

## ELECTRONIC SUPPLEMENTARY INFORMATION

### Synthesis, Spectroscopy and Electronic Structure of Vinylidene and Alkynyl Complexes in the Cycloheptatrienyl Tungsten Series $[\text{W}(\text{C}=\text{CHR})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^+$ and $[\text{W}(\text{C}\equiv\text{CR})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^{n+}$ ( $n = 0$ or $1$ ).

Hannah N. Lancashire,<sup>a</sup> Neil J. Brown,<sup>b</sup> Laura Carthy,<sup>a</sup> David Collison,<sup>c\*</sup> Emma C. Fitzgerald,<sup>a</sup> Ruth Edge,<sup>c</sup> Madeleine Helliwell,<sup>a</sup> Mark Holden,<sup>a</sup> Paul J. Low,<sup>b\*</sup> Joseph J.W. McDouall<sup>a\*</sup> and Mark W. Whiteley<sup>a\*</sup>

<sup>a</sup>*School of Chemistry, University of Manchester, Manchester M13 9PL, UK*

<sup>b</sup>*Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, UK*

<sup>c</sup>*EPSRC National Service for EPR Spectroscopy, School of Chemistry, University of Manchester, Manchester, M13 9PL, UK*

Corresponding Authors. Email [Mark.Whiteley@manchester.ac.uk](mailto:Mark.Whiteley@manchester.ac.uk); [p.j.low@durham.ac.uk](mailto:p.j.low@durham.ac.uk); [joe.mcdouall@manchester.ac.uk](mailto:joe.mcdouall@manchester.ac.uk)

Page 1: Figure ESI-1. B3LYP/Def2-SVP Frontier orbitals of **6-H**

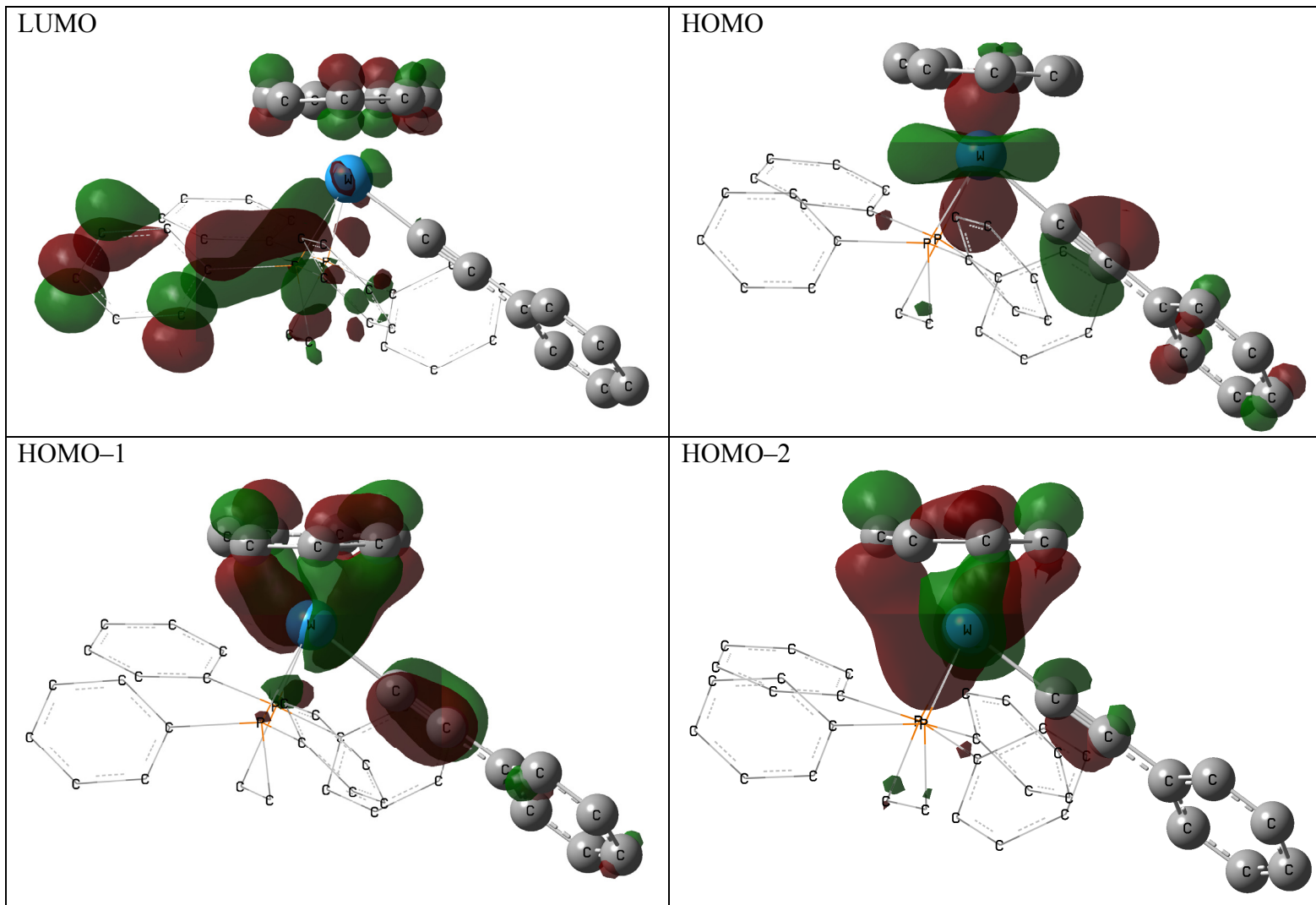
Page 2: Figure ESI-2. B3LYP/Def2-SVP Spin density of **[6-H]<sup>+</sup>**

