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## PAPER

# Synthesis, spectroscopy and electronic structure of the vinylidene and alkynyl complexes $[W(C=CHR)(dppe)(\eta-C_7H_7)]^+$ and $[W(C=CR)(dppe)(\eta-C_7H_7)]^{n+}$ (n = 0 or 1)<sup>†</sup>

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The first examples of vinylidene complexes of the cycloheptatrienyl tungsten system  $[W(C=CHR)(dppe)(\eta-C_7H_7)]^+$  (dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>; R = H, 3; Ph, 4; C<sub>6</sub>H<sub>4</sub>-4-Me, 5) have been synthesised by reaction of [WBr(dppe)( $\eta$ -C<sub>7</sub>H<sub>7</sub>)], **1**, with terminal alkynes HC=CR; a one-pot synthesis of 1 from [WBr(CO)<sub>2</sub>( $\eta$ -C<sub>7</sub>H<sub>7</sub>)] facilitates its use as a precursor. The X-ray structure of 4[PF<sub>6</sub>] reveals that the vinylidene ligand substituents lie in the pseudo mirror plane of the  $W(dppe)(\eta-C_7H_7)$ auxiliary (vertical orientation) with the phenyl group located syn to the cycloheptatrienyl ring. Variable temperature <sup>1</sup>H NMR investigations on  $[W(C=CH_2)(dppe)(\eta-C_2H_2)][PF_6]$ , 3, estimate the energy barrier to rotation about the W= $C_{\alpha}$  bond as  $62.5 \pm 2 \text{ kJ mol}^{-1}$ ; approximately 10 kJ mol $^{-1}$  greater than for the molybdenum analogue. Deprotonation of 4 and 5 with KOBu<sup>t</sup> yields the alkynyls  $[W(C \equiv CR)(dppe)(\eta - C_7H_7)]$  (R = Ph, 6; C<sub>6</sub>H<sub>4</sub>-4-Me, 7) which undergo a reversible one-electron oxidation at a glassy carbon electrode in  $CH_2Cl_2$  with  $E_{\frac{1}{2}}$  values approximately 0.12 V negative of Mo analogues. The 17-electron radicals  $[6]^+$  and  $[7]^+$  have been investigated by spectroelectrochemical IR, UV-visible and EPR methods. The electronic structures of representative vinylidene (3) and alkynyl (6) complexes have been investigated at the B3LYP/Def2-SVP level. In both cases, electronic structure is characterised by a frontier orbital with significant metal  $d_{z^2}$  character and this dominates the structural and spectroscopic properties of the system.

#### Introduction

Complexes of highly unsaturated carbon-chain ligands<sup>1,2</sup> are the focus of significant current activity in organometallic chemistry with the expectation of future applications as molecular materials in electronic,<sup>3</sup> magnetic<sup>4</sup> and optical<sup>5</sup> devices. Two series of complexes central to the development of this chemistry are the metallacumulenylidenes M{=(C),=CR<sub>2</sub>} and alkynyl/poly-ynyl complexes M{-(C=C),-C=CR} and in a sequence of investigations, we have demonstrated the capacity of the cycloheptatrienyl molybdenum auxiliary Mo(dppe)(η-C<sub>7</sub>H<sub>7</sub>) to support systems of this type.<sup>6-10</sup> A key requirement for materials applications will be an in-depth understanding of the factors which control

the interaction between the metal centre and the carbon chain ligand and our recent studies, supported by electronic structure calculations,<sup>9,10</sup> suggest that cycloheptatrienyl complexes of the Group 6 metals have a significant contribution to make in this respect. Thus, by comparison with analogous cyclopentadienyl based, Group 8 complexes, M(dppe)Cp (M = Fe or Ru),<sup>11,12</sup> the energy ordering of the d-orbital manifold in the Mo(dppe)(n- $C_7H_7$ ) fragment is altered by strong  $\delta$  interactions between the  $e_2$  level of the C<sub>7</sub>H<sub>7</sub> ring and the  $d_{xy}$  and  $d_{x^2-y^2}$  metal orbitals<sup>13,14</sup> resulting in a metal-centred HOMO incorporating substantial d<sub>z<sup>2</sup></sub> character.<sup>9,10</sup> The  $d_{z^2}$  symmetry of the HOMO in Mo(dppe)( $\eta$ - $C_7H_7$ ) complexes is manifest both in the structural chemistry of cumulenvlidene derivatives9 and in the redox chemistry of the alkynyl and poly-ynyl systems<sup>8,10</sup> where the limited effect of a one-electron oxidation process in perturbation of the alkynyl ligand may, in part, be attributed to a poor symmetry match between the metal  $d_{z^2}$  HOMO (directed towards the centre of the cycloheptatrienyl ring) and the alkynyl  $\pi$ -orbitals.

To explore further the relationship between frontier orbital symmetry and the structural and redox chemistry of cumulenylidene and alkynyl complexes, we now report the progression of our studies to cycloheptatrienyl tungsten systems based on the W(dppe)( $\eta$ -C<sub>7</sub>H<sub>7</sub>) auxiliary. The principal objectives of this

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Scheme 1 Routes to the preparation of  $[WX(CO)_2(\eta-C_7H_7)]$ , R = Me, Pr<sup>*n*</sup>.

investigation were first to establish that a metal-centred  $d_{z^2}$  HOMO is a consistent feature of the cycloheptatrienyl Group 6 metal series and secondly to evaluate, by a combined experimental and theoretical approach, the effect of the 5d orbital set of W *vs.* the 4d set of Mo upon the electronic structure and chemical reactivity of carbon chain complexes of these systems.

#### **Results and discussion**

#### Synthesis of [WBr(dppe)(η-C<sub>7</sub>H<sub>7</sub>)]

The chemistry of the W(dppe)( $\eta$ -C<sub>7</sub>H<sub>7</sub>) system was initiated more than a decade ago,<sup>15</sup> but our investigations were impeded by the poor accessibility of precursor complexes of the type [WX(dppe)( $\eta$ -C<sub>7</sub>H<sub>7</sub>)]; the synthetic challenges involved have been well documented.<sup>15,16</sup> Recently however, we have developed a direct synthesis<sup>9</sup> of [MoBr(dppe)( $\eta$ -C<sub>7</sub>H<sub>7</sub>)] from the dicarbonyl precursor [MoBr(CO)<sub>2</sub>( $\eta$ -C<sub>7</sub>H<sub>7</sub>)] and this led to a re-evaluation of the analogous tungsten chemistry. Most known complexes of the cycloheptatrienyl tungsten system are derived from [WX(CO)<sub>2</sub>( $\eta$ -C<sub>7</sub>H<sub>7</sub>)] (X = halide) which is obtained in a four step synthesis from W(CO)<sub>6</sub> in relatively low overall yield (Scheme 1).<sup>17</sup>

The final step, involving CO substitution by halide X, is reported to proceed in very low yield for X = Br or  $Cl^{18}$  and therefore the majority of syntheses utilise the iodide derivative [WI(CO)<sub>2</sub>(n- $C_{7}H_{7}$ ] as an entry to further chemistry of W( $\eta$ -C<sub>7</sub>H<sub>7</sub>) complexes. In the current investigation, the initial objective was to develop an improved route to the bromide derivative  $[WBr(CO)_2(\eta - C_7H_7)]$ , this being preferred to the commonly employed iodide system on the basis of activation to carbonyl substitution<sup>19</sup> and lability of the W-X bond. Two modifications to the reaction sequence outlined in Scheme 1 have been effected. First,  $[W(CO)_3(\eta-C_7H_7)]^+$  can be conveniently obtained in good yield as the  $PF_6^-$  salt by direct reaction of  $[W(CO)_3(NCR)_3]$  with  $[C_7H_7][PF_6]$ ,<sup>20</sup> thus avoiding the need to isolate the cycloheptatriene complex  $[W(CO)_3(\eta-C_7H_8)]$ . Secondly, modification of the conditions (reduced reaction time and reagent excess) in the reaction of  $[W(CO)_3(\eta-C_7H_7)]^+$  with NaBr, reliably gave product yields in excess of 60%.

The availability of gram quantities of  $[WBr(CO)_2(\eta-C_7H_7)]$ facilitated an investigation of its direct reaction with dppe. As reported previously, reaction of  $[WI(CO)_2(\eta-C_7H_7)]$  with dppe affords the ring-slipped adduct [WI(CO)<sub>2</sub>(dppe)( $\eta^3$ -C<sub>7</sub>H<sub>7</sub>)] which is resistant to loss of CO even in refluxing toluene.<sup>21</sup> However, in a modification to the procedure recently developed for the analogous chemistry of molybdenum,9 a mixture of  $[WBr(CO)_2(\eta-C_7H_7)]$  and one half equivalent of dppe was added to a refluxing 1:1 toluene/xylene solution followed one hour later by a second half equivalent of dppe. This procedure gave moderate yields of [WBr(dppe)( $\eta$ -C<sub>7</sub>H<sub>7</sub>)], 1, formed as a mixture with [W(CO)(dppe)(η-C<sub>7</sub>H<sub>7</sub>)]Br<sup>15</sup> and small quantities of [W(CO)<sub>4</sub>(dppe)] (IR, v(C=O) cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>) 2017, 1915 (sh), 1901, 1879),<sup>22</sup> which were separated from 1, by column chromatography on alumina. The identity of complex 1 was confirmed by microanalysis, mass spectrometry (see Experimental), <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy (Table 1) and by a single crystal X-ray structural study as the CH<sub>2</sub>Cl<sub>2</sub> solvate (Fig. 1).



