

Synthesis and structure of a series of tungsten(II) and tungsten(VI) diyanyl and diyndiyl complexes

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Oxidation of the diyanyl and diyndiyl complexes $[\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3\text{Cp}^*]$ (**1**) and $[\{\text{W}(\text{CO})_3\text{Cp}^*\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})]$ (**2**) affords the corresponding dioxo compounds $[\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{O})_2\text{Cp}^*]$ (**4**) and $[\{\text{W}(\text{O})_2\text{Cp}^*\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})]$ (**6**) via oxo–peroxo intermediates. The molecular structures are consistent with a degree of mixing between the carbon orbitals of the $\text{C}_4(\text{H})$ fragment and the d^4 , but not the d^0 , metal centres. A simple synthesis of the useful reagent $\text{WCl}(\text{CO})_3\text{Cp}^*$ is also described.

Introduction

Diyanyl and diyndiyl complexes are of interest as they represent not only extended analogues of metal acetylide complexes, but also metal stabilised C_4 fragments which behave as novel carbon sources with unusual reactivity. Di- and poly-yndiyl complexes have also been suggested as candidates for use as molecular-scale wires in the emerging field of molecular circuitry.^{1,2} While initial studies were centred on polymeric materials,³ the majority of more recent reports concerned with this class of compound have described the synthesis, electrochemical properties, chemical reactivity and electronic structure of discrete molecular species.^{4–8} However, despite the interest in this class of compound, there are relatively few pairs of diyanyl and diyndiyl complexes featuring the same combination of metal and supporting ligands which have been structurally characterised (Table 1). Direct comparisons of the structural parameters

associated with these closely related carbon-rich ligands are therefore often unclear, and further hampered by the relatively low precision of many of the structures reported.

The ready preparation of $[\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3\text{Cp}]$ (**1-H**) from the CuI catalysed condensation of $[\text{WCl}(\text{CO})_3\text{Cp}]$ with $\text{HC}\equiv\text{CC}\equiv\text{CH}$ in amine solvents has permitted the diyanyl chemistry of the $\text{W}(\text{CO})_3\text{Cp}$ fragment to be explored in considerable detail.⁹ However, similar studies of the diyndiyl complex $[\{\text{W}(\text{CO})_3\text{Cp}\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})]$ (**2-H**) have been limited by the low solubility of this material in common solvents.¹⁰ In the case of $[\text{W}\{(\text{C}\equiv\text{C})_n\text{Ph}\}(\text{CO})_3\text{Cp}^*]$ ($n = 1, 2$) chemical oxidation ($\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$) affords the unusual oxo–peroxo species $[\text{W}\{(\text{C}\equiv\text{C})_n\text{Ph}\}(\text{O})_2(\text{O})\text{Cp}^*]$, and subsequent treatment with PPh_3 results in abstraction of an oxygen atom to give the dioxo species $[\text{W}\{(\text{C}\equiv\text{C})_n\text{Ph}\}(\text{O})_2\text{Cp}^*]$, with the molecular structures of the acetylide derivative having been described.^{11,12}

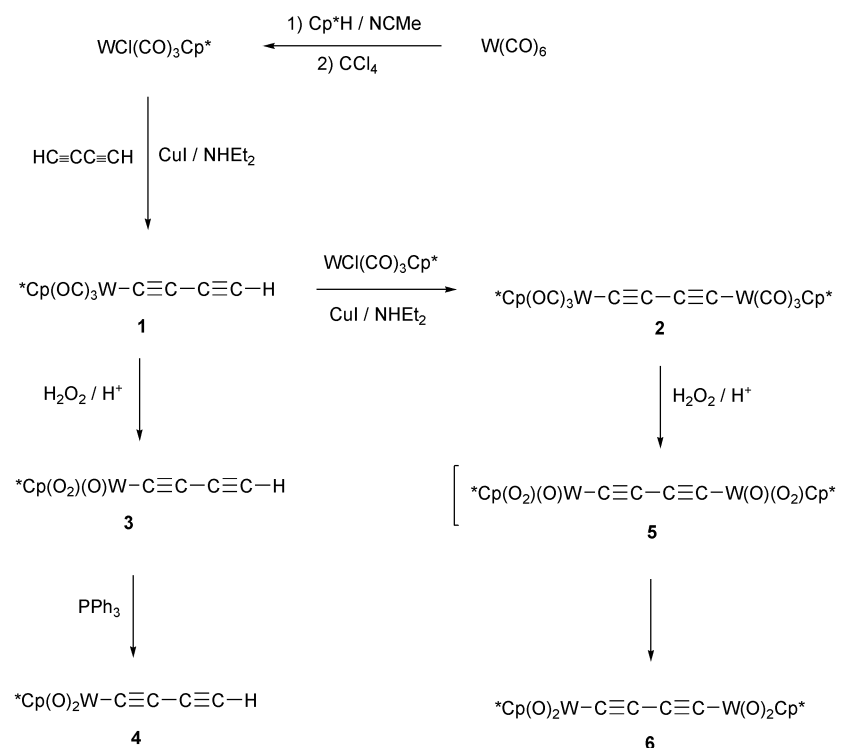
With the Cp^* group expected to improve the solubility of the diyndiyl complex and aid crystallisation, we considered that the $\text{W}(\text{L}_x)\text{Cp}^*$ fragment [$\text{L}_x = (\text{CO})_3, (\text{O})(\text{O})_2, (\text{O})_2$] could provide a suitable platform for extending the structural chemistry

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Table 1 Selected bond lengths (Å) and angles (°) associated with comparable pairs of diyanyl and diyndiyl complexes

