

## A Combined Stopped-Flow, Electrospray Ionization Mass

### Spectrometry and $^{31}\text{P}$ NMR study on the Acetic Acid-Mediated

### Fragmentation of the Hydroxo-Chalcogenide Cluster

$[\text{W}_3\text{Se}_4(\text{OH})_3(\text{dmpe})_3]^+$  (dmpe = 1, 2-bis(dimethylphosphanyl)ethane) to yield the dinuclear  $[\text{W}_2\text{Se}_2(\mu\text{-Se})_2(\mu\text{-CH}_3\text{CO}_2)(\text{dmpe})_2]^+$  complex.

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**Figure 3S, 4S.** ESI-MS/MS for species generated from  $[\text{W}_3\text{Se}_4(\text{OH})_2(\text{CH}_3\text{CO}_2)(\text{dmpe})_3]^+$  ( $[\mathbf{1}_1]^+$ ).

**Figure 5S.** ESI-MS/MS for species generated from  $[\text{W}_3\text{Se}_4(\text{OH})(\text{CH}_3\text{CO}_2)_2(\text{dmpe})_3]^+$  ( $[\mathbf{1}_2]^+$ ).

**Figure 6S.** ESI-MS/MS for species generated from  $[\text{W}_2\text{Se}_2(\mu\text{-Se})_2(\mu\text{-CH}_3\text{CO}_2)(\text{dmpe})_2]^+$  ( $[\mathbf{2}]^+$ ).

ESI-MS/MS for species generated from  $[\text{W}_3\text{Se}_4(\text{OH})_3(\text{dmpe})_3]^+$  ( $[\mathbf{1}]^+$ ).

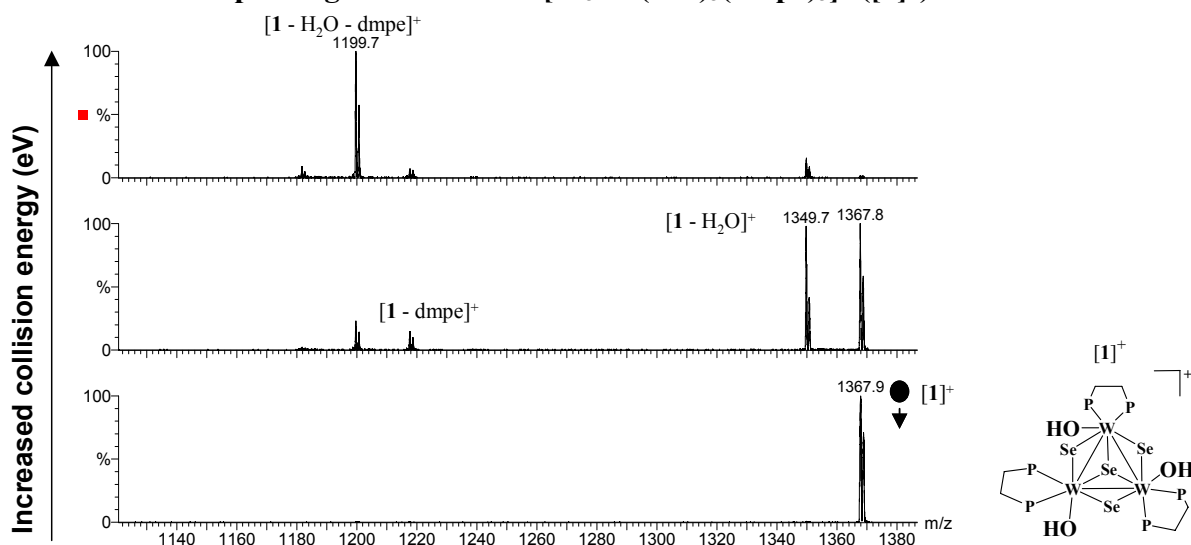


Figure 1S, ESI-MS/MS for species  $[\text{W}_3\text{Se}_4(\text{OH})_3(\text{dmpe})_3]^+$  ( $[\mathbf{1}]^+$ ).