**Fig. 1** Molecular structure of complex **1**, with thermal ellipsoids plotted at 50% probability. Hydrogen atoms, and solvent of crystallisation omitted for clarity. Key bond lengths (Å) and angles (°):W(1)–Br(1), 2.505(3); W(1)–P(1), 2.469(3); W(1)–P(2), 2.462(3); P(1)–W(1)–P(2), 78.60(9); P(1)–W(1)–Br(1), 83.31(9); P(2)–W(1)–Br(1), 83.92(9).

Table 1	<sup>1</sup> H,	${}^{13}C{}^{1}H{}^{1}$	and ${}^{31}P$	${}^{1}H$	NMR	data <sup>a</sup>

	<sup>1</sup> H NMR			<sup>13</sup> C{ <sup>1</sup> H} NMR				<sup>31</sup> P{ <sup>1</sup> H} NMR	
	R	$C_7H_7$	dppe	$\overline{C_{\alpha}}$	$C_{\beta}$	R	$\mathrm{C}_{7}\mathrm{H}_{7}$	dppe	
1	_	5.15	2.30, m, 4H, PCH <sub>2</sub> ; 7.28–8.19, m, PPh <sub>2</sub>						40.3 {228}
2	2.53, t, (7.4), 2H, H <sub><math>\beta</math></sub> ; 1.29, q, 2H, H <sub><math>\gamma</math></sub> ; 3.79, t, (7.2), 2H, H <sub><math>\delta</math></sub>	4.79, t, {3}	2.72, m, 2H; 3.01, m, 2H, PC <i>H</i> <sub>2</sub> ; 7.58–6.97, m, PPh <sub>2</sub>	307.7, t, {14}	_	56.4, $C_{\beta}$ ; 24.0, $C_{\gamma}$ ; 80.6, $C_{\delta}$	84.6	29.9, m, PCH <sub>2</sub> ; 136.8–128.7, PPh <sub>2</sub>	30.8 {321}
3	4.78, br, 1H; 5.69, br, 1H; C=CH <sub>2</sub>	5.04	2.58, br, 2H; 2.86, br, 2H, PC <i>H</i> <sub>2</sub> ; 7.85–7.01, m, PPh <sub>2</sub>	348.6, t, {25}	103.2, t, {9}	_	87.0	28.0, m, PCH <sub>2</sub> ; 137.8–126.0, PPh <sub>2</sub>	34.7 {316}
4 <sup><i>b</i></sup>	5.74, t, $\{12.3\}$ , C=CHPh; 7.78-6.55, m, C=CHC <sub>6</sub> H <sub>5</sub>	5.07, t, {3}	2.68, m, 2H; 2.95, m, 2H, PCH <sub>2</sub> ; 7.78–6.55, m, PPh <sub>2</sub>	352.2, t, {27}	123.2, t, {10}	136.2–127.1, Ph	87.5	28.3, m, PCH <sub>2</sub> ; 136.2–127.1, PPh <sub>2</sub>	34.4 {316}
5	5.67, t, $\{12.0\}$ , C==CHC <sub>6</sub> H <sub>4</sub> Me; 6.91, d, $\{7.6\}$ , 2H; 6.37, d, $\{7.6\}$ , 2H, C <sub>6</sub> H <sub>4</sub> Me; 2.20, 3H, C <sub>6</sub> H <sub>4</sub> Me	4.96, t, {3}	2.58, m, 2H; 2.85, m, 2H, PCH <sub>2</sub> ; 7.68–6.86, m, PPh <sub>2</sub>	352.2, t, {26}	122.8, t, {10}	138.0–125.3, <i>C</i> <sub>6</sub> H <sub>4</sub> Me; 21.1, C <sub>6</sub> H <sub>4</sub> Me	86.9	28.0, m, PCH <sub>2</sub> ; 138.0–125.3, PPh <sub>2</sub>	34.7 {317}
6	6.83, m, 2H; 6.65, m, 1H; 5.94, d, $\{5.6\}$ , 2H: C $\equiv$ CC $_{\epsilon}H_{5}$ .	4.84	2.26, br, 2H; 2.44, br, 2H, PC <i>H</i> <sub>2</sub> ; 7.84–7.25, m, PPh <sub>2</sub>	130.2, t, {22}	120.7	140.1–121.7, Ph	81.3	28.6, m, PCH <sub>2</sub> ; 140.4–121.7 PPh <sub>2</sub>	43.6 {329}
7	6.54, d, {7.6}, 2H; 5.74, d, {7.6}, 2H, C $\equiv$ CC <sub>6</sub> H <sub>4</sub> Me; 2.07, 3H, C $\equiv$ CC <sub>6</sub> H <sub>4</sub> Me	4.73	2.15, m, 2H; 2.32, m, 2H, PCH <sub>2</sub> ; 7.72–7.14, m, PPh <sub>2</sub>	not observed	121.7	$141.9-125.9, C_{6}H_{4}Me; 21.0, C_{6}H_{4}Me$	82.5	29.7, m, PCH <sub>2</sub> ; 141.9–125.9, PPh <sub>2</sub>	41.5 {321}

<sup>*a*</sup> 400 MHz <sup>1</sup>H, 100 MHz <sup>13</sup>C{<sup>1</sup>H}, 162 MHz <sup>31</sup>P{<sup>1</sup>H} NMR spectra unless stated otherwise; d = doublet, t = triplet, q = quintet, m = multiplet, br = broad; chemical shifts downfield from SiMe<sub>4</sub>, coupling constants in Hz, J(H-H) as (), J(H-P) or J(C-P) as {}; in CD<sub>2</sub>Cl<sub>2</sub> solution unless stated otherwise, labelling as in Scheme 2. All spectra recorded at ambient temperature. Spectra for complexes 1, 6 and 7 recorded with a trace of cobaltocene added to the solution to prevent accumulation of paramagnetic W(I) species by aerial oxidation. <sup>*b* 31</sup>P NMR spectrum in CDCl<sub>3</sub>.

#### Carbene and vinylidene complexes $[W{(C)_n=CR_2}(dppe)(\eta-C_7H_7)]^+$

The synthetic protocol outlined above unlocks the chemistry of the cycloheptatrienyl tungsten system to a series of advances based upon the electron-rich,  $d^6$ , W(dppe)( $\eta$ -C<sub>7</sub>H<sub>7</sub>) auxiliary. To commence the investigation, the reactions of [WBr(dppe)(η- $C_{7}H_{7}$  with terminal alkynes HC=CR to give carbene and vinylidene products were explored. An extensive series of iron, ruthenium and molybdenum, carbene and vinylidene complexes of general formulation  $[M = CR_2](dppe)(\eta - L)^+ \{M = Fe, L =$  $Cp^{23}$  or  $Cp^{*}$ ;<sup>24</sup> M = Ru, L = Cp;<sup>25,26</sup> M = Mo, L =  $C_7H_7^{9}$  has been developed, based on the reaction of metal halide precursor complexes  $[MX(dppe)(\eta-L)]$  with terminal alkynes HC=CR in methanol in the presence of a halide acceptor such as  $NH_4[PF_6]$  or  $K[PF_6]$ . The method depends upon ionisation of the halide ligand and subsequent addition of the alkyne to the d6 metal centre which promotes alkyne to vinylidene isomerisation. It was therefore our expectation that the d<sup>6</sup> tungsten centre of  $[WBr(dppe)(\eta-C_7H_7)]$ would exhibit analogous reactivity.

The outcome of the reactions of  $[WBr(dppe)(\eta-C_7H_7)]$  with terminal alkynes HC=CR is summarised in Scheme 2 and characterisation details for the complexes described are presented in Table 1 and the Experimental section.

Clearly the cycloheptatrienyl tungsten centre is able to support a range of metallacumulenylidene systems in an equivalent manner to the molybdenum analogue. The 2-oxacyclopentylidene  $[W(CCH_2CH_2CH_2O)(dppe)(\eta-C_7H_7)][PF_6],2$ , was isolated as an orange solid from the reaction of 3-butyn-1-ol/K[PF<sub>6</sub>] under reflux in methanol. Similarly the vinylidene complexes  $[W(C=CHR)(dppe)(\eta-C_7H_7)][PF_6], (R = H, 3; R = Ph, 4; R =$  $C_6H_4$ -4-Me, 5) were obtained by reaction of [WBr(dppe)( $\eta$ - $C_7H_7$ )] with HC=CSiMe<sub>3</sub>, HC=CPh or HC=CC<sub>6</sub>H<sub>4</sub>-4-Me respectively and K[PF<sub>6</sub>] under methanol reflux. In common with their molybdenum counterparts, the vinylidene complexes were stable in refluxing methanol with no evidence for methoxide addition at  $C_{\alpha}$ . The availability of a series of carbene and vinylidene complexes  $[M{(C)_n=CR_2}(dppe)(\eta-C_7H_7)]^+$  (M = Mo or W, n = 0 or 1) allows a direct comparison of spectroscopic and structural data for molybdenum and tungsten analogues. The  ${}^{13}C{}^{1}H$  NMR chemical shift data for  $C_{\alpha}$  of the Mo and W carbene and vinylidene systems are summarised in Table 2 from which it is evident that the tungsten derivatives exhibit a shift of  $\delta C_{\alpha}$  to high field by approximately 20 ppm. In each case the  $C_{\alpha}$  resonance is a triplet with  ${}^{2}J(P-C)$  values similar for the two metals but slightly smaller for the tungsten derivatives.

