+$  (right) cationic clusters in  $CH_3CN$  at 20V.

## 2. $^{31}P\{^1H\}$ NMR spectra of $[W_3S_4H_3(edpp)_3]^+$ and $[W_3S_4D_2H(edpp)_3]^+$ species



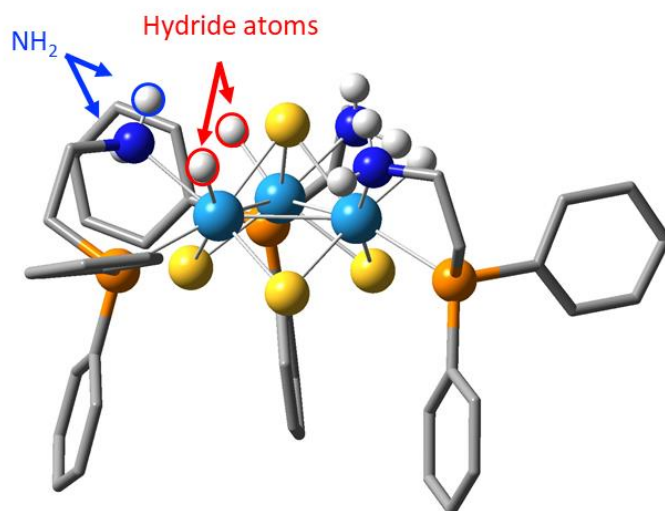
**Figure S2.**  $^{31}P\{^1H\}$ -NMR spectra of  $[W_3S_4H_3(edpp)_3]BPh_4$  (top) and  $[W_3S_4D_2H(edpp)_3]BPh_4$  (bottom) in  $CD_3CN$ .

### 3. FT-IR spectra of $[\text{W}_3\text{S}_4\text{H}_3(\text{edpp})_3]^+$ and $[\text{W}_3\text{S}_4\text{D}_2\text{H}(\text{edpp})_3]^+$ compounds



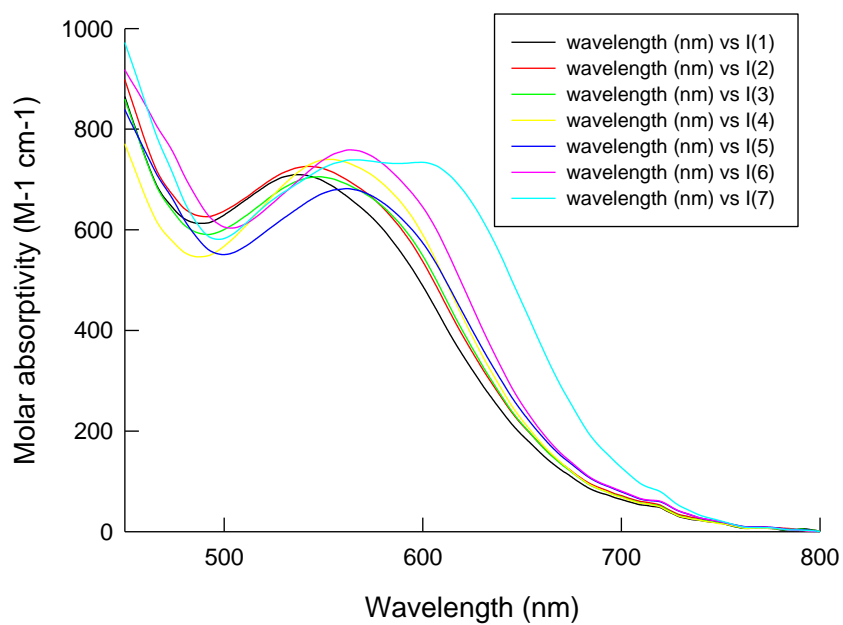
**Figure S3.** FT-IR spectra of  $[\text{W}_3\text{S}_4\text{H}_3(\text{edpp})_3]^+$  (red) and  $[\text{W}_3\text{S}_4\text{D}_2\text{H}(\text{edpp})_3]^+$  (blue).

### 4. Spatial positions of the hydridic and protonic H atoms in the trimetallic cluster



**Figure S4.** Front view of the  $[\text{W}_3\text{S}_4\text{H}_3(\text{edpp})_3]^+$  cationic cluster. The hydride atoms and  $\text{NH}_2$  groups are highlighted; the other H atoms have been omitted for clarity.

## 5. Calculated UV-vis spectra for further species formed upon addition of HCl/HBr



**Figure S5.** Spectra calculated for the different intermediates formed in the reaction of  $[W_3S_4H_3(edpp)_3]^+$  with HBr in acetonitrile solution at 25.0°C. The spectra were obtained from the fit of the spectral changes.