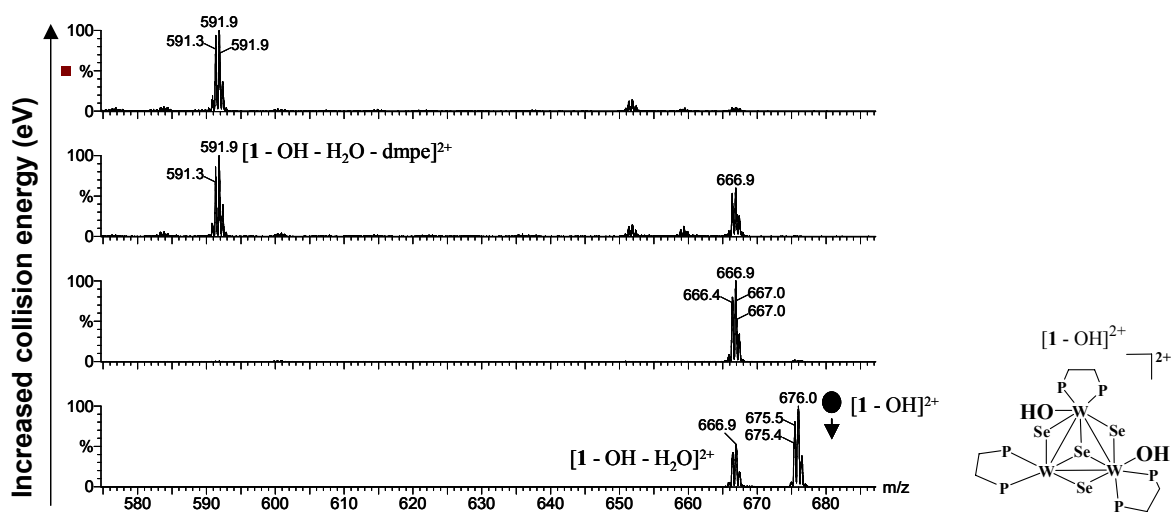


Figure 2S, ESI-MS/MS for species  $[\text{W}_3\text{Se}_4(\text{OH})_2(\text{dmpe})_3]^{2+}$  ( $[\mathbf{1} - \text{OH}]^{2+}$ ).

ESI-MS/MS for species generated from  $[\text{W}_3\text{Se}_4(\text{OH})_s(\text{CH}_3\text{CO}_2)(\text{dmpe})_3]^+$  ( $[\text{I}_1]^+$ ).

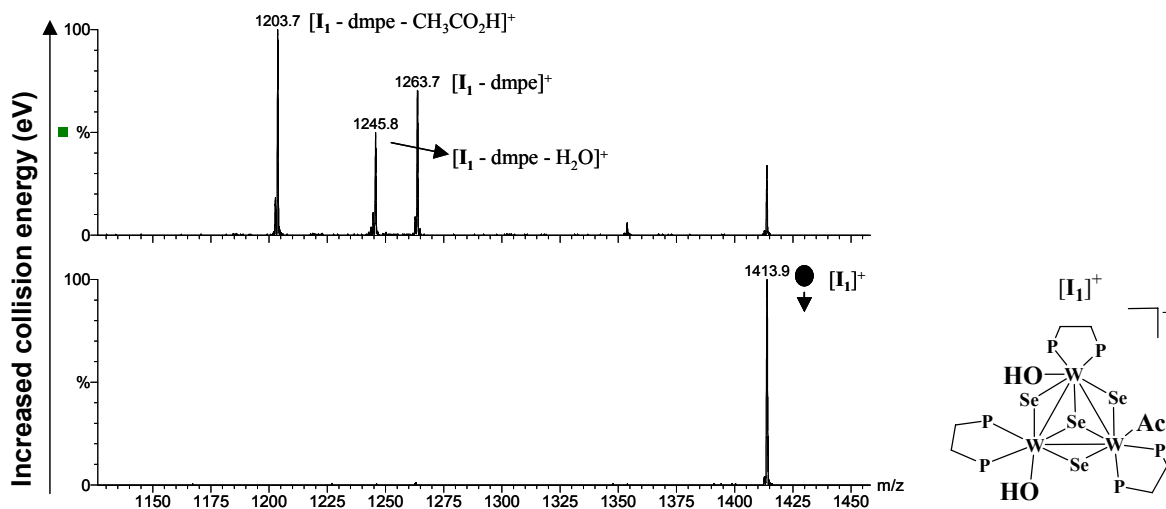


Figure 3S. ESI-MS/MS for species  $[\text{W}_3\text{Se}_4(\text{OH})_2(\text{CH}_3\text{CO}_2)(\text{dmpe})_3]^+$  ( $[\text{I}_1]^+$ ).