#### Structural studies

We have previously reported structural studies on the cycloheptatrienyl molybdenum carbene and vinylidene complexes  $[Mo(CCH_2CH_2CH_2O)(dppe)(\eta-C_7H_7)]^+$ ,<sup>27</sup> and  $[Mo(C=CHR)-(dppe)(\eta-C_7H_7)]^+$  (R = Ph<sup>7</sup> or (CH<sub>2</sub>)<sub>3</sub>OH<sup>27</sup>). A key observation from this work is the orientation of the carbene or vinylidene ligand substituents with respect to the pseudo mirror plane which

**Table 2** Comparison of <sup>13</sup>C NMR shifts<sup>*a*</sup> for  $C_{\alpha}$  in complexes  $[M\{(C)_n = CR_2\}(dppe)(\eta - C_7H_7)]^+$ 

	$(C)_n = CR_2$	$(C)_n = CR_2$							
	CCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> O		C=CH <sub>2</sub>		C=C(H)Ph				
М	$\overline{\delta\mathrm{C}_{lpha}}$	Solvent	$\overline{\delta \mathrm{C}_{lpha}}$	Solvent	$\overline{\delta \mathrm{C}_{lpha}}$	Solvent			
Mo W	331.7 {18} 307.7 {14}	acetone- $D_6$ , $CD_2Cl_2$	368.0 {30} 348.6 {25}	$\begin{array}{c} CD_3CN\\ CD_2Cl_2 \end{array}$	372.8 {32} 352.2 {27}	acetone- $D_6$ , $CD_2Cl_2$			

<sup>*a*  $^{2}$ *J*(P–C) values in Hz in parentheses {}.</sup>



Scheme 2 *Reagents and conditions* (i) dppe  $(\frac{1}{2}$  equivalent), toluene/xylene (1:1), reflux 1 h, then further dppe  $(\frac{1}{2}$  equivalent) reflux 3 h. (ii) HC=C(CH<sub>2</sub>)<sub>2</sub>OH, in methanol, K[PF<sub>6</sub>], reflux 3 h. (iii) HC=CR (R = SiMe<sub>3</sub>, Ph or C<sub>6</sub>H<sub>4</sub>-4-Me) in methanol, K[PF<sub>6</sub>], reflux 2–3 h. (iv) (R = Ph or C<sub>6</sub>H<sub>4</sub>-4-Me), excess KOBu' in thf, 40 min.

bisects the Mo(dppe)( $\eta$ -C<sub>7</sub>H<sub>7</sub>) fragment. Thus the oxacarbene ring of [Mo(CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O)(dppe)( $\eta$ -C<sub>7</sub>H<sub>7</sub>)]<sup>+</sup>, is disposed orthogonal to the mirror plane in a horizontal alignment whereas in each of the vinylidene complexes, the substituents lie in the mirror plane and are assigned to a vertical configuration. By

contrast, structural studies on the  $[M\{(C)_n = CR_2\}(dppe)(\eta-L)]^+$ (*n* = 0 or 1; L = Cp or Cp\*; M = Fe or Ru) series reveal that carbenes adopt a vertical configuration,<sup>25</sup> whilst vinylidenes are horizontal.<sup>28</sup> In terms of the classical, self-consistent field (SCF) calculations on these systems,<sup>29</sup> it appears that the preferred plane of the  $\pi$ -interaction of the Mo(dppe)( $\eta$ -C<sub>7</sub>H<sub>7</sub>) auxiliary

Bond lengths/Å			
W(1)–P(1)	2.5037(18)	W(1)–C(2)	2.328(6)
W(1) - P(2)	2.5032(18)	W(1) - C(3)	2.323(6)
W(1) - C(8)	1.941(7)	W(1)-C(4)	2.331(6)
C(8) - C(9)	1.323(9)	W(1) - C(5)	2.290(6)
C(9) - C(10)	1.463(9)	W(1) - C(6)	2.339(6)
W(1)–C(1)	2.280(6)	W(1)–C(7)	2.357(6)
Bond angles (°)			
P(1)-W(1)-P(2)	80.19(6)	W(1)-C(8)-C(9)	172.4(5)
P(1)-W(1)-C(8)	78.40(19)	C(8) - C(9) - C(10)	128.8(6)
P(2)-W(1)-C(8)	81.03(19)	Ct-W(1)-C(8)	138
$Ct = centroid of C_7$	H <sub>7</sub> ring		

with the vacant p-orbital of the cumulenylidene  $C_{\alpha}$  carbon is the converse of that in the  $[M\{(C)_n = CR_2\}(dppe)(\eta-L)]^+$  (M = Fe or Ru) series and a recent DFT investigation on the vinylidene complex  $[Mo(C = CH_2)(dppe)(\eta-C_7H_7)]^+$  has confirmed that the atypical orientation of vinylidene ligands in the cycloheptatrienyl molybdenum system can be attributed to a  $\pi$ -interaction between the cumulenylidene LUMO and the metal  $d_{z^2}$  based HOMO of the Mo(dppe)( $\eta$ -C<sub>7</sub>H<sub>7</sub>) unit.<sup>9</sup> The main purpose of the current study was therefore to establish the ligand orientation preference imposed by the W(dppe)( $\eta$ -C<sub>7</sub>H<sub>7</sub>) auxiliary.

The crystallographically determined structure of  $[W(C=CHPh)(dppe)(\eta-C_7H_7)][PF_6]$ , **4** with the crystallographic numbering scheme is illustrated in Fig. 2. The asymmetric unit of **4** contains two molecules; in one of these the cycloheptatrienyl ring is disordered over two sites and therefore the discussion here is focussed on the non-disordered molecule although structural parameters are very similar in each case. Important bond lengths and angles for the non-disordered molecule are given in Table 3 and it is evident that the key  $W=C_{\alpha}$  (1.941(7) Å) and  $C_{\alpha}-C_{\beta}$  (1.323(9) Å) distances of the vinylidene ligand lie within normal ranges.<sup>30</sup> However the principal structural feature of interest



Fig. 2 Molecular structure of complex 4, with thermal ellipsoids plotted at 50% probability. Hydrogen atoms [except H(9)] and  $PF_6^-$  counter anion omitted for clarity. The figure illustrates one of two crystallographically independent molecules in the asymmetric unit.

in 4 is the orientation of the vinylidene ligand which adopts a vertical configuration with the more bulky Ph substituent located in the syn position relative to the cycloheptatrienyl ring in accord with the structures of the molybdenum analogues; this result suggests that the vertical orientation of the vinylidene ligand substituents is a consistent feature of the Group 6 metal systems,  $M(dppe)(\eta-C_7H_7)$  (M = Mo or W). The dihedral angle between the planes defined by Ct–W–C(8) and C(8)–C(9)–C(10) (Ct represents the centroid of the cycloheptatrienyl ring) is 1.5° in 4 (cf.  $[Mo(C=CHPh)(dppe)(\eta-C_7H_7)][BF_4]$ , 10.6°) indicating a small deviation from the precise vertical configuration. An additional salient structural feature of 4 is the large Ct-W-C(8) angle (138°). This is similar to that observed in the molybdenum analogue (135°),<sup>7</sup> and consistent with the optimum value  $(135°)^{31}$ for a  $\pi$ -interaction between the cumulenylidene LUMO and a metal d<sub>2</sub> based HOMO.

#### **Dynamic NMR Investigations**

Variable temperature <sup>1</sup>H NMR studies on complexes of the type  $[M{=(C)_n=CH_2}(dppe)(\eta-L)]^+$  (n = 0, L = Cp, M = Fe<sup>32</sup> or Ru;<sup>33</sup>  $n = 1, L = C_7 H_7, M = Mo^7$  and  $[M(=CH_2)(CO)_2(PPh_3)Cp]^+$  (M = Mo or W)<sup>34</sup> in which the carbene or vinylidene H substituents are disposed in a vertical orientation may be employed to confirm low temperature solution conformations and to estimate activation energies to rotation about the  $M=C_{\alpha}$  bond. In the case of  $[Mo(C=CH_2)(dppe)(\eta-C_7H_7)]^+$  the two vinylidene hydrogen substituents are inequivalent in the low temperature <sup>1</sup>H NMR spectrum consistent with a vertical vinylidene orientation with two discrete vinylidene proton environments located syn or anti to the cycloheptatrienyl ring. From the coalescence temperature of 268 K ( $\pm$ 3 K) in CD<sub>3</sub>CN, the energy barrier to rotation about the Mo= $C_{\alpha}$  bond in [Mo(C=CH<sub>2</sub>)(dppe)( $\eta$ -C<sub>7</sub>H<sub>7</sub>)]<sup>+</sup> was estimated as 51.9  $\pm 1$  kJ mol<sup>-1</sup>,<sup>7</sup> significantly larger than the equivalent parameter in complexes of the type [M(C=CHR)(dppe)Cp]+  $(M = Fe^{23} \text{ or } Ru^{35})$ . The synthesis of the tungsten analogue  $[W(C=CH_2)(dppe)(\eta-C_7H_7)][PF_6]$ , 3, now permits an evaluation of the effect of the identity of the metal on the  $M=C_{\alpha}$  rotation barrier in the complexes  $[M(C=CH_2)(dppe)(\eta-C_7H_7)]^+$ .

