Synthesis, Spectroscopy and Electronic Structure of Vinylidene and Alkynyl Complexes in the Cycloheptatrienyl Tungsten Series \([W(C=CHR)(dppe)(\eta^1-C_7H_7)]^+\) and \([W(C≡CR)(dppe)(\eta^1-C_7H_7)]^n^+\) (n = 0 or 1).

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**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 \([6-\text{H}]^+\) (isosurface value is 0.004 au)

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

<table>
<thead>
<tr>
<th>Mulliken Spin Densities</th>
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<tbody>
<tr>
<td>W</td>
</tr>
<tr>
<td>(C_a) (alkynyl)</td>
</tr>
<tr>
<td>(C_b) (alkynyl)</td>
</tr>
<tr>
<td>(\text{ortho}-C) (alkynyl(\text{C}_6\text{H}_5))</td>
</tr>
<tr>
<td>(\text{para}-C) (alkynyl (\text{C}_6\text{H}_5))</td>
</tr>
</tbody>
</table>

The hydrogens of the alkynyl \(\text{C}_6\text{H}_5\) all have spin densities < 0.003.
**Figure ESI-3** Cyclic voltammogram of complex 6 recorded in CH$_2$Cl$_2$ / [NBu$_4$][PF$_6$], (0.2M).

![Cyclic voltammogram of complex 6](image)

**Figure ESI-4** Cyclic voltammogram of complex 7 recorded in CH$_2$Cl$_2$ / [NBu$_4$][PF$_6$], (0.2M).

![Cyclic voltammogram of complex 7](image)