	M–C _α	C _α ≡C _β	C _β –C _γ	C _γ ≡C _δ	Bond angles ^a	Ref.
$\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3\text{Cp}^*$	2.143(6)	1.169(8)	1.422(8)	1.212(8)	174.5(5), 175.9(6), 179.4(6)	This work
$\{\text{W}(\text{CO})_3\text{Cp}^*\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})$	2.127(7)	1.226(10)	1.376(14)	1.226(10)	178.9(8), 179.3(10), 179.3(10), 178.9(8)	This work
$\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{O})_2\text{Cp}^*$	2.082(4)	1.202(5)	1.379(5)	1.200(6)	175.4(3), 178.0(4), 176.8(4)	This work
$\{\text{W}(\text{O})_2\text{Cp}^*\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})$	2.072(4)	1.217(5)	1.375(7)	1.217(5)	177.6(3), 179.3(5), 179.3(5), 177.6(3)	This work
$\text{Re}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3(\text{tBu}_2\text{bpy})$	2.114(8)	1.199(10)	1.369	1.19(1)	175.2(6), 178.3(8), 179.8(10)	27
$\text{Re}(\text{C}\equiv\text{CC}\equiv\text{CPh})(\text{CO})_3(\text{tBu}_2\text{bpy})$	2.126(5)	1.198(7)	1.385	1.189(7)	175.7(5), 177.4(6), 178.6(6)	27
$\{\text{Re}(\text{CO})_3(\text{tBu}_2\text{bpy})\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})$	2.13(2)	1.19(2)	1.43(4)	1.19(2)	176(1), 178(2), 178(2), 176(1)	28
$\text{Fe}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_2\text{Cp}^*$	1.907(4)	1.207(5)	1.378(6)	1.153(6)	178.0(4), 179.0(5), 178.2(6), 175(3)	20
$\{\text{Fe}(\text{CO})_2\text{Cp}^*\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})$	1.933(4)	1.197(5)	1.398(7)	1.197(5)	178.0(4), 178.0(6), 178.0(6), 178.0(4)	20
$\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CPh})(\text{PPh}_3)_2\text{Cp}$	1.994(4)	1.206(5)	1.389(6)	1.200(6)	178.3(3), 169.5(4), 175.9(4), 176.9(4)	29
$\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})^b$	2.00(1)	1.20(2)	1.38(2)	1.25(2)	177(1), 178(2), 175(1), 170(1)	29
$\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})^c$	2.01(1)	1.22(1)	1.39(1)	1.22(1)	175(1), 177(1), 177(1), 175(1)	29
$\{\text{Ru}_2(\mu\text{-ap})_4\}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)$	2.075(9)	1.207(11)	1.406(11)	1.208(11)	179.5(8), 177.1(9), 178.4(11), 178.5(10)	21
$\{\text{Ru}_2(\mu\text{-ap})_4\}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)_2$	1.938(11)	1.216(13)	1.394(15)	1.208(14)	178.5(9), 177.7(11), 178.3(12), 170.3(11)	21
$\{\text{Ru}_2(\mu\text{-ap})_4\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})$	1.956(9)	1.228(13)	1.386(16)	1.227(15)	175.3(8), 172.2(11), 176.2(13), 174.7(13)	14
$\{\text{Ru}_2(\mu\text{-ap})_4\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})$	2.047(14)	1.258(16)	1.33(2)	1.258(16)	177.8(12), 176.1(19), 176.1(19), 177.8(12)	14
$\text{Pt}(\text{C}\equiv\text{CC}\equiv\text{CH})_2(\text{dppe})$	2.20(1)	1.17(2)	1.36(2)	1.16(2)	171.7(9), 176(1), 175(1)	2f
$\text{cyclo-}\{\text{Pt}(\text{C}\equiv\text{CC}\equiv\text{C})(\text{dppe})\}_4$	2.027(8)	1.17(1)	1.40(1)	1.22(1)	176(1), 179(1), 178(1), 177(1)	2f
	2.00(1)	1.24(2)	1.38(2)	1.21(2)	175.9(8), 177.5(9), 177(1), 177.3(8)	

^a Bond angles from metal centre M–C_α≡C_β, C_α≡C_β–C_γ, C_β–C_γ≡C_δ, C_γ≡C_δ–R. ^b thf Solvate. ^c Methanol solvate.



Scheme 1 Synthesis of tungsten diynyl and diydiyl complexes used in this work.

associated with diynyl and diydiyl complexes of tungsten, and permit a comparison of diynyl and diydiyl ligands in formally d^4 and d^0 metal complexes. We report here the synthesis, structures and electrochemical properties of the complexes $[\text{W}(\text{C}\equiv\text{CC}\equiv\text{CR})(\text{L}_x)\text{Cp}^*]$ [$\text{R} = \text{H}$, $\text{W}(\text{L}_x)\text{Cp}^*$].

Results and discussion

A modification of the procedure described previously for the preparation of $[\text{WCl}(\text{CO})_3\text{Cp}]$ was used in the preparation of the pentamethylcyclopentadienyl analogue $[\text{WCl}(\text{CO})_3\text{Cp}^*]$.¹³ An acetonitrile solution of $[\text{W}(\text{CO})_6]$ containing pentamethylcyclopentadiene was heated at reflux to give an orange-brown solution, presumed to contain the corresponding hydride $[\text{WH}(\text{CO})_3\text{Cp}^*]$, after 48 h. Treatment of the solution with CCl_4 gave the chloride $\text{WCl}(\text{CO})_3\text{Cp}^*$ in excellent yield (>90%) after chromatographic purification. This procedure has the distinct advantage of avoiding the time-consuming preparation of $[\text{W}(\text{NCMe})_3(\text{CO})_3]$.¹³

The reaction of $\text{WCl}(\text{CO})_3\text{Cp}^*$ with $\text{HC}\equiv\text{CC}\equiv\text{CH}$ in NHEt_2 catalysed by CuI proceeded rather more slowly than in the case of the Cp analogue (24 h, 0°C to ambient), and afforded yellow $[\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3\text{Cp}^*]$ (**1**) in 77 % yield. The diydiyl complex $[\{\text{W}(\text{CO})_3\text{Cp}^*\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})]$ (**2**) was obtained from the reaction of **1** with an equivalent of $\text{WCl}(\text{CO})_3\text{Cp}^*$ under CuI/NHEt_2 conditions in excellent yield (90%) as a bright yellow precipitate, which was isolated and crystallised from CH_2Cl_2 -hexane.

Oxidation of **1** ($\text{H}_2\text{O}_2/\text{H}^+$, benzene, 7 days) afforded a very pale yellow coloured solution from which $[\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{O})_2(\text{O})\text{Cp}^*]$ (**3**) was isolated as large block-shaped crystals after crystallisation from acetone. Treatment of **3** with PPh_3 afforded the dioxo diynyl complex $[\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{O})_2\text{Cp}^*]$ (**4**) in good yield after crystallisation from ethanol-hexane.

Chemical oxidation of **2** under the same $\text{H}_2\text{O}_2/\text{H}^+$ conditions resulted in rapid bleaching of the characteristic yellow colour of the carbonyl complex. After 12 h, ^1H NMR and ES-MS analysis of an extract indicated the complete consumption of the starting material ($\delta_{\text{Cp}^*} = 2.11$) and the presence of both $[\{\text{W}(\text{O})(\text{O}_2)\text{Cp}^*\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})]$ (**5**) ($\delta_{\text{Cp}^*} = 2.26$; ES-MS m/z 805 $[\text{M} + \text{Na}]^+$, 789 $[\text{M} + \text{Na} - \text{O}]^+$) and $[\{\text{W}(\text{O})_2\text{Cp}^*\}_2$ -

$(\mu\text{-C}\equiv\text{CC}\equiv\text{C})]$ (**6**) ($\delta_{\text{Cp}^*} = 2.27$, *vide infra*). After 4 days, spectroscopic analysis of the reaction mixture indicated the complete conversion of **2** to **6**, and the bis(dioxo) diydiyl complex **6** was isolated in moderate yield after workup and crystallisation. In contrast to the diynyl complexes, the intermediate oxo-peroxo diydiyl complex **5** is not stable with respect to **6**.

Each complex (Scheme 1) was characterised by the usual spectroscopic methods (as a mixture with **6** in the case of **5**) and single crystal X-ray diffraction for **1-4** and **6** (*vide infra*). Although the majority of terminal diynyl complexes reported to date give rise to a single $\nu(\text{C}\equiv\text{C})$ band,¹ the IR spectra of the diynyl complexes **1**, **3** and **4** each contained two $\nu(\text{C}\equiv\text{C})$ bands arising from the $\text{W}-\text{C}\equiv\text{C}$ and $\text{C}\equiv\text{CH}$ alkynyl moieties. While the carbonyl bands in the diydiyl complex **2** obscured the $\nu(\text{C}\equiv\text{C})$ band, the single $\nu(\text{C}\equiv\text{C})$ band was clearly observed for the dioxo diynyl **6**. In the case of the oxo-containing species, the IR spectra contained $\nu(\text{W}=\text{O})$ bands (942, **3**; 931, **4**; 937, **5**; 934, **6** cm^{-1}), as well as $\nu(\text{O}-\text{O})$ in the case of **3** (852 cm^{-1}) and **5** (856 cm^{-1}). The ^1H NMR chemical shift of the diynyl proton in **1** (δ 2.03), **3** (δ 2.50) and **4** (δ 2.51) reflects the nature of the metal fragment, indicating some degree of electronic information is propagated from the metal centre through the diynyl ligand.