Remarkably, the <sup>1</sup>H NMR spectrum of **3** in CD<sub>3</sub>CN reveals that the vinylidene protons are inequivalent at ambient temperature (293 K) consistent with a vertical ligand orientation and a high activation energy to rotation about the W=C<sub>a</sub> bond. On warming above 293 K, the vinylidene proton resonances broaden and a coalescence temperature of 330 K ( $\pm$ 5 K) in CD<sub>3</sub>CN was determined giving an estimated barrier to rotation about the W=C<sub>a</sub> bond in **3** as 62.5  $\pm$ 2 kJ mol<sup>-1</sup>. This is considerably larger than the equivalent parameter for the molybdenum analogue determined in the same solvent and may indicate an enhanced  $\pi$ interaction between the vinylidene ligand and the metal 5d orbitals. A related metal-dependency of rotation barriers has been reported for the Group 6 carbene complexes [M(=CH<sub>2</sub>)(CO)<sub>2</sub>(PPh<sub>3</sub>)Cp]<sup>+</sup> [M = W, 35 kJ mol<sup>-1</sup>; M = Mo, < 28 kJ mol<sup>-1</sup>].<sup>34</sup>

#### Alkynyl complexes $[W(C \equiv CR)(dppe)(\eta - C_7H_7)]$

The vinylidene complexes **4** and **5** undergo deprotonation on treatment with KOBu<sup>t</sup> in thf to afford alkynyl complexes  $[W(C \equiv CR)(dppe)(\eta - C_7H_7)]$  (R = Ph, **6**; R = C<sub>6</sub>H<sub>4</sub>-4-Me, **7**;

**Table 4** Electrochemical, IR and UV-visible data for the alkynyl complexes  $[M(C \equiv CR)(dppe)(\eta - C_7H_7)]^{n+}$   $(n = 0 \text{ or } 1)^a$ 

Complex		Electrochemical data <sup>b</sup>	IR data <sup>e</sup>			UV/visible data <sup>d</sup>		
R	М		n = 0	<i>n</i> = +1	$\Delta v (C \equiv C)$	n = 0	<i>n</i> = +1	
Ph	Mo	-0.72	2045	2032	-13	32700 (21000), 27000 (12200) 18900 (1000)	33300 (15600), 28300 (8400), 18900 (2100) sb 16900 (4800)	
Ph	W	-0.84	2042, 1991 (w)	2029	-13	(12200), 10000 (1000) 34300 (8120), 25300 (3640), 19100 (650)	34700 (6100), 29200 (3140), 26300 (2030), 20000 (970), sh, 18000 (1600)	
C <sub>6</sub> H <sub>4</sub> -4-Me	Mo	-0.72	2050	2017	-33	32680 (18300), 27100 (12800), 19200 (800)	28250 (7800), 16600 (5300)	
C <sub>6</sub> H <sub>4</sub> -4-Me	W	-0.86	2048, 2036 (sh)	2012, 2002 (sh)	-35	25700 (7200), 20700 (1950)	29800 (7500), 25500 (4970), 20500 (1600), 17600 (1270)	

<sup>*a*</sup> Data for M = Mo from reference 10. <sup>*b*</sup>  $E_{\frac{1}{2}}$  (V), by cyclic voltammetry at a glassy carbon working electrode, Ag/AgCl reference electrode. All potentials are reported *vs.* FeCp<sub>2</sub>/FeCp<sub>2</sub><sup>+</sup> (FeCp<sub>2</sub>/FeCp<sub>2</sub><sup>+</sup> = 0.00 V) at a scan rate of 0.100 V s<sup>-1</sup> from 0.2 M [NBu<sub>4</sub><sup>*n*</sup>][PF<sub>6</sub>]/CH<sub>2</sub>Cl<sub>2</sub> solutions at ambient temperature. <sup>*c*</sup>  $v(C \equiv C)/cm^{-1}$ , spectroelectrochemical measurement in 0.1 M [NBu<sub>4</sub><sup>*n*</sup>][PF<sub>6</sub>]/CH<sub>2</sub>Cl<sub>2</sub>. <sup>*d*</sup>  $v_{max}/cm^{-1}$ , ( $\epsilon/M^{-1} cm^{-1}$ ) determined by spectroelectrochemical methods in 0.1 M [NBu<sub>4</sub><sup>*n*</sup>][PF<sub>6</sub>]/CH<sub>2</sub>Cl<sub>2</sub>.

Scheme 2) which were isolated as red–brown solids following purification by chromatography on Celite. The deprotonation reactions proceeded to completion only with a large excess of base, probably reflecting the high stability and low acidity of the vinylidenes **4** and **5** conferred by the strongly electron donating  $W(dppe)(\eta-C_7H_7)$  auxiliary. Complexes **6** and **7** were characterised as summarised in Tables 1 and 4 and the Experimental section. Key spectroscopic features are the IR active  $v(C \equiv C)$  stretching bands which (with the exception of band splitting in **7**) are almost identical to the molybdenum analogues (see Table 4),<sup>6,10</sup> and in the <sup>13</sup>C NMR spectrum, the characteristic triplet resonance for the alkynyl  $C_{\alpha}$  carbon which is shifted to high field by *ca*. 10 ppm as a result of substitution of Mo with W.

The redox behaviour of complexes 1, 6 and 7 was investigated by cyclic voltammetry at a glassy carbon electrode in CH<sub>2</sub>Cl<sub>2</sub> (details as in Table 4). Under these conditions, each of the complexes undergoes a diffusion controlled  $(i_p/v^{\frac{1}{2}})$  is constant for scan rates  $v = 50-500 \text{ mV s}^{-1}$ ), chemically reversible one-electron oxidation with the separation between cathodic and anodic peak potentials comparable to that determined for ferrocene under identical conditions. The formal reduction potentials  $E_{\frac{1}{2}}$  for **6** and 7 are approximately 120 mV to negative potential of the Mo analogues. In principle, the results of the cyclic voltammetry indicate that the 17-electron radicals  $[W(C = CR)(dppe)(\eta - C_7H_7)]^+$  $(R = Ph, [6]^+; R = C_6H_4-4-Me, [7]^+)$  are isolable synthetic targets. However, whilst the radicals were undoubtedly generated by reaction of 6 and 7 with [FeCp<sub>2</sub>][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub>, isolation as pure materials was impeded by slow decomposition to the carbonyl complex<sup>36</sup> [W(CO)(dppe)( $\eta$ -C<sub>7</sub>H<sub>7</sub>)]<sup>+</sup>, [v(CO), CH<sub>2</sub>Cl<sub>2</sub>, 1940 cm<sup>-1</sup>]<sup>15</sup> and therefore in the investigations described below,  $[6]^+$  and [7]<sup>+</sup> were generated *in situ* or studied by spectroelectrochemical techniques.

## Spectroelectrochemical IR, UV-visible and EPR investigations on the alkynyl radicals $[W(C \equiv CR)(dppe)(\eta - C_7H_7)]^+$

A key feature of the redox chemistry of metal alkynyl systems is the negative shift in the IR active  $v(C \equiv C)$  stretch resulting from one-electron oxidation to the 17-electron radical cations. The magnitude of the negative shift in  $v(C \equiv C)$  acts as a good first order indicator of the metal vs. alkynyl ligand character of the redox active frontier orbital within a series of similar complexes. Thus the large negative shifts of  $v(C \equiv C)$  upon oxidation observed for  $[Ru(C \equiv CR)(dppe)Cp^*]^{n+}$ , (> 100 cm<sup>-1</sup>) are consistent with depopulation of an orbital with a substantial degree of C=C bonding character, and significant radical-ligand character in the cations [Ru(C=CR)(dppe)Cp\*]+.12 Although less extensively documented, available data from Os(dppe)Cp\* based ynyl systems also supports the notion of substantially ligandbased frontier orbitals in the 5d analogues.<sup>37</sup> Similar analyses of the shift in alkynyl stretching frequency upon oxidation,  $\Delta v$ (C=C), for the iron complexes [Fe(C=CR)(dppe)Cp\*]<sup>0/+</sup> are complicated by splitting of the v(C = C) band by Fermi coupling.<sup>38</sup> However, it is generally agreed that the 3d cation-radical systems feature more substantial metal-localised radical character than their 4d (Ru) or 5d (Os) counterparts.<sup>11</sup> By contrast with the ruthenium complexes, the  $Mo(\eta-C_7H_7)$  complexes which also contain a 4d6 formal electron configuration, feature a more metalcentred oxidation process, with less alkynyl ligand character and consequently much smaller shifts in  $v(C \equiv C)$ .<sup>10</sup> Given the essentially identical structure of the complexes [M(C=CR)(dppe)(η- $C_{7}H_{7}$ ] (M = Mo or W) with those of the group 8 complexes  $M(C \equiv CR)(dppe)Cp^*$ , a comparison of the shift in  $v(C \equiv C)$ following one-electron oxidation should provide a good indicator of the effect of 4d vs. 5d orbital overlap upon the metal-alkynyl interaction.