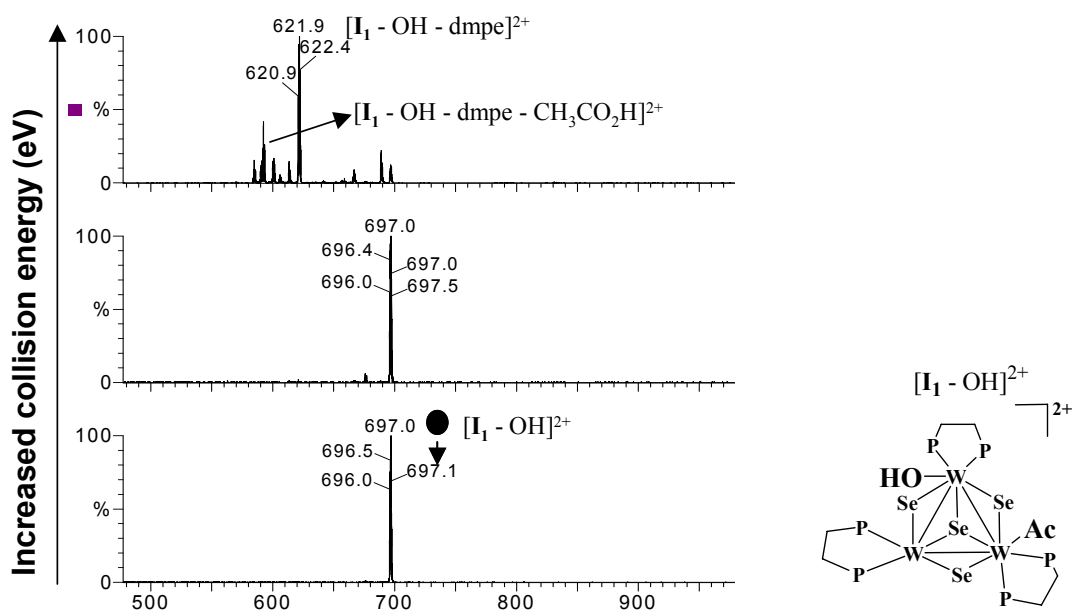


Figure 4S. ESI-MS/MS for species  $[\text{W}_3\text{Se}_4(\text{OH})(\text{CH}_3\text{CO}_2)(\text{dmpe})_3]^{2+}$  ( $[\text{I}_1 - \text{OH}]^+$ ).

ESI-MS/MS for species generated from  $[\text{W}_3\text{Se}_4(\text{OH})(\text{CH}_3\text{CO}_2)_2(\text{dmpe})_3]^+$  ( $[\text{I}_2]^+$ ).