The observation of $^1J_{\text{CW}}$ and $^2J_{\text{CW}}$ coupling constants assisted the assignment of C(1) and C(2) in the ^{13}C NMR spectra of **1** and **4**. While it is difficult to accurately assess the specific role of through-bond and through-space components to the magnitude of a coupling constant, the significantly larger $^1J_{\text{CW}}$ observed for C(1) in **4** is indicative of a stronger and shorter σ -bond between these nuclei. The C(3) and C(4) resonances did not exhibit coupling to the metal centre, and the more intense signal was tentatively assigned to C(4), being bound to the terminal proton. For complexes **2**, **3** and **6** coupling of the C_4 nuclei to ^{183}W could not be resolved and only tentative assignments are given.

The electron impact (EI) ionisation mass spectra of the various complexes were in agreement with the proposed structures. The electrospray (ES) mass spectrum of **2** shows $[\text{M} + \text{Na}]^+$ at m/z 877 together with the fragment ion at m/z 827 $[(\text{M} + \text{H} - \text{CO})^+]$ and a peak at m/z 1731 assigned to $[2\text{M} + \text{Na}]^+$. Similar aggregates with alkali metal ions have been observed in the ES-mass spectra of related complexes.^{2f}

Table 2 Crystallographic details for complexes **1–4** and **6**

	1	2	3	4	6
Formula	C ₁₇ H ₁₆ O ₃ W	C ₃₀ H ₃₀ O ₆ W ₂ ·2CH ₂ Cl ₂	C ₁₄ H ₁₆ O ₃ W	C ₁₄ H ₁₆ O ₂ W	C ₂₄ H ₃₀ O ₄ W ₂
<i>M_w</i> /g mol ⁻¹	452.15	1024.09	416.12	400.12	750.18
<i>T</i> /K	120(2)	120(2)	120(2)	120(0)	120(2)
<i>λ</i> /Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	<i>Pnma</i>	<i>P</i> $\bar{1}$	<i>P2₁/n</i>	<i>Pbca</i>	<i>Pbca</i>
<i>Z</i>	4	1	4	8	4
<i>a</i> /Å	19.110(1)	6.695(1)	7.779(1)	12.547(1)	12.609(1)
<i>b</i> /Å	10.804(1)	11.497(1)	13.840(1)	12.687(1)	12.104(1)
<i>c</i> /Å	7.429(1)	11.647(1)	12.730(1)	17.081(2)	15.469(1)
<i>α</i> /°	90	89.00(1)	90	90	90
<i>β</i> /°	90	84.61(1)	98.20(1)	90	90
<i>γ</i> /°	90	84.98(1)	90	90	90
<i>V</i> /Å ³	1533.90(7)	888.98(15)	1357.04(9)	2719.0(4)	2360.89(15)
<i>D_c</i> /g cm ⁻³	1.958	1.913	2.037	1.955	2.111
<i>μ</i> /mm ⁻¹	7.537	6.805	8.509	8.484	9.763
Reflections collected/unique	16022/1853	10090/4448	15600/3424	28375/2964	16192/3396
<i>R₁</i> / <i>wR₂</i> (all data)	0.0300, 0.0446	0.0398, 0.0943	0.0277, 0.0506	0.0273, 0.0650	0.0320, 0.0624

Table 3 Selected bond lengths (Å) and angles (°)

	1	2	3	4	6
W–C(1)	2.143(6)	2.127(7)	2.093(4)	2.082(4)	2.072(4)
C(1)–C(2)	1.169(8)	1.226(10)	1.215(5)	1.202(5)	1.217(5)
C(2)–C(3)	1.422(8)	1.376(14)	1.387(6)	1.379(5)	1.375(7)
C(3)–C(4)	1.212(8)		1.187(6)	1.200(6)	
W–Cp(0)	2.116	2.005	2.083	2.092	2.091
W–O(1)			1.724(3)	1.735(3)	1.733(3)
W–O(2)			1.929(3)	1.724(3)	1.723(3)
W–O(3)			1.929(3)		
O(2)–O(3)			1.465(5)		
W–C(21)	2.012(4)	1.995(8)			
W–C(22)	2.023(5)	2.005(8)			
W–C(23)	2.012(4) ^a	1.971(9)			
C(21)–O(21)	1.141(5)	1.154(11)			
C(22)–O(22)	1.140(6)	1.135(11)			
C(23)–O(23)	1.141(5) ^a	1.171(12)			
W–C(1)–C(2)	174.5(5)	178.9(8)	176.9(3)	175.4(3)	177.6(3)
C(1)–C(2)–C(3)	175.9(6)	179.3(10)	177.3(4)	178.0(4)	179.3(5)
C(2)–C(3)–C(4)	179.4(6)		178.9(5)	176.8(4)	

^a For C(23)/O(23) read C(21A)/O(21A).

The redox properties of **1–4** and **6** were investigated using cyclic and thin-layer voltammetry. However, these studies were hampered by the chemical and electrochemical irreversibility of the redox processes. The tricarbonyl diyndyl complex **1**, underwent a single irreversible oxidation, and while two oxidation waves could be observed in the CV of the diyndyl complex **2**, the chemically irreversible nature of the first process precludes any confident discussion of the transmission of electronic events on the basis of this data. Compound **4**, which features a metal centre in higher formal oxidation state, undergoes a single reduction in CH₂Cl₂ [*E*_{1/2}(**4**) = –1.38 V vs. Pt wire pseudo-reference, 0.1 M NBu₄BF₄, *E*_{1/2}(Fc/Fc⁺) = 0.46 V], which becomes more chemically reversible at sub-ambient temperatures, and which was shown by thin layer voltammetry using an equimolar internal ferrocene standard to be a one-electron process. The electrochemical response of the binuclear diyndyl complex [$\{W(O)_2Cp^*\}_2(\mu-C\equiv CC\equiv C)$] was measured in NCME, due to the limited solubility of the material in dichloromethane at low temperatures. The CV was characterised by a single irreversible reduction process, with a peak potential at –1.27 V relative to an internal ferrocene standard (*E*_{1/2} = 0.40 V). Thin-layer voltammetry indicated a series of ECE processes were involved in this reduction, and we were unable to quantify electronic interactions between the metal centres using these electrochemical methods.

Molecular structures

The structural parameters associated with numerous diyndyl and diyndyl complexes have been established through X-ray diffraction studies, although there are relatively few examples of families for which both diyndyl and diyndyl ligands have been crystallographically characterised for the same metal fragments (Table 1). In principle, comparisons between the diyndyl and diyndyl forms can reveal information about the underlying electronic structure. However, it is rare that the structural analyses are sufficiently precise, or the magnitude of the effects sufficiently great, for such comparisons to be useful in practice.¹⁴ However, with good quality crystal specimens available for the compounds **1**, **2**, **3**, **4** and **6** we decided to attempt a comparative structural study for the tungsten series, both as a function of complex type (diyndyl vs. diyndyl) and metal d count (d⁴ vs. d⁰). The crystallographic details are summarised in Table 2, with selected bond lengths and angles given in Table 3. Plots of complex **1** (Fig. 1), **2** (Fig. 2), **3** (Fig. 3), **4** (Fig. 4) and **6** (Fig. 5) are illustrated below.