The shift in  $v(C \equiv C)$  resulting from one-electron oxidation of 6 and 7 to the corresponding radicals [6]<sup>+</sup> and [7]<sup>+</sup> was investigated by synthetic and spectroelectrochemical methods. Addition of [FeCp<sub>2</sub>][PF<sub>6</sub>] to red-brown, CH<sub>2</sub>Cl<sub>2</sub> solutions of 6 and 7 resulted in the rapid formation of deep red  $([6]^+)$  or deep pink  $([7]^+)$  solutions of the 17-electron radicals for which IR data were immediately recorded; results were confirmed by an IR spectroelectrochemical analysis (Fig. 3) which also demonstrated the reversibility of the changes in the IR spectra. In both cases the negative shifts in  $v(C \equiv C)$  resulting from one-electron oxidation are small (6/[6]<sup>+</sup>,  $-13 \text{ cm}^{-1}$ ;  $7/[7]^+$ ,  $-35 \text{ cm}^{-1}$ ) and almost identical to the Mo series (see Table 4); (the interpretation of the data for  $7/[7]^+$  is complicated by band splitting in both 7 and [7]<sup>+</sup>, however both bands assigned to v(C = C) in complex 7 are Raman inactive and consequently the splitting is attributed to Fermi coupling effects).<sup>38</sup> The very similar response in  $v(C \equiv C)$  resulting from one-electron



Complex	$A_{iso}(^{183}W)/G$	$a_{iso}(^{31}P)/G$	$a_{iso}(^{1}\mathrm{H})/\mathrm{G}$	$g_{ m iso}$
[1]+	61	26	Ь	1.952
<b>[6]</b> +	50	24	4.3	1.978
[ <b>7</b> ]⁺	50	24	4.2	1.977

<sup>a</sup> X-band solution spectra in CH<sub>2</sub>Cl<sub>2</sub> at 273 K ([1]<sup>+</sup>) or 193 K ([6]<sup>+</sup>, [7]<sup>+</sup>); hyperfine couplings in Gauss. <sup>b</sup> hyperfine coupling to <sup>1</sup>H not resolved.

 $(590 \text{ nm}); M = W, 18000 \text{ cm}^{-1} (555 \text{ nm})]$  consistent with the higher lying 5d orbitals of the tungsten centre; the change in position of this absorption may also account for the marked contrast in the colours of the 17-electron radicals  $[M(C \equiv CPh)(dppe)(\eta - C_7H_7)]^+$ (M = Mo, deep blue; M = W, deep red). Consistent with the description of oxidation of these W-alkynyl complexes in terms of metal-centred redox processes, weak W d-d bands were observed near 12,000 cm<sup>-1</sup> (Fig. 4).

X-band EPR spectra of the radicals [1]<sup>+</sup>, [6]<sup>+</sup> and [7]<sup>+</sup> were recorded on CH<sub>2</sub>Cl<sub>2</sub> solutions of the complexes generated in situ at 193 K by addition of  $[FeCp_2][PF_6]$  to the 18-electron precursors; Fig. 5 illustrates a representative spectrum obtained for  $[6]^+$  and details of the EPR parameters extracted from the spectra are presented in Table 5. The spectra of the tungsten complexes are slightly less well resolved than for their Mo analogues<sup>10,15,39</sup> but hyperfine couplings to <sup>183</sup>W and <sup>31</sup>P were determined in all cases and for the alkynyl derivatives it was possible to estimate the hyperfine to the hydrogens of the  $C_7H_7$  ring. By comparison with Mo analogues,  $a_{iso}({}^{31}P)$  is slightly larger for the W complexes; values for  $A_{iso}(^{183}W)$  are similar to those determined previously for metal centred cation radical complexes.<sup>40</sup> The shift in  $g_{iso}$ , typically from 1.996 for the Mo alkynyl complexes to 1.978 for the W series, is consistent with the larger spin orbit coupling constant for the 5d metal.



Fig. 5 X-band solution spectrum of  $[W(C \equiv CPh)(dppe)(\eta - C_7H_7)]^+$ , [6]<sup>+</sup>, recorded as a first derivative spectrum in CH2Cl2 at 193 K.

#### Electronic structure calculations

Density functional calculations were performed on the vinylidene complex  $[W(C=CH_2)(dppe)(\eta-C_7H_7)]^+$ , denoted 3-H to distinguish experimental and calculated parameters, the C=CH<sub>2</sub> rotational transition state of 3-H, (3-H<sup>\*</sup>), and the alkynyl complexes [W(C=CPh)(dppe)( $\eta$ -C<sub>7</sub>H<sub>7</sub>)]<sup>n+</sup>, 6-H and [6-H]<sup>+</sup>, using the Gaussian03 suite of programs.41 All calculations employed the



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oxidation of directly analogous complexes [M(C=CR)(dppe)(n- $C_{7}H_{7}$ ] (M = Mo or W; R = Ph or  $C_{6}H_{4}$ -4-Me) suggests that the metal alkynyl interaction is almost independent of the 4d vs. 5d character of the metal centre; this result is in marked contrast to the vinylidenes  $[M(C=CH_2)(dppe)(\eta-C_2H_2)]^+$  (M = Mo or W) where the barrier to rotation about  $M = C_{\alpha}$  is significantly increased for the 5d metal.

To probe further, the effects of substitution of Mo by W in these systems, comparisons between  $6/[6]^+$ ,  $7/[7]^+$  and their Mo analogues were extended to UV-visible and EPR studies. The UVvisible electronic absorption spectra were recorded by spectroelectrochemical methods in CH<sub>2</sub>Cl<sub>2</sub> under identical conditions to those previously reported for the Mo analogues;<sup>10</sup> experimental spectra for  $6/[6]^+$  are shown in Fig. 4. The principal result features the position of the band at the red end of the visible region in the radical cations, which for the Mo analogues has been assigned to a LMCT (alkynyl to metal) transition on the basis of a TD-DFT treatment.<sup>10</sup> In the tungsten complexes this band is of reduced intensity and shifted to higher energy by ca.  $1000 \text{ cm}^{-1} [cf. [M(C = CPh)(dppe)(\eta - C_7H_7)]^+, M = Mo, 16900 \text{ cm}^{-1}$ 



Fig. 4 Spectroelectrochemical UV-visible spectra for 6 (dotted line)/[6]+(solid line) recorded in 0.1 M NBu<sub>4</sub>PF<sub>6</sub>/CH<sub>2</sub>Cl<sub>2</sub>.

**Table 6** Important bond lengths (Å) and angles (°) for complex **3-H** and the rotational transition state **3-H**<sup>\*</sup> from structures optimized using the BP86 and B3LYP functionals and the Def2-SVP basis. For atom numbering, see Fig. 2

	3-Н		3-H <sup>≠</sup>		
Bond lengths	BP86	B3LYP	BP86	B3LYP	
W(1)-P(1)	2.553	2.582	2.507	2.534	
W(1) - P(2)	2.572	2.601	2.511	2.539	
W(1) - C(8)	1.942	1.944	1.982	1.985	
C(8) - C(9)	1.332	1.321	1.329	1.318	
W(1) - C(1)	2.326	2.325	2.340	2.345	
W(1) - C(2)	2.357	2.354	2.381	2.386	
W(1) - C(3)	2.346	2.345	2.337	2.339	
W(1) - C(4)	2.353	2.352	2.383	2.387	
W(1) - C(5)	2.319	2.320	2.337	2.340	
W(1) - C(6)	2.401	2.401	2.448	2.458	
W(1)-C(7)	2.430	2.429	2.450	2.460	
Angles					
P(1)-W(1)-P(2)	80.99	80.53	79.99	79.92	
P(1)-W(1)-C(8)	80.87	81.33	82.81	83.64	
P(2)-W(1)-C(8)	83.35	83.99	85.53	86.31	
W(1)-C(8)-C(9)	178.83	178.90	178.36	178.02	
Ct-W(1)-C(8)	135.52	135.07	129.65	128.71	
W(1)–C(8)–C(9)–H(9)	3.49	1.51	98.72	101.44	
$Ct = centroid of C_7 H_7 rin_2$	g.				

Def2-SVP basis set of Ahlrichs *et al.*<sup>42,43</sup> For W, this basis constitutes a relativistic effective potential with 60 electrons treated in the core.<sup>44</sup> All structures were fully optimized using both the BP86<sup>45</sup> and B3LYP<sup>46</sup> functionals for purposes of comparison, starting from crystal geometries where X-ray data were available. All structures were confirmed as minima or transition states through vibrational analysis.