Page 2: Table ESI-1. B3LYP/Def2-SVP Mulliken spin densities on selected atoms of **[6-H]<sup>+</sup>**.

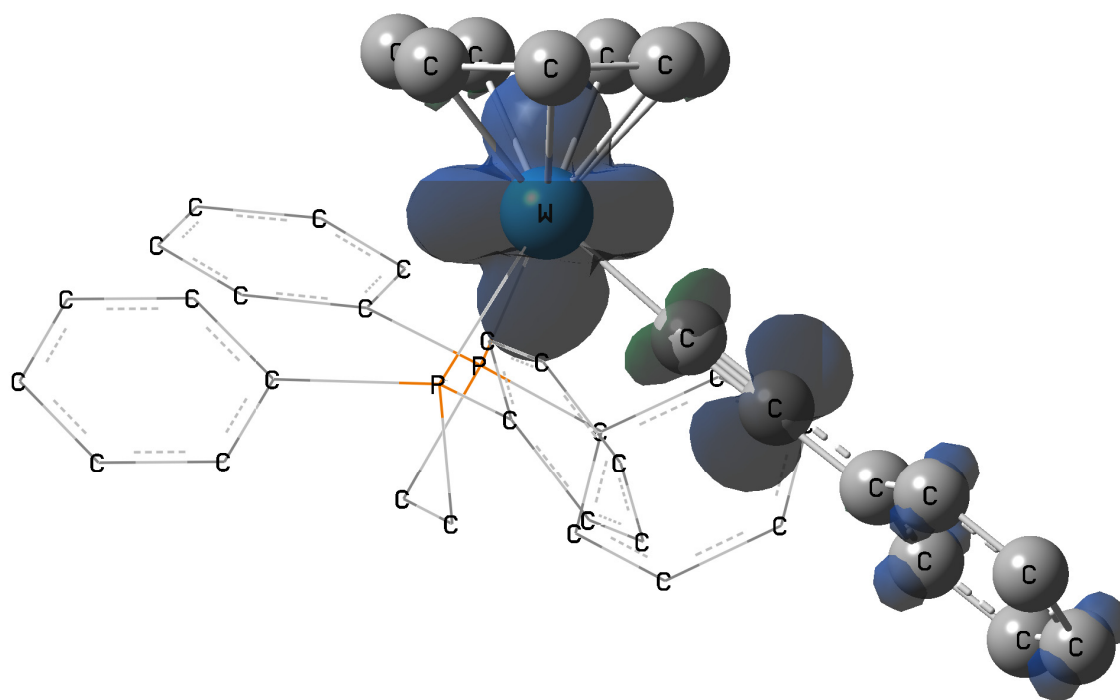
Page 3: Figure ESI-3. Cyclic voltammetric scan for alkynyl complex **6**