The W(CO)₃Cp* fragment is common to both the diyndyl complex **1**, which rests on a crystallographic mirror plane passing through the C₄ ligand, the Cp* ring and C(1)–W(1)–C(22) similar to the symmetry element found in the solid-state structure of [W(C≡CC≡CSiMe₃)(CO)₃Cp],^{9a} and the diyndyl

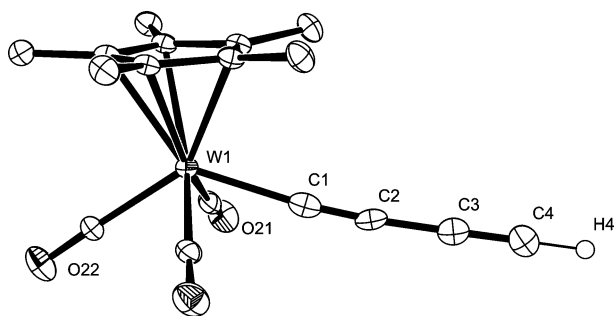


Fig. 1 A plot of compound **1**, showing the atom labelling scheme. Of the hydrogen atoms, only H(4) is shown. Symmetry transformations used to generate equivalent atoms $x, y, z = x, -y + 1/2, z$.

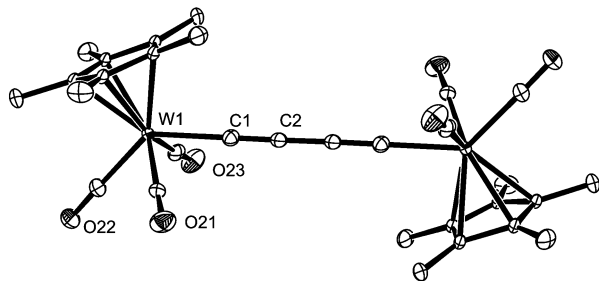


Fig. 2 The molecular structure of compound **2**. Hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms $x, y, z = -x + 1, -y + 1, -z + 1$.

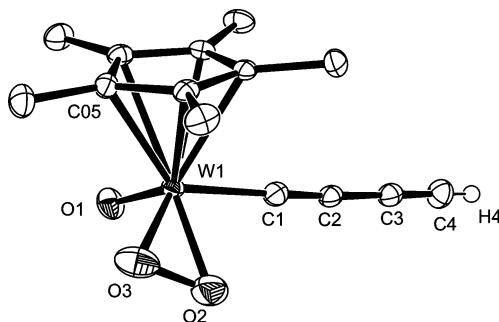


Fig. 3 A diagram illustrating the molecular structure of **3**. All hydrogen atoms except H(4) have been omitted for clarity.

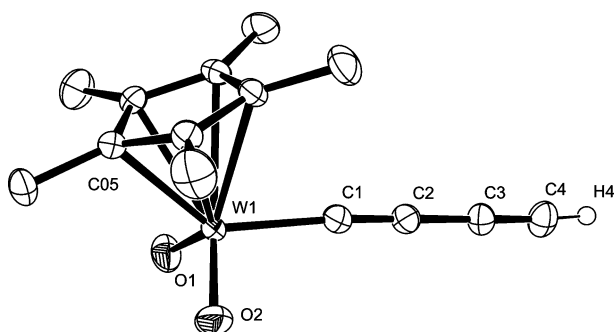


Fig. 4 The molecular structure of compound **4**. All hydrogen atoms except H(4) have been omitted for clarity.

complex **2**, which contains an inversion centre at the midpoint of the all-carbon ligand. The angles between the ligands subtended by the metal centre are comparable [**1**: C(21)–W–C(22) 78.8(1)°; C(22)–W–C(1) 129.3(2)°; C(21)–W–C(21A) 116.5(2)°. **2**: C(21)–W–C(22) 78.6(4)°; C(23)–W–C(22) 77.8(4)°; C(22)–W–C(1) 130.6(3)°; C(21)–W–C(23) 113.3(4)°] and define a metal geometry similar to that observed in the solid-state structure of diynyl complexes of $W(CO)_3Cp$.^{9a,e,15} Within each complex, the W–CO bond lengths are indistinguishable [**1**: 2.012(4), 2.023(5) Å; **2**: 1.971(9), 1.995(8), 2.005(8) Å], and do not reflect the differences in relative *cis* or *trans* orientation of the carbonyl

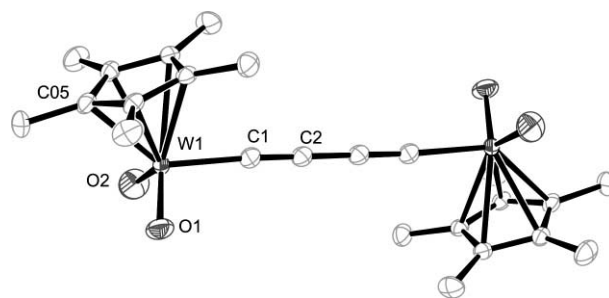


Fig. 5 The molecular structure of compound **6**. Hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms $x, y, z = -x, -y + 2, -z$.

groups to the diyn(di)yl ligand. However there is a distinct contraction in the distance between the metal centre and the centroid of the $\eta^5-C_5Me_5$ ligand in the diyndiyl compound **2** (2.00₅ Å) compared with that in **1** (2.11₆ Å).

As with the tricarbonyl compounds described above, the formally W(vi) complex **3** contains a seven coordinate tungsten centre. The W=O(1) [1.724(3) Å], W–O(2, 3) [1.929(3) Å] and O(2)–O(3) [1.465(5) Å] bond lengths are similar to those reported for $[W(CH_2SiMe_3)(O)(O_2)Cp']$ ($Cp' = Cp$,¹⁶ Cp^{*17}) and are reflected in the formal description of **3** as an oxo-peroxo complex. The complex did not suffer from the problems of crystal decay and disorder which have plagued some of the previous structural characterisations of $W(O)(O_2)Cp'$ -containing complexes.^{11,16,17} The O(2)–O(3) bond gives rise to an acute O(2)–W–O(3) bond angle [44.6(2)°] and prevents O(3) from adopting a position fully *trans* to the diynyl group. The tungsten centre subtends an angle of 108.9(2)° between O(2) and O(3). Overall the metal fragment geometry is comparable to those of other structurally characterised tungsten oxo-peroxo compounds.^{16–18}

The W=O bond lengths in the dioxo complexes $[W(C\equiv C\equiv CH)(O)_2Cp^*]$ (**4**) [1.724(3), 1.735(3) Å] and $\{[W(O)_2-Cp^*]_2(\mu-C\equiv C\equiv C)\}$ (**6**) [1.723(3), 1.733(3) Å] are comparable, and do not differ from the W=O(1) bond length observed in $[W(C\equiv C\equiv CH)(O)(O_2)Cp^*]$ (**3**) and related complexes.^{11,18b,19} There is little difference in the angles between the oxo ligands and C(1) subtended by the metal centres [**4**/**6**: O(1)–W–O(2) 108.1(2)/108.2(2)°; O(1)–W–C(1) 103.5(2)/101.9(1)°; O(2)–W–C(1) 102.1(2)/102.7(2)°]. The W–Cp*(centroid) distance is identical in the dioxo complexes [2.09₂ (**4**), 2.09₁ (**6**) Å], although the individual distances between the metal centre and C(01–05) illustrate the strong *trans* influence of the oxo-ligands. Thus, in each structure, the W(1)–C(05) distance [**4**: 2.288(4); **6**: 2.313(3) Å] of the Cp* ligand is shorter than the other four W–C distances which are in the range 2.411(4)–2.484(4) Å.