Optimisation of the geometry of **3-H** showed that the minimum energy structure has the plane of the C=CH<sub>2</sub> moiety aligned perpendicular to the plane of the C<sub>7</sub>H<sub>7</sub> ring, in accord with the observed structure of **4** shown in Fig. 2. The transition state for rotation of the vinylidene ligand around the W-C<sub> $\alpha$ </sub>-C<sub> $\beta$ </sub> axis (**3-H**<sup>\*</sup>) has the C=CH<sub>2</sub> plane aligned 'horizontal', essentially parallel to the C<sub>7</sub>H<sub>7</sub> plane. Some key geometric parameters for these structures are given in Table 6 and may be compared directly with those of **4** shown in Table 3. It can be seen that the main differences in the geometries of **3-H** and **3-H**<sup>\*</sup>, apart from the rotation of the C=CH<sub>2</sub> group, are the reduction by some 6° of the Ct-W(1)-C(8) angle and the general lengthening of the W-C distances of the C<sub>7</sub>H<sub>7</sub> ring (except for W-C(3) which eclipses the C=C bond and is shortened slightly in the transition state).

The rotational barrier for the **3-H**  $\rightarrow$  **3-H**<sup>\*</sup> conversion is calculated to be 70.7 (BP86)/67.2 (B3LYP) kJ mol<sup>-1</sup>. The inclusion of zero-point energies reduces these to 67.8 (BP86)/64.0 (B3LYP) kJ mol<sup>-1</sup> in good agreement with the experimentally determined value of 62.5 ± 2 kJ mol<sup>-1</sup>. In our previous work<sup>9</sup> we calculated the rotational barrier for the Mo-analogue of **3** to be about 45 kJ mol<sup>-1</sup>, which compares with the experimental value of around 52 kJ mol<sup>-1</sup> observed in dynamic NMR experiments. The current calculations concur with the experimental findings that the W systems have larger rotational barriers than the Mo analogues. To investigate the origin of this difference we

Table 7B3LYP/Def2-SVP orbital components (%) of HOMO-1 of $[M(C=CH_2)(dppe)(\eta-C_7H_7)]^+$  (M = Mo or W) (sum of orbital populationson non-hydrogen atoms only)

М	Metal	$C = C(H_2)$	C <sub>7</sub> (H <sub>7</sub> )	$P_2$
Мо	56	8	27	2
W ( <b>3-H</b> )	53	12	18	2

carried out a population analysis on **3-H** and its Mo analogue at the B3LYP/Def2-SVP level (for the Mo-analogue we used the structure obtained previously in reference 9). There is remarkable qualitative and quantitative similarity between the frontier orbital energies and compositions of the W and Mo systems but a key difference is between the HOMO-1 of **3-H** and its Mo-analogue. This orbital consists of  $\pi$ -type bonding interactions between  $C_{\alpha}$  and the metal centre in the  $[M(dppe)(\eta-C_7H_7)]^+$  (M = W, Mo) fragment (we have previously established the importance of this interaction in dictating the orientational preference of these systems<sup>9</sup>). On rotation of the C=CH<sub>2</sub> unit, this  $\pi$ -bonding interaction is removed and so it must be significant in determining the rotational energy barrier. The HOMO-1 orbital is shown in Fig. 6 and its composition in Table 7.



**Fig. 6** HOMO-1 orbital of **3-H** at the B3LYP/Def2-SVP level. For clarity only the hydrogens of the C=CH<sub>2</sub> group are shown and the dppe unit is shown in wireframe. Isosurface value is 0.04 au.

Inspection of Table 7 reveals that the bonding HOMO-1 orbital of **3-H** contains slightly more C==CH<sub>2</sub> character and less metal character than in the Mo-analogue. Moreover, the contribution of the C<sub>7</sub>H<sub>7</sub> ring is substantially less in **3-H** than in the Mo analogue, indicating a change in the balance of the bonding between the metal and the C<sub>7</sub>H<sub>7</sub> ring or the C==CH<sub>2</sub> ligand. The M==C==CH<sub>2</sub> m-interaction is therefore more efficient in the tungsten derivative **3-H** and consequently this complex features a larger rotational barrier, as observed experimentally in the dynamic NMR studies described above.

For the alkynyl complex **6-H**, we wished to establish the nature of the HOMO orbital and compare it with the analogous Mo system. For reasons that we have described elsewhere<sup>10</sup> the HOMO of  $[Mo(C=CPh)(dppe)(\eta-C_7H_7)]$  is dominated by the  $d_{z^2}$  orbital

	Energy/eV	Orbital composition (%)					
Orbital		metal	C <sub>7</sub> (H <sub>7</sub> )	C≡C	C <sub>6</sub> (H <sub>5</sub> )	<b>P</b> <sub>2</sub>	
LUMO	-1.10	7 (14)	17 (34)	1 (2)	0(2)	12 (12)	
HOMO	-3.94	61 (62)	4 (4)	16 (16)	9 (9)	4 (3)	
HOMO-1	-4.82	23 (24)	40 (37)	23 (25)	6 (6)	4 (4)	
HOMO-2	-5.08	44 (47)	39 (37)	6 (6)	2 (2)	3 (3)	

**Table 8** B3LYP/Def2-SVP orbital energies and compositions of  $[W(C \equiv CPh)(dppe)(\eta - C_7H_7)]$ , 6-H (values in parentheses for Mo analogue)



Fig. 7 HOMO orbital of 6-H at B3LYP/Def2-SVP level. For clarity hydrogens are omitted and the dppe unit is shown in wireframe. Isosurface value is 0.04 au.

of the metal. Fig. 7 shows the HOMO of **6-H** and it can be seen that it has the same character as the analogous Mo system.

# Table 8 presents a population analysis of the frontier molecular orbitals of **6-H** alongside equivalent data for the Mo analogue<sup>10</sup> (shown in parentheses). The degree of similarity is striking and MO plots for the HOMO-1 and HOMO-2 of **6-H** (see ESI<sup>†</sup>) confirm strong $\delta$ interactions between the C<sub>7</sub>H<sub>7</sub> ring and the tungsten d<sub>xy</sub> and d<sub>x<sup>2</sup>-y<sup>2</sup></sub> orbitals, identical to the Mo analogue and key to the establishment of a HOMO with substantial metal d<sub>z<sup>2</sup></sub> character.<sup>10</sup>

For the 17-electron radical cation [6-H]<sup>+</sup>, spin density distribution is again dominated by the metal  $d_{z^2}$  orbital with B3LYP/Def2-SVP computed Mulliken spin densities revealing significant localisation of spin density at the W centre (W: 0.980,  $C_{\alpha}$ : -0.123,  $C_{\beta}$ : 0.234, see ESI<sup>†</sup>). Finally the shift in the alkynyl  $\nu$ (C=C) stretching frequency resulting from one-electron oxidation of **6-H** to [6-H]<sup>+</sup> was examined. We find  $v(C \equiv C) = 2039 \text{ cm}^{-1}$  $(BP86)/2126 \text{ cm}^{-1}$  (B3LYP) in 6-H and  $v(C \equiv C) = 2000 \text{ cm}^{-1}$  $(BP86)/2091 \text{ cm}^{-1}$  (B3LYP) in [6-H]<sup>+</sup>, giving a shift,  $\Delta v(C = C) =$  $-39 \text{ cm}^{-1}$  (BP86)/ $-35 \text{ cm}^{-1}$  (B3LYP). Both levels of calculation slightly exaggerate the shift but obtain the correct trend. The BP86 functional gives better agreement with experiment for the position of the stretching wavenumber but the B3LYP functional is slightly better at predicting the magnitude of the shift. The small experimental shift in  $v(C \equiv C)$  resulting from one-electron oxidation of 6 to  $[6]^+$  is therefore consistent with the highly metalbased frontier orbital character found in the calculated electronic structures of these systems.