Page 3: Figure ESI-4 Cyclic voltammetric scan for alkynyl complex **7**

**Figure ESI-1** B3LYP/Def2-SVP Frontier orbitals of **6-H** (isosurface value is 0.04 au)



**Figure ESI-2** B3LYP/Def2-SVP Spin density of  $[\mathbf{6-H}]^+$  (isosurface value is 0.004 au)

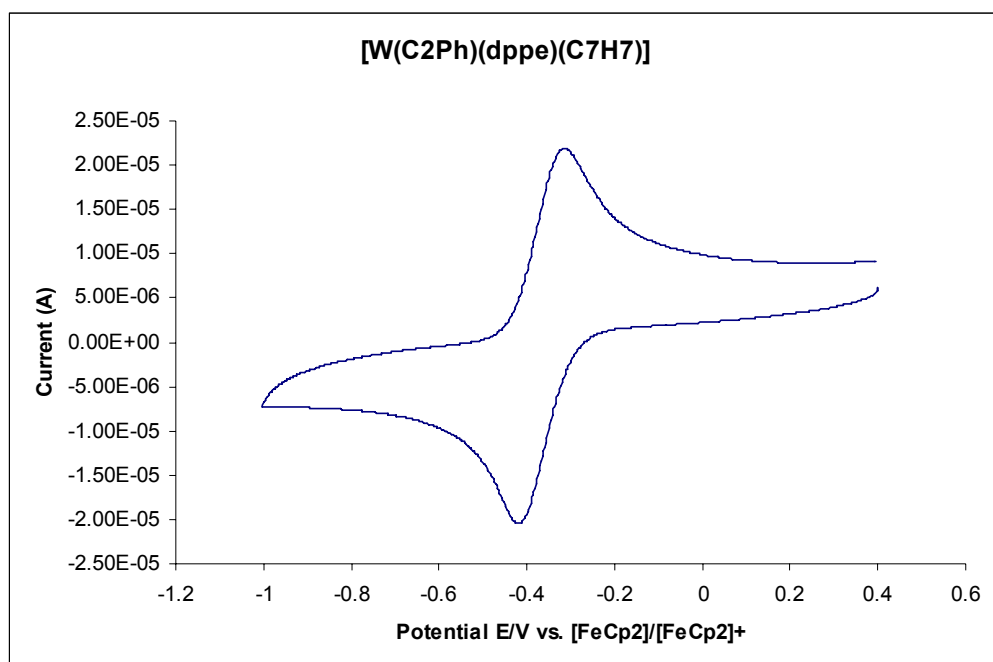


**Table ESI-1** B3LYP/Def2-SVP Mulliken spin densities on selected atoms of  $[\mathbf{6-H}]^+$

| Mulliken Spin Densities                                 |        |
|---|--------|
| W   | 0.980  |
| C <sub>α</sub> (alkynyl)                                | -0.123 |
| C <sub>β</sub> (alkynyl)                                | 0.234  |
| <i>ortho</i> -C (alkynylC <sub>6</sub> H <sub>5</sub> ) | 0.056  |
| <i>para</i> -C (alkynyl C <sub>6</sub> H <sub>5</sub> ) | 0.063  |

The hydrogens of the alkyne C<sub>6</sub>H<sub>5</sub> all have spin densities < 0.003.

**Figure ESI-3** Cyclic voltammogram of complex **6** recorded in CH<sub>2</sub>Cl<sub>2</sub> / [NBu<sub>4</sub><sup>n</sup>][PF<sub>6</sub>], (0.2M).



**Figure ESI-4** Cyclic voltammogram of complex **7** recorded in CH<sub>2</sub>Cl<sub>2</sub> / [NBu<sub>4</sub><sup>n</sup>][PF<sub>6</sub>], (0.2M).