It is of interest to examine the effect the various combinations of metal oxidation state and supporting ligands have on the bond lengths along the W–C≡C–C≡C–R (R = H, W) chain. The diynyl ligand in **1** [C(1)–C(2) 1.169(8), C(2)–C(3) 1.422(8), C(3)–C(4) 1.212(8) Å] shows the expected alternating short–long–short separations similar to that found in the analogous compound $[W(C\equiv C\equiv CH)(CO)_3Cp]$ (**1-H**) [1.191(5), 1.376(6), 1.176(6) Å], while the W–C(1) distances are identical [1.2143(6); **1-H** 2.148(4) Å].^{9e}

From the data in Table 3 it can be seen that substitution of the diynyl proton for a $W(CO)_3Cp^*$ moiety has only a limited effect, if any, upon the W–C separation, but has a greater effect on the structure of the four carbon chain. In comparison with **1**, the C≡C triple bonds in **2** are elongated [**1**: 1.169(8), 1.212(8) Å vs. **2**: 1.23(1) Å], and the central C–C single bond contracted [**1**: 1.422(8) Å vs. **2**: 1.38(1) Å]. Variation in C–C bond lengths between diynyl and diyndiyl complexes has been observed in $[Fe(C\equiv C\equiv CH)(CO)_2Cp^*]$ and $\{[Fe(CO)_2Cp^*]_2(\mu-C\equiv C\equiv C)\}$,²⁰ and the 2-anilinopyridinate complexes $\{[Ru_2(\mu-ap)_4]\{C\equiv C\equiv CSiMe_3\}$ and $\{[Ru_2(\mu-ap)_4]\}_2(\mu-C\equiv C\equiv C)\}$.^{14,21}

In both cases it has been suggested that the bond length variation may be due to an increase in the cumulenic character of the C₄ fragment in the diyndiyl complexes. However, in light of the growing body of electronic structure information which is available,^{1,2c,7,22} we believe that these variations arise simply from an extension of the conjugation pathlength through the mixing of an additional d_π set in the HOMO.

The polycarbon ligands in the W(vi) complexes [W(C≡CC≡CH)(O)(O₂)Cp*] (**3**), [W(C≡CC≡CH)(O)₂Cp*] (**4**) and [$\{W(O)_2Cp^*\}_2(\mu-C\equiv C\equiv C)$] (**6**) show the usual alternating short–long–short C–C separations, and there is little doubt that these compounds are best described as diyndyl (**3**, **4**) and diyndiyl (**6**) complexes (Table 3). The W–C(1) distance in the W(vi) complexes are shorter than that found in the W(II) tricarbonyl complexes **1** and **2** (Table 3). This bond length contraction can be attributed to the decreased size of the W(vi) centre relative to W(II) and the increased electrostatic attraction between the metal and C(1). This latter aspect, which would result in a stronger W–C σ-bonding interaction in W(C≡CC≡CH)(O)₂Cp* is consistent with the greater ¹J_{CW} coupling constant observed for this complex. In contrast to the changes in the structure observed between **1** and **2**, replacement of the diyndyl proton in W(C≡CC≡CH)(O)₂Cp* by a second W(O)₂Cp* moiety to give **6** has no effect of any significance upon the structure of the C₄ chain (Table 3). This structural evidence strongly suggests that there is no significant interaction between the carbon fragment and the W(vi) metal centre through the π-framework.

Poly(ynyl) and poly(yndiyl) ligands often display a degree of curvature, the cumulative effects of which can lead to remarkably pronounced distortions of the “linear” ligand.^{2f,g,4,23} These structural distortions are not accounted for by computational studies, and are usually attributed to “crystal packing forces”. In the present set of diyndyl and diyndiyl complexes, the diyndiyl compounds **2** and **6** contain almost linear C₄ chains, and an examination of the packing motifs reveals the absence of any significant intermolecular interactions. The diyndyl ligands in **1**, **3** and **4** are arguably more distorted, and it is interesting to compare the packing motifs in these structures. The tricarbonyl complex **1** adopts a layered motif (Fig. 6) in which the diyndyl ligand from one molecule is directed so as to “rest” between the C13 methyl groups of an adjacent, symmetry related molecule. This weak interaction (C4 ... C13' 3.467 Å) is suggested to be responsible for the gentle convex curve of the diyndyl ligand. The oxo(peroxo) complex **3** adopts a stacked structure along the *a*-axis, in which the diyndyl ligands from molecules in one stack are directed into the void space between three adjacent stacks. The only obvious intermolecular contacts occur between H4 and the adjacent peroxo ligand (H4 ... O2' 2.65₈ Å, H4 ... O3' 2.62₀ Å), and the diyndyl ligand in **3** is the nearest to linear of those described here. The most significant intermolecular interactions are found in the solid-state structure of the dioxo species **4**. The compounds pack in a series of infinite head-to-tail chains. The Cp* rings of sequential molecules within each chain are located on opposite sides of the chain

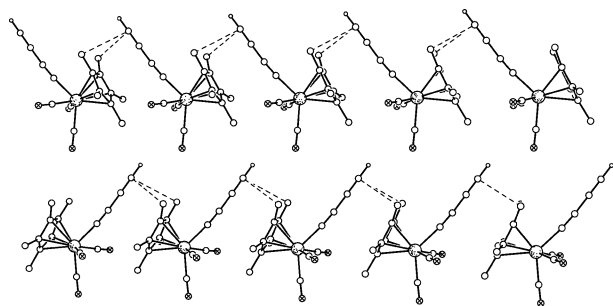


Fig. 6 An illustration of the layered structure of **1**. The dotted line indicates the closest intermolecular contact between C4 and C13 on adjacent molecules within a layer.

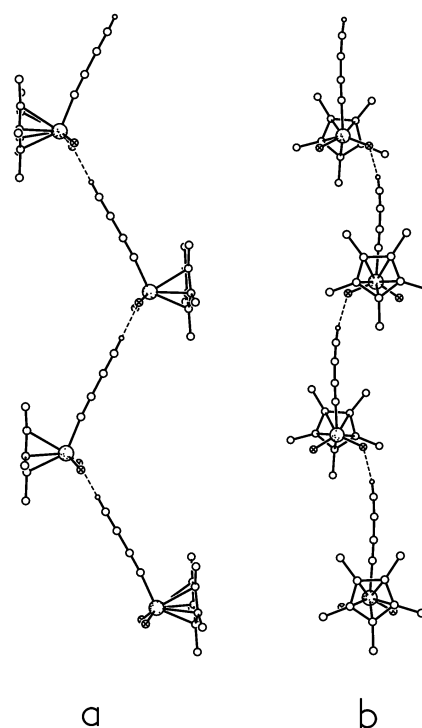


Fig. 7 Two perspective views of the chain like motif in the crystal structure of **4**.

(Fig. 7(a)) and the intermolecular separation between H4 and O1 on an adjacent molecule is 2.17₅ Å, suggestive of an interaction which could be responsible for the gentle curvature of the diyndyl ligand (Fig. 7(b)). There are no close contacts between molecules in adjacent chains.