#### Conclusions

A simple, one-pot synthesis of  $[WBr(dppe)(\eta-C_7H_7)]$  from  $[WBr(CO)_2(\eta-C_7H_7)]$  has opened up investigations into the chemistry of the electron-rich, d<sup>6</sup>, cycloheptatrienyl tungsten auxiliary W(dppe)( $\eta$ -C<sub>7</sub>H<sub>7</sub>). The reactions of [WBr(dppe)( $\eta$ -C<sub>7</sub>H<sub>7</sub>)] with terminal alkynes in refluxing methanol proceed with alkyne to vinylidene isomerisation to afford oxacyclocarbene and vinylidene complexes of general formulation  $[W{(C)_n = CR_2}(dppe)(\eta (C_7H_7)$ ]<sup>+</sup> (n = 0 or 1). An X-ray structural study on the phenylvinylidene complex  $[W(C=CHPh)(dppe)(\eta-C_7H_7)][PF_6],$ reveals that, in common with the Mo analogue, the vinylidene ligand adopts a vertical orientation consistent with a strong interaction between a filled metal  $d_{z^2}$  orbital and the vacant p orbital on  $C_{\alpha}$  of the vinylidene ligand. Variable temperature <sup>1</sup>H NMR investigations on  $[W(C=CH_2)(dppe)(\eta-C_7H_7)][PF_6]$ demonstrate that the energy barrier to rotation about the W= $C_{\alpha}$ bond is approximately 10 kJ mol-1 larger than for the analogous molybdenum complex. Deprotonation of the vinylidenes  $[W(C=CHR)(dppe)(\eta-C_7H_7)][PF_6]$  yields the alkynyl complexes  $[W(C \equiv CR)(dppe)(\eta - C_7H_7)]$  which can be reversibly oxidised to the 17-electron radicals  $[W(C = CR)(dppe)(\eta - C_7H_7)]^+$ . Substitution of Mo by its 5d counterpart W in the alkynyl complexes  $[M(C = CR)(dppe)(\eta - C_7H_7)]^{n+}$  has a relatively small effect on the electronic properties of the system with the key parameter  $\Delta v(C = C)$  (the shift in the alkynyl stretching frequency resulting from one-electron oxidation) essentially identical for Mo and W analogues. Electronic structure calculations confirm the  $d_{z^2}$ 

character of the HOMO in the W(dppe)( $\eta$ -C<sub>7</sub>H<sub>7</sub>) fragment and successfully model the increase in activation energy to metal- $C_{\alpha}$  bond rotation in [W(C=CH\_2)(dppe)(\eta-C\_7H\_7)]^+, which can be attributed to the stronger M= $C \pi$ -bonding interactions in the [HOMO-1]. The alkynyl complexes  $[W(C \equiv CR)(dppe)(\eta - C_7H_7)]$ also feature a strongly metal-based  $d_{r^2}$  HOMO, in common with their Mo counterparts and this can account for the very similar spectroscopic properties of the two series of complexes. Fundamentally, the exchange of W in place of Mo in the vinylidene complexes  $[M(C=CHR)(dppe)(\eta-C_7H_7)]^+$  and alkynyl complexes  $[M(C \equiv CR)(dppe)(\eta - C_7H_7)]^{n+}$  results in limited effects only. The dominant feature which controls the electronic structure and chemical properties of these systems is the strong  $\delta$  bonding between the metal and the  $e_2$  level of the  $C_7H_7$  ring leading to substantial metal  $d_{r^2}$  character in frontier orbitals and this overrides the more subtle effects resulting from replacement of the 4d orbital set of Mo with the 5d set of W.

#### Experimental

#### General procedures

The preparation, purification and reactions of the complexes described were carried out under dry nitrogen. All solvents were dried by standard methods, distilled and deoxygenated before use. The complex  $[W(CO)_3(\eta-C_7H_7)][PF_6]$  was prepared by a published procedure.20 NMR spectra were recorded on a Varian Inova 400  $(400 \text{ MHz}^{1}\text{H}, 100 \text{ MHz}^{13}\text{C}{^{1}\text{H}}, 162 \text{ MHz}^{31}\text{P}{^{1}\text{H}})$  spectrometer. Infrared spectra were obtained on a Perkin Elmer FT RX1 spectrometer and MALDI mass spectra were recorded using a Micromass/Waters TOF Spec 2E instrument. Microanalyses were conducted by the staff of the Microanalytical Service of the School of Chemistry, University of Manchester. Cyclic voltammograms were recorded ( $v = 100 \text{ mV s}^{-1}$ ) from 0.2 M [NBu<sub>4</sub>][PF<sub>6</sub>], CH<sub>2</sub>Cl<sub>2</sub> solutions ca.  $1 \times 10^{-4}$  M in analyte using a three-electrode cell equipped with a glassy carbon working electrode, Pt wire counter electrode and Ag/AgCl reference electrode. All redox potentials are reported with reference to an internal standard of the ferrocene/ferrocenium couple (FeCp<sub>2</sub> + = 0.00 V). UVvisible and IR spectroelectrochemical experiments were performed at room temperature with an air-tight OTTLE cell equipped with Pt minigrid working and counter electrodes, a Ag wire reference electrode and CaF2 windows47 using either a Nicolet Avatar spectrometer or a Perkin Elmer Lambda 900 spectrophotometer. EPR experiments were conducted on a Bruker BioSPin EMX microspectrometer at X-band (9 GHz); spectra are the average of 16 scans. Spectral analysis and simulation was carried out using Bruker WinEPR software (Bruker Biospin Ltd.).

#### Preparation of [WBr(CO)<sub>2</sub>(η-C<sub>7</sub>H<sub>7</sub>)]

A solution of  $[W(CO)_3(\eta-C_7H_7)][PF_6]$  (4.76 g, 9.44 mmol) in AR acetone (70 cm<sup>3</sup>) was treated with NaBr (1.41 g, 13.69 mmol) and the reaction mixture stirred for 1 h to give a green solution before the solvent was removed *in vacuo* over a period of 30 min. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 cm<sup>3</sup>) and the resulting solution filtered, treated with hexane and the volume reduced to yield [WBr(CO)<sub>2</sub>( $\eta$ -C<sub>7</sub>H<sub>7</sub>)] as a dark green solid; yield 3.17 g (82%).

#### Preparation of [WBr(dppe)(η-C<sub>7</sub>H<sub>7</sub>)], 1

A mixture of xylene (50 cm<sup>3</sup>) and toluene (50 cm<sup>3</sup>) was heated to reflux point then dppe (1.21 g, 3.04 mmol) and [WBr(CO)<sub>2</sub>(η- $(C_{7}H_{7})$ ] (2.50 g, 6.08 mmol) were added to the solution as a mixture of solids. After 1 h the reaction mixture was treated with additional dppe (1.21 g, 3.04 mmol) and reflux continued for 3 h. The resulting solution was filtered hot to remove  $[W(CO)(dppe)(\eta-C_7H_7)]Br$ , then evaporated to dryness. The green-brown residue, dissolved in CH<sub>2</sub>Cl<sub>2</sub> was transferred to an alumina/n-hexane chromatography column. A yellow band, [W(CO)4(dppe)], was eluted first using n-hexane-CH<sub>2</sub>Cl<sub>2</sub> (1:1) followed by a red band. The required product eluted as a green band using n-hexane-CH<sub>2</sub>Cl<sub>2</sub>/acetone (2:2:1) solvent mixture as eluant. The green band was collected, solvent removed, and the residue recrystallised from CH<sub>2</sub>Cl<sub>2</sub>-nhexane to give [WBr(dppe)( $\eta$ -C<sub>7</sub>H<sub>7</sub>)] as a green solid, yield 0.97 g (21%). Cyclic voltammetry:  $E_{\perp} = -0.77$  V vs. FeCp<sub>2</sub>/FeCp<sub>2</sub><sup>+</sup>. Anal. Calcd. (%) for C<sub>33</sub>H<sub>31</sub>WP<sub>2</sub>Br: C, 52.6; H, 4.1. Found: C, 52.3; H, 4.0. Mass (MALDI): m/z 753 (M<sup>+</sup>), 673 (M<sup>+</sup> - Br).

#### Preparation of [W(CCH2CH2CH2C)(dppe)(η-C7H7)][PF6], 2

A mixture of [WBr(dppe)( $\eta$ -C<sub>7</sub>H<sub>7</sub>)] (0.40 g, 0.53 mmol), 3-butyn-1-ol (0.19 g, 2.71 mmol) and K[PF<sub>6</sub>] (0.20 g, 1.09 mmol) in AR methanol (40 cm<sup>3</sup>) was heated at reflux for 3 h and the resulting deep orange solution was evaporated to dryness. The residue was recrystallised from CH<sub>2</sub>Cl<sub>2</sub>-diethyl ether and the resulting orange solid washed with toluene. A further recrystallisation from acetone–diethyl ether gave **2** as an orange solid; yield 0.07 g (15%). Anal. Calcd. (%) for C<sub>37</sub>H<sub>37</sub>WOP<sub>3</sub>F<sub>6</sub>: C, 50.0; H, 4.2. Found: C, 49.6; H, 3.8. Mass (MALDI): m/z 744 (M<sup>+</sup> + H), 673 (M<sup>+</sup> -CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O).

#### Preparation of [W(C=CH<sub>2</sub>)(dppe)(η-C<sub>7</sub>H<sub>7</sub>)][PF<sub>6</sub>], 3

A mixture of  $[WBr(dppe)(\eta-C_7H_7)]$  (0.49 g, 0.65 mmol), HC=CSiMe<sub>3</sub> (0.21 g, 2.14 mmol) and K[PF<sub>6</sub>] (0.24 g, 1.30 mmol) in AR methanol (40 cm<sup>3</sup>) was heated at reflux for 2 h and the resulting orange solution was evaporated to dryness. The orange residue, dissolved in CH<sub>2</sub>Cl<sub>2</sub> was transferred to a Celite/n-hexane chromatography column, and the product eluted as an orange band using n-hexane–CH<sub>2</sub>Cl<sub>2</sub> (1:1) solvent mixture as eluant. The orange band was collected, solvent removed, the residue was recrystallised from CH<sub>2</sub>Cl<sub>2</sub>-diethyl ether and the resulting solid washed with toluene. A further recrystallisation from acetone– diethyl ether gave **3** as a yellow solid; yield 0.33 g (60%). Mass (MALDI): m/z 699 (M<sup>+</sup>). HR ES+-MS (m/z): 699.1588 (WC<sub>35</sub>H<sub>33</sub>P<sub>2</sub> requires 699.1561).