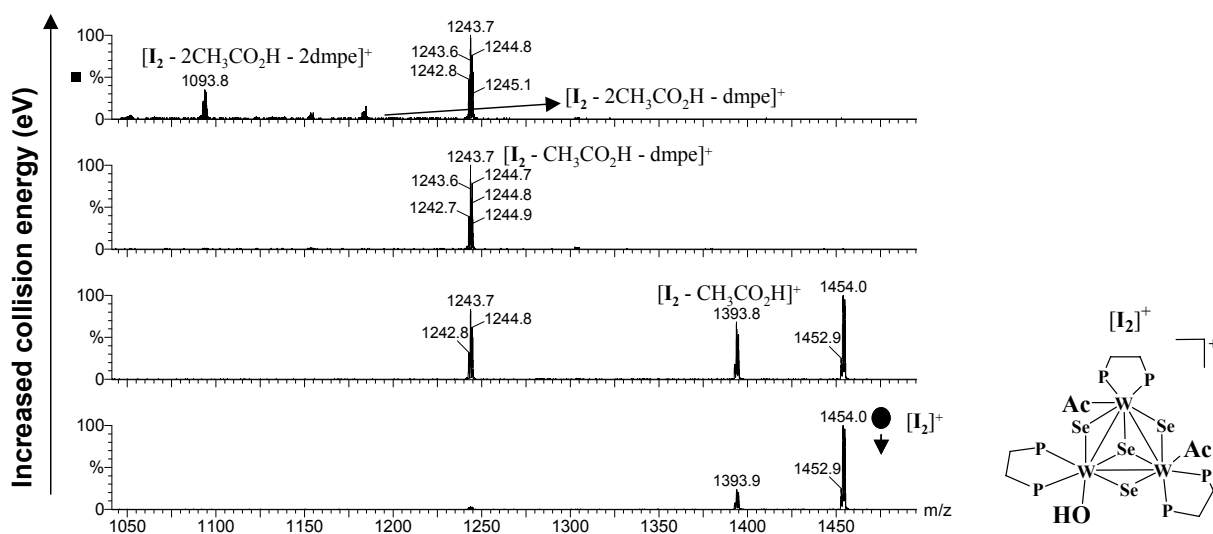


Figure 5S ESI-MS/MS for species  $[\text{W}_3\text{Se}_4(\text{OH})(\text{CH}_3\text{CO}_2)_2(\text{dmpe})_3]^+$  ( $[\text{I}_2]^+$ ).

ESI-MS/MS for species generated from  $[\text{W}_2\text{Se}_2(\mu\text{-Se})_2(\mu\text{-CH}_3\text{CO}_2)(\text{dmpe})_2]^+$  ( $[\text{2}]^+$ ).

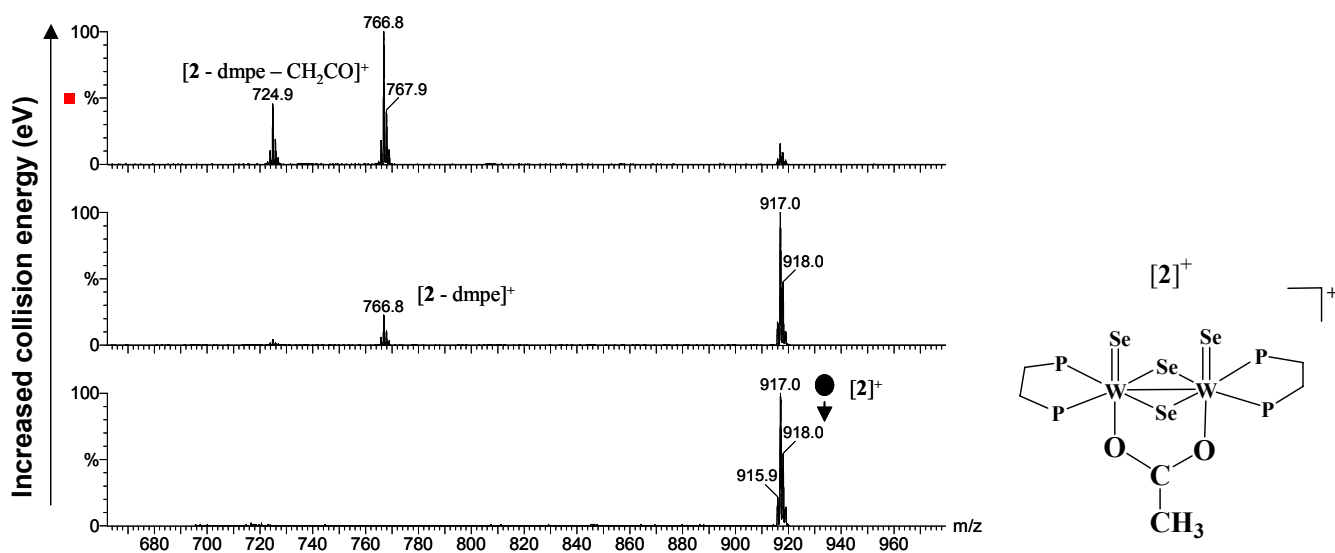


Figure 6S ESI-MS/MS for species  $[\text{W}_2\text{Se}_2(\mu\text{-Se})_2(\mu\text{-CH}_3\text{CO}_2)(\text{dmpe})_2]^+$  ( $[\text{2}]^+$ ).