Electronic structure

The basic electronic structure of metal complexes featuring σ-bonded acetylide and higher polyyndyl and diyl ligands is well established.^{1,2c,7,22} The most significant bonding interaction comes from the strong interaction of the carbon based σ-type orbital with a radial hybrid orbital from the metal ligand fragment. In the case of octahedral (or quasi-octahedral) metal complexes, this strong σ-type M–C bonding interaction is complemented by a π interaction between the filled yndyl π orbitals and the metal-based t_{2g} orbitals of appropriate symmetry. The vacant C≡C π* orbitals are well removed from the metal–ligand fragment orbitals, and this large energy gap results in only a very limited contribution from M–C back-bonding to the bonding description.

The variations in C≡C and C–C bond lengths observed between **1** and **2**, which are large in comparison to the changes observed in other pairs of diyndyl and diyndiyl complexes (Table 1), suggests a degree of mixing between the metal d and carbon π systems in these tungsten complexes which contain formally d⁴ metal centres. The shorter W–C bond lengths in **4** and **6** when compared to **1** and **2**, together with the large ¹J_{CW} coupling constant observed in the case of **4**, is consistent with the decreased size of the W(vi) centre and an increased electrostatic component to the σ-bond. Given that the bond lengths associated with the carbon fragment in the W(vi) (*i.e.* d⁰) complexes **4** and **6** are identical, and display little evidence for conjugation, it would appear that oxidation of the metal centre has lowered the energy of the metal based orbitals to such an extent as to effectively decouple them from the filled carbon frontier orbitals. These suggestions are strongly supported by electronic structure calculations on the acetylide complex [W(C≡CPh)(O)₂Cp*], describing an essentially acetylide centred HOMO with negligible metal character, which were reported while this study was in progress.²⁴

Conclusion

We have prepared and structurally characterised a series of tungsten(II) and (VI) diynyl and diyndiyl complexes. While the standard electrochemical methods used to assess "electronic interactions" in bimetallic bridged systems were hampered by the poor electrochemical response of the complexes, the structural evidence indicates that in the case of W(II) (d^4), but not W(VI) (d^0), diyndiyl complexes, a delocalised electronic structure is involved. Deviations from linearity in the C_4 ligand of the diynyl complexes can be accounted for by relatively weak intermolecular interactions.

Experimental

General conditions

Reagents were purchased and used as received, unless stated otherwise. Solvents were dried according to standard methods and distilled prior to use with the exception of benzene, which was used in the oxidation reactions as received. Reactions were carried out under dry high purity nitrogen, using standard Schlenk techniques, unless stated otherwise. Buta-1,3-diyne was prepared according to the literature procedure,^{9a} and used with the necessary degree of respect. This material is highly sensitive to detonation in the solid state, and should only be prepared and manipulated by an experienced experimentalist.

Instrumental measurements

Infrared spectra were recorded on a Nicolet Avatar FT-IR spectrometer. NMR spectra were obtained from Varian Mercury 200 or 400, and Inora500 spectrometers. ^1H spectra were recorded at 200, 300, 500 MHz; ^{13}C spectra were recorded at 126 MHz. All spectra were obtained using CDCl_3 and referenced against the solvent resonances. ES mass spectra were obtained using a Micromass LCT mass spectrometer; EI mass spectra and accurate mass determinations were obtained using a Micromass Autospec mass spectrometer. Cyclic voltammetry experiments were recorded using an EG&G Versastat II instrument in CH_2Cl_2 -acetonitrile containing 0.1 M $[\text{NBu}_4]\text{PF}_6$. Solutions were purged with argon and experiments conducted with a platinum working electrode, and platinum wire reference and counter electrodes, at sub-ambient temperatures. Carbon, hydrogen and nitrogen microanalyses were obtained using an Exeter Analytical CE-440 Elemental Analyser.

Crystallography

Data were collected on a Bruker SMART CCD area diffractometer (ω -scans) using graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data processing was carried out using SAINT software.²⁵ The structures were solved by Patterson methods and refined by full matrix least squares on F^2 using the SHELXTL suite of programs.²⁶ Hydrogen atoms were found or placed and refined using a riding model.

CCDC reference numbers 196749–196753.

See <http://www.rsc.org/suppdata/dt/b2/b212074g/> for crystallographic data in CIF or other electronic format.

$\text{WCl}(\text{CO})_3\text{Cp}^*$

A suspension of $\text{W}(\text{CO})_6$ (5.13 g, 14.6 mmol) in freshly distilled and degassed acetonitrile (75 ml) was treated with pentamethylcyclopentadiene (3.88 g, 28.5 mmol) and the mixture brought to reflux. After 48 h, 8 ml of dry CCl_4 was added and the solution allowed to cool with stirring. The solvent was removed to give a dark red solid, which was extracted (CH_2Cl_2) and loaded onto a short column of silica in hexane. Elution with dichloromethane-hexane (1 : 1) gave an orange band. The solvent was removed to give $\text{WCl}(\text{CO})_3\text{Cp}^*$ (5.79 g, 91%) as a red-orange powder which was collected, washed with a small portion of

cold hexane and dried in air. IR (CH_2Cl_2): $\nu(\text{CO})$: 2032, 1939 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 2.172 (s, Cp^*).

$\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3\text{Cp}^*$ (1)

A sample of $\text{WCl}(\text{CO})_3\text{Cp}^*$ (1.99 g, 4.53 mmol) was dissolved in NH_2Et_2 (25 ml)–thf (5 ml) and treated with CuI (100 mg, 0.53 mmol), followed immediately and rapidly by buta-1,3-diyne (6 ml of a 1.58 M solution in thf). The solution was protected from the light and allowed to stir in an ice bath for 24 h. Removal of the solvent gave a dark residue which was extracted with the minimum volume of CH_2Cl_2 and purified by column chromatography on alumina. Elution with dichloromethane-hexane (1/1) gave a yellow band, from which $[\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3\text{Cp}^*]$ precipitated as a yellow powder (3.47 mmol, 77%) upon concentration, which was collected, washed with cold hexane and dried in air. This compound is light sensitive and best kept in a freezer. Crystals suitable for X-ray study were obtained by diffusion of hexane into a CH_2Cl_2 solution of **1**. Found: C, 44.90; H, 3.56. $\text{C}_{17}\text{H}_{16}\text{O}_3\text{W}$ requires: C, 45.16; H, 3.57%. IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{C})$ 2138, 1995; $\nu(\text{CO})$ 2029, 1941 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 2.12 (s, 15H, Cp^*), 2.03 (s, 1H, $\text{C}\equiv\text{C}-\text{H}$). ^{13}C NMR (126 MHz, CDCl_3): δ 105.0 (C_5Me_5), 10.90 (C_5Me_5), 232.3 (CO, $J = 59 \text{ Hz}$), 216.1 (CO, $^1J_{\text{CW}} = 71 \text{ Hz}$), 85.98 (C1, $^1J_{\text{CW}} = 47 \text{ Hz}$), 108.4 (C2, $^2J_{\text{CW}} = 11 \text{ Hz}$), 71.03 (C3), 62.74 (C4). EI mass spectrum: m/z 453 [(M + H)⁺], 425 [(M + H - CO)⁺].