#### Preparation of [W(C=CHPh)(dppe)(η-C<sub>7</sub>H<sub>7</sub>)][PF<sub>6</sub>], 4

A mixture of [WBr(dppe)( $\eta$ -C<sub>7</sub>H<sub>7</sub>)] (0.55 g, 0.73 mmol), HC=CPh (0.42 g, 4.12 mmol) and K[PF<sub>6</sub>] (0.28 g, 1.52 mmol) in AR methanol (40 cm<sup>3</sup>) was heated at reflux for 2 h and the resulting deep orange solution was evaporated to dryness. The residue was recrystallised from CH<sub>2</sub>Cl–diethyl ether and the resulting orange solid washed with toluene. A further recrystallisation from acetone–diethyl ether gave **4** as an orange solid; yield 0.54 g (80%). Anal. Calcd. (%) for C<sub>41</sub>H<sub>37</sub>WP<sub>3</sub>F<sub>6</sub>: C, 53.5; H, 4.0. Found: C, 53.5; H, 3.7. Mass (MALDI): m/z 775 (M<sup>+</sup>), 673 (M<sup>+</sup> – C=CHPh).

#### Preparation of [W(C=CHC<sub>6</sub>H<sub>4</sub>-4-Me)(dppe)(η-C<sub>7</sub>H<sub>7</sub>)][PF<sub>6</sub>], 5

A mixture of [WBr(dppe)( $\eta$ -C<sub>7</sub>H<sub>7</sub>)] (0.81 g, 1.08 mmol), HC=CC<sub>6</sub>H<sub>4</sub>-4-Me (0.62 g, 5.35 mmol) and K[PF<sub>6</sub>] (0.39 g, 2.12 mmol) in AR methanol (80 cm<sup>3</sup>) was heated at reflux for 2 h and the resulting orange solution was evaporated to dryness. The orange residue, dissolved in CH<sub>2</sub>Cl<sub>2</sub> was transferred to a Celite/n-hexane chromatography column, and the product eluted as an orange band using n-hexane–CH<sub>2</sub>Cl<sub>2</sub> (1:1) solvent mixture as eluant. The orange band was collected, solvent removed, the residue was recrystallised from CH<sub>2</sub>Cl<sub>2</sub>-diethyl ether and the resulting solid washed with toluene. A further recrystallisation from acetone–diethyl ether gave **5** as an orange solid; yield 0.82 g (82%). Anal. Calcd. (%) for C<sub>42</sub>H<sub>39</sub>WP<sub>3</sub>F<sub>6</sub>: C, 54.0; H, 4.2. Found: C, 53.5; H, 4.0. Mass (MALDI): m/z 789 (M<sup>+</sup>), 673 (M<sup>+</sup> – C==C(H)C<sub>6</sub>H<sub>4</sub>-4-Me).

#### Preparation of [W(C=CPh)(dppe)(η-C<sub>7</sub>H<sub>7</sub>)], 6

A mixture of  $[W(C=CHPh)(dppe)(\eta-C_7H_7)][PF_6]$  (0.27 g, 0.29 mmol) and KOBu<sup>1</sup> (0.33 g, 2.95 mmol) in thf (50 cm<sup>3</sup>) was stirred at room temperature for 40 min then the resulting redbrown solution was evaporated to dryness. The residue, dissolved in CH<sub>2</sub>Cl<sub>2</sub> was transferred to a Celite/n-hexane chromatography column, and the product eluted as a red band using n-hexane-CH<sub>2</sub>Cl<sub>2</sub> (1:1) as eluant. The red band was collected, solvent removed, and the residue, dissolved in diethyl ether, was filtered through a Celite covered sinter. The volume of solvent was reduced and the solution left in the freezer overnight at -20 °C leading to precipitation of the product. The mother liquors were removed by syringe and the remaining solid dried *in vacuo* to give **6** as a red–brown solid; yield 0.13 g, (58%). Mass (MALDI): m/z 774 (M<sup>+</sup>), 673 (M<sup>+</sup> – C<sub>2</sub>Ph). HR ES+-MS (m/z): 774.1801 (C<sub>41</sub>H<sub>36</sub>P<sub>2</sub>W requires 774.1796).

#### Preparation of [W(C=CC<sub>6</sub>H<sub>4</sub>-4-Me)(dppe)(η-C<sub>7</sub>H<sub>7</sub>)], 7

Complex 7 was prepared as a red-brown solid by an identical procedure to that described for **6** starting from [W(C=CHC<sub>6</sub>H<sub>4</sub>-4-Me)(dppe)( $\eta$ -C<sub>7</sub>H<sub>7</sub>)][PF<sub>6</sub>] (0.40 g, 0.43 mmol) and KOBu<sup>t</sup> (0.48 g, 4.29 mmol); yield 0.24 g, (71%). HR ES+-MS (*m/z*): 788.1962 (C<sub>42</sub>H<sub>39</sub>P<sub>2</sub>W requires 788.1953).

#### X-Ray crystal structures of $[WBr(dppe)(\eta-C_7H_7)]\cdot CH_2Cl_2$ , 1.CH<sub>2</sub>Cl<sub>2</sub> and $[W(C=CHPh)(dppe)(\eta-C_7H_7)][PF_6]$ , 4[PF\_6].

The majority of details of the structure analyses carried out on complexes  $1 \cdot CH_2Cl_2$  and  $4[PF_6]$  are given in Table 9. Single crystals of  $1 \cdot CH_2Cl_2$  were obtained by vapour diffusion of diethyl ether into a  $CH_2Cl_2$  solution of the complex to give green needles; single crystals of  $4[PF_6]$  were obtained by vapour diffusion of diethyl ether into a  $CH_2Cl_2$  solution of the complex to give orange plates. X-ray data for  $1 \cdot CH_2Cl_2$  were collected with an Oxford Diffraction X-Calibur 2 Diffractometer equipped with an Oxford-Cryosystems low-temperature device, by means of Mo-K $\alpha$  ( $\lambda = 0.7103$  Å) radiation and  $\omega$  scans. Data were corrected for Lorentz, polarisation and absorption factors. Data collection, cell refinement and data reduction were carried out with Oxford Diffraction Ltd., CrysAlis CCD and CrysAlis RED software. X-Ray data for  $4[PF_6]$  was collected with a Bruker AXS

Table 9 Crystal data and refinement parameters

$C_{34}H_{33}P_2BrCl_2W_1$	$C_{41}H_{37}P_3F_6W, 4[PF_6]$
1.CH <sub>2</sub> Cl <sub>2</sub>	
838.20	920.47
100(2)	100(2)
Orthorhombic	Monoclinic
Pcab	$P2_1/c$
23.3121(10)	33.250(5)
9.3925(4)	12.061(5)
27.8933(15)	18.645(5)
90.00	104.641(5)
6107.5(5); 8	7234(4); 8
5.395	3.388
3.15-28.54	1.27-26.42
-30/30,	-38/41; -15/8;
-12/12,-35/36	-22/23
7189	40504
4653	14741
0.0731	0.0512
0.2155	0.0954
99.3	99.3
	$\begin{array}{c} C_{34}H_{33}P_2BrCl_2W,\\ 1\cdot CH_2Cl_2\\ 838.20\\ 100(2)\\ Orthorhombic\\ Pcab\\ 23.3121(10)\\ 9.3925(4)\\ 27.8933(15)\\ 90.00\\ 6107.5(5); 8\\ 5.395\\ 3.15-28.54\\ -30/30,\\ -12/12,-35/36\\ 7189\\ 4653\\ 0.0731\\ 0.2155\\ 99.3 \end{array}$

Diffractometer using monochromated Mo-K $\alpha$  ( $\lambda = 0.7103$  Å) radiation and  $\omega$  scans; an absorption correction was applied with the aid of the SADABS program.48 Both structures were solved by direct methods with refinement by full-matrix least squares based on F<sup>2</sup> against all reflections; SHELXS-97,49 was employed for the computing structure solutions and SHELXL-97,50 for the computing structure refinements. In the structure of  $1 \cdot CH_2 Cl_2$ , the anisotropic displacement parameters of the atoms C(1)-C(7) of the cycloheptatrienyl ring, C(29)-C(34) of the dppe ligand, and Br(1) were disordered and restrained since they tended to become unrealistic (NPD). Constraints were applied to the cycloheptatrienyl ring, Br(1) and C(29)-C(34), all non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions. The asymmetric unit of  $4[PF_6]$ contains two molecules; in one of the cations the cycloheptatrienyl ring is disordered over two sites, the occupancy of which was constrained to sum to unity with restraints applied to the geometry of the two disordered components. All non-hydrogen atoms were refined anisotropically with constraints applied to the disordered cycloheptatrienyl ring described above; hydrogen atoms were included in calculated positions.

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