$\{\text{W}(\text{CO})_3\text{Cp}^*\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})$ (2)

A mixture of $\text{WCl}(\text{CO})_3\text{Cp}^*$ (1.02 g, 2.26 mmol) and $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3\text{Cp}^*$ (1.02 g, 2.32 mmol) in diethylamine (35 ml) was treated with CuI (100 mg, 0.53 mmol) and the solution stirred under nitrogen and in the dark for 16 h. The yellow precipitate formed was isolated and washed with a small portion of cold hexane yielding $\text{Cp}^*(\text{CO})_3\text{WC}\equiv\text{CC}\equiv\text{CW}(\text{CO})_3\text{Cp}^*$ (1.73 g, 90%) as a yellow powder. Crystals suitable for X-ray study were obtained by diffusion of hexane into a solution of **2** in CH_2Cl_2 . Found: C, 41.92; H, 4.93. $\text{C}_{30}\text{H}_{30}\text{O}_6\text{W}_2$ requires: C, 42.18; H, 3.54%. IR (CH_2Cl_2): $\nu(\text{CO})$ 2025, 1940 cm^{-1} . ^1H NMR (200 MHz, CDCl_3): δ 2.11 (s, Cp^*). ^{13}C NMR (126 MHz, CDCl_3): δ 120.3 (C_5Me_5), 10.94 (C_5Me_5), 220.5, 216.0 (CO), 119.7 (C1), 106.5 (C2). ES mass spectrum: m/z 1731 [(2M + Na)⁺], 877 [(M + Na)⁺], 827 [(M + H - CO)⁺].

$\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{O}_2)(\text{O})\text{Cp}^*$ (3)

The complex $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3\text{Cp}^*$ (0.523 g, 1.16 mmol) was dissolved in benzene (30 ml) in an open flask. To this solution 15 ml of 35% hydrogen peroxide and 10 drops of concentrated sulfuric acid were added. The orange solution formed was stirred vigorously; open to air and in the dark, for 5 days, after which time the solution was pale yellow in colour. The organic layer was separated and washed with deionised water (3 × 20 ml). The aqueous layer and washings were washed with a portion of benzene (20 ml) and the organic washings combined and dried with magnesium sulfate. Benzene was removed under vacuum to produce a yellow powdery residue. This residue was recrystallised from hot acetone to yield $[\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{O}_2)(\text{O})\text{Cp}^*]$ (0.807 mmol, 70%) as a pale yellow powder. Crystals suitable for X-ray study were obtained by slow evaporation of an acetone solution of **3**. Found: C, 37.45; H 3.70. $\text{C}_{14}\text{H}_{16}\text{O}_3\text{W}$ requires: C, 40.41; H, 3.88%. IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{C})$ 2160, 2010; $\nu(\text{W}=\text{O})$ 942; $\nu(\text{O}-\text{O})$ 852 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 2.25 (s, 15H, Cp^*); 2.45 (s, 1H, $\text{C}\equiv\text{C}-\text{H}$). ^{13}C NMR (126 MHz, CDCl_3): δ 121.3 (C_5Me_5), 10.96 (C_5Me_5), 114.1 (C1), 79.56 (C2), 72.13 (C3), 68.50 (C4). EI mass spectrum: m/z 417 [(M + H)⁺].

$\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{O})_2\text{Cp}^*$ (4)

A sample of $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{O}_2)(\text{O})\text{Cp}^*$ (0.404 g, 0.972 mmol) was partially dissolved in benzene (50 ml), treated with PPh_3

(0.255 g, 0.971 mmol) and allowed to stir in the dark. After 90 min the solvent was removed and the residue was extracted (CH_2Cl_2) and loaded onto a short column of silica in hexane. Elution with dichloromethane gave a yellow band. The solvent was removed to give $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{O})_2\text{Cp}^*$ (0.849 mmol, 87%) which was recrystallised from hot acetone to give a pale yellow powder. Crystals suitable for X-ray study were obtained from ethanol and hexane. Found: C, 41.95; H, 4.10. $\text{C}_{14}\text{H}_{16}\text{O}_2\text{W}$ requires: C, 42.02; H, 4.03%. IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{C})$ 2156, 2010; $\nu(\text{W}=\text{O})$ 931 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ_{H} 2.27 (s, 15H, Cp*); 2.51 (s, 1H, C=C-H). ^{13}C NMR (126 MHz, CDCl_3): δ 120.5 (C_5Me_5), 11.06 (C_5Me_5), 111.9 (C1, $^1J_{\text{CW}} = 136$ Hz), 110.7 (C2, $^2J_{\text{CW}} = 26$ Hz), 68.01 (C3), 71.32 (C4). EI mass spectrum: m/z 400 [M^+].

$\text{Cp}^*(\text{O})_2\text{WC}\equiv\text{CC}\equiv\text{CW}(\text{O})_2\text{Cp}^*$ (6)

The diyndiyl complex $\text{Cp}^*(\text{CO})_3\text{WC}\equiv\text{CC}\equiv\text{CW}(\text{CO})_3\text{Cp}^*$ (0.244 g, 0.285 mmol) was partially dissolved in benzene (60 ml) and treated with 15 ml of 35% hydrogen peroxide and 10 drops of concentrated sulfuric acid. The orange solution was vigorously stirred, open to air, for 4 days, to give an almost colourless pale yellow solution. The organic layer was separated and washed with deionised water (3×20 ml). The aqueous layer and washings were washed with a portion of benzene (20 ml) and the organic washings combined and dried with magnesium sulfate. Benzene was removed under vacuum to produce a pale yellow powdery residue which was recrystallised from hot acetone to afford $\text{Cp}^*(\text{O})_2\text{WC}\equiv\text{CC}\equiv\text{CW}(\text{O})_2\text{Cp}^*$ (0.0916 mmol, 32%) as a pale yellow powder. Crystals suitable for X-ray study were obtained by vapour diffusion of hexane and a solution of **6** in acetone. Found: C, 38.01; H, 4.26. $\text{C}_{24}\text{H}_{30}\text{O}_4\text{W}_2$ requires: C, 38.43; H, 4.03%. IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{C})$ 2017; $\nu(\text{W}=\text{O})$ 935 cm^{-1} . ^1H NMR (200 MHz, CDCl_3): δ 2.27 (s, Cp*). ^{13}C NMR (126 MHz, CDCl_3): δ 120.6 (C_5Me_5), 11.12 (C_5Me_5), 119.6 (C1), 110.5 (C2). EI mass spectrum: m/z 1523 [(2M + Na) $^+$], 773 [(M + Na) $^+$].

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References

- P. J. Low and M. I. Bruce, *Adv. Organomet. Chem.*, 2001, **48**, 71.
- See, for example: (a) M. Akita, A. Sakurai and Y. Moro-oka, *Chem. Commun.*, 1999, 101; (b) A. Sakurai, M. Akita and Y. Moro-oka, *Organometallics*, 1999, **18**, 3241; (c) W. E. Meyer, A. J. Amoroso, C. R. Horn, M. Jaeger and J. A. Gladysz, *Organometallics*, 2001, **20**, 1115; (d) F. Paul, W. E. Meyer, L. Toupet, H. Jiao, J. A. Gladysz and C. Lapinte, *J. Am. Chem. Soc.*, 2000, **122**, 9405; (e) P. J. Low, A. J. Carty, K. A. Udachin and G. D. Enright, *Chem. Commun.*, 2001, 411; (f) M. I. Bruce, K. Costuas, J.-F. Halet, B. C. Hall, P. J. Low, B. K. Nicholson, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 2002, 383; (g) M. I. Bruce, B. C. Hall, P. J. Low, M. E. Smith, B. W. Skelton and A. H. White, *Inorg. Chim. Acta*, 2000, **300–302**, 633.
- (a) Y. Fujikura, K. Sonogashira and N. Hagihara, *Chem. Lett.*, 1975, 1067; (b) K. Sonogashira, S. Takahashi and N. Hagihara, *Macromolecules*, 1977, **10**, 879; (c) K. Sonogashira, S. Kataoka, S. Takahashi and N. Hagihara, *J. Organomet. Chem.*, 1978, **160**, 319; (d) S. Takahashi, M. Kariya, T. Yatake, K. Sonogashira and N. Hagihara, *Macromolecules*, 1978, **11**, 1063; (e) K. Sonogashira, K. Ohga, S. Takahashi and N. Hagihara, *J. Organomet. Chem.*, 1980, **188**, 237.

- J. Stahl, J. C. Böhring, E. B. Bauer, T. B. Peters, W. Mohr, J. M. Martín-Alvarez, F. Hampel and J. A. Gladysz, *Angew. Chem., Int. Ed.*, 2002, **41**, 1872.
- F. Paul and C. Lapinte, *Coord. Chem. Rev.*, 1998, **178–180**, 431.
- M. I. Bruce, P. J. Low, K. Costuas, J.-F. Halet, S. P. Best and G. A. Heath, *J. Am. Chem. Soc.*, 2000, **122**, 1949.
- S. Kheradmandan, K. Heinze, H. W. Schmalle and H. Berke, *Angew. Chem., Int. Ed.*, 1999, **38**, 2270.
- T. Ren, *Organometallics*, 2002, **21**, 732.
- (a) M. I. Bruce, M. Ke, P. J. Low, B. W. Skelton and A. H. White, *Organometallics*, 1998, **17**, 3539; (b) M. I. Bruce, B. W. Skelton, A. H. White and N. N. Zaitseva, *J. Chem. Soc., Dalton Trans.*, 1996, 3151; (c) M. I. Bruce, B. C. Hall, P. J. Low, M. E. Smith, B. W. Skelton and A. H. White, *Inorg. Chim. Acta*, 2000, **300–302**, 633; (d) M. I. Bruce, P. J. Low, N. N. Zaitseva, S. Kahal, J.-F. Halet, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 2000, 2939; (e) M. I. Bruce, P. J. Low, M. Ke, B. D. Kelly, B. W. Skelton, M. E. Smith, A. H. White and N. B. Witton, *Aust. J. Chem.*, 2001, **54**, 453; (f) M. I. Bruce, M. E. Smith, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 2001, **637**, 484.
- M. I. Bruce, J.-F. Halet, S. Kahal, P. J. Low, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1999, **578**, 155.
- C.-W. Shiu, C.-J. Su, C.-W. Pin, Y. Chi, P. S.-M. Peng and G.-H. Lee, *J. Organomet. Chem.*, 1997, **545–546**, 151.
- Y. Chi, personal communication.
- N. W. Hoffman, *Inorg. Chim. Acta.*, 1984, **88**, 59.
- T. Ren, G. Zou and J. C. Alvarez, *Chem. Commun.*, 2000, 1197.
- M. I. Bruce, B. D. Kelly, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1999, 847.
- P. Legzdins, E. C. Phillips, S. J. Rettig, L. Sánchez, J. Trotter and V. C. Yee, *Organometallics*, 1988, **7**, 1877.
- J. W. Fallor and Y. Ma, *Organometallics*, 1988, **7**, 559.
- (a) D. Chakraborty, M. Bhattacharjee, R. Krätzner, R. Siefken, H. W. Roesky, I. Usón and H.-G. Schmidt, *Organometallics*, 1999, **18**, 106; (b) P. Legzdins, E. C. Phillips, J. Trotter and V. C. Yee, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1995, **C51**, 2498.
- (a) P. Legzdins, S. J. Rettig, K. J. Ross and J. E. Veltheer, *J. Am. Chem. Soc.*, 1991, **113**, 4361; (b) A. A. Eagle, E. R. T. Tiekink and C. G. Young, *J. Chem. Soc., Chem. Commun.*, 1991, 1746; (c) A. A. Eagle, C. G. Young and E. R. T. Tiekink, *Organometallics*, 1992, **11**, 2934; (d) Z. Xiao, R. W. Gable, A. G. Wedd and C. G. Young, *J. Am. Chem. Soc.*, 1996, **118**, 2912.
- M. Akita, M.-C. Chung, A. Sakurai, S. Sugimoto, M. Terada, M. Tanaka and Y. Moro-oka, *Organometallics*, 1997, **16**, 4882.
- G. Xu and T. Ren, *Organometallics*, 2001, **20**, 2400.
- (a) O. F. Koentjoro, R. Rousseau and P. J. Low, *Organometallics*, 2001, **20**, 4502; (b) P. Belanzoni, N. Re, A. Sgamellotti and C. Florinai, *J. Chem. Soc., Dalton Trans.*, 1998, 1825; (c) M. Brady, W. Weng, Y. Zhou, J. W. Seyler, A. J. Amoroso, A. M. Arif, M. Böhme, G. Frenking and J. A. Gladysz, *J. Am. Chem. Soc.*, 1997, **119**, 775 and references therein.
- (a) T. B. Peters, Q. L. Zheng, J. Stahl, J. C. Böhring, A. M. Arif, F. Hampel and J. A. Gladysz, *J. Organomet. Chem.*, 2002, **641**, 53; (b) W. Mohr, J. Stahl, F. Hampel and J. A. Gladysz, *Inorg. Chem.*, 2001, **40**, 3263; (c) T. B. Peters, J. C. Böhring, A. M. Arif and J. A. Gladysz, *Organometallics*, 1999, **18**, 3261; (d) R. Dembinski, T. Lis, S. Szafert, C. L. Mayne, T. Bartik and J. A. Gladysz, *J. Organomet. Chem.*, 1999, **578**, 229; (e) B. Bartik, R. Dembinski, T. Bartik, A. M. Arif and J. A. Gladysz, *New J. Chem.*, 1997, **21**, 739; (f) M. I. Bruce, B. C. Hall, B. W. Skelton, M. E. Smith and A. H. White, *J. Chem. Soc., Dalton Trans.*, 2002, 995; (g) V. W.-W. Yam, S. H.-F. Chong, C.-C. Ko and K.-K. Cheung, *Organometallics*, 2000, **19**, 5092.
- Y. F. Cheng, D. L. Phillips, G. Z. He, C.-M. Che and Y. Chi, *Chem. Phys. Lett.*, 2001, **338**, 308; a referee notes that the contraction of the d orbitals in the high oxidation state is also consistent with the observed trends.
- Bruker (1998a). SAINT-NT V5.1. Data Reduction Software. Bruker Analytical X-ray Instruments Inc., Madison, WI, USA.
- Bruker (1998b). SHELXTL-NT. Version 5.1. Bruker Analytical X-ray Instruments Inc., Madison, WI, USA.
- V. W.-W. Yam, S. H.-F. Chong and K.-K. Cheung, *Chem. Commun.*, 1998, 2121.
- V. W.-W. Yam, V. C.-Y. Lau and K.-K. Cheung, *Organometallics*, 1996, **15**, 1740.
- M. I. Bruce, B. C. Hall, B. D. Kelly, P. J. Low, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1999, 3719.