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Bridging alkenyl species from the protonation of ditungsten, tungsten–molybdenum and dimolybdenum transverse alkyne complexes with HCl and $\mathrm{CF_3COOH}$. Crystal structure of $[\mathrm{WMoCl}\{\mu\text{-}(E)\text{-HC=CHPh}\}(\mathrm{CO})_4(\eta^5\text{-C}_5\mathrm{H}_5)_2]$

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Abstract

Some Group 6 transition metal complexes with bridging alkyne ligands $[\mathrm{MM'}(\mu\text{-HCCMe})(\mathrm{CO})_4(\eta^5\text{-C}_5\mathrm{H}_5)_2]$ [MM' = $\mathrm{W_2}$ **1**; WMo **2**; $\mathrm{Mo_2}$ **3**] and $[\mathrm{WMo}(\mu\text{-HCCPh})(\mathrm{CO})_4(\eta^5\text{-C}_5\mathrm{H}_5)_2]$ (**5**) were treated with hydrogen chloride to afford respectively $[\mathrm{MM'Cl}(\mu\text{-HC=CHMe})(\mathrm{CO})_4(\eta^5\text{-C}_5\mathrm{H}_5)_2]$ [MM'=$\mathrm{W_2}$ (**6**); WMo (**7a**); $\mathrm{Mo_2}$ (**8**)] and $[\mathrm{WMoCl}(\mu\text{-HC=CHPh})(\mathrm{CO})_4(\eta^5\text{-C}_5\mathrm{H}_5)_2]$ (**9a**). Similarly, the complexes $[\mathrm{WMo}(\mu\text{-HCCMe})(\mathrm{CO})_4(\eta^5\text{-C}_5\mathrm{H}_5)_2]$ (**2**) and $[\mathrm{MM'}(\mu\text{-HCCPh})(\mathrm{CO})_4(\eta^5\text{-C}_5\mathrm{H}_5)_2]$ [MM' = $\mathrm{W_2}$ (**4**); WMo (**5**)] were treated with trifluoroacetic acid to give respectively $[\mathrm{WMo}(\mathrm{CF_3COO})(\mu\text{-HC=CHMe})(\mathrm{CO})_4(\eta^5\text{-C}_5\mathrm{H}_5)_2]$ (**7b**) and $[\mathrm{MM'}(\mathrm{CF_3COO})(\mu\text{-HC=CHPh})(\mathrm{CO})_4(\eta^5\text{-C}_5\mathrm{H}_5)_2]$ [MM' = $\mathrm{W_2}$ (**10**); WMo (**9b**)]. All the products **6**–**10** result from anti Markovnikov addition of a proton to the bridging alkyne groups in **1**–**5**, and contain (E)-alkenyl ligands, μ-HC=CHR, σ-bonded to one metal centre and π-bonded to the other. The metal centre to which the alkenyl ligand is σ-bonded in **6**–**10** is also coordinated by a conjugate base ($\mathrm{Cl^-}$ or $\mathrm{CF_3COO^-}$).

In the case of **9a** a single-crystal X-ray diffraction study shows that the W centre has been formally oxidised from W(+1) to W(+3), with both the alkenyl and chloro groups σ-bonded to it, while the Mo centre is π-coordinated by the alkenyl group and remains in oxidation state (+1).

Keywords: Tungsten; Molybdenum; Protonation; Alkenyl; Crystal structure

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1. Introduction

Bimetallic complexes containing bridging alkenyl groups $[\mu\text{-R}^1\mathrm{C{=}CR^2R^3}]$ have been prepared by a variety of methods [1–5]. One method pertinent to this work is the direct protonation of complexes possessing a bridging alkyne group [6]. In the case of mixed metal alkyne complexes such protonation can in principle lead to isomeric bonding modes for the alkenyl group, since this group can bridge the metal atoms asymmetrically by σ-bonding to one metal centre and π-bonding to the other. In one previous study of the Group 6 Group 10 alkyne-bridged species $[\mathrm{NiM}(\mu\text{-RC}_2\mathrm{R'})(\mathrm{CO})_2(\eta^5\text{-C}_5\mathrm{H}_5)(\eta^5\text{-C}_5\mathrm{H}_4\mathrm{Me})]$ (M = W, Mo), protonation with trifluoroacetic acid afforded only the complexes $[\mathrm{NiM}(\mathrm{CO_2CF_3})(\mu\text{-RC=CHR'})(\mathrm{CO})_2(\eta^5\text{-C}_5\mathrm{H}_5)(\eta^5\text{-C}_5\mathrm{H}_4\mathrm{Me})]$, in which the alkenyl ligand σ-bonded to the Group 6 metal and π-bonded to the nickel atom [7]. Our interest in Group 6 bimetallic complexes containing bridging alkyne ligands [8–11] has now led us to study the reactions of various heteronuclear tungsten–molybdenum alkyne-bridged complexes, $[\mathrm{WMo}(\mu\text{-R}^1\mathrm{CCR}^2)(\mathrm{CO})_4(\eta^5\text{-C}_5\mathrm{H}_5)_2]$ [$\mathrm{R^1}$ = H; $\mathrm{R^2}$ = Me (**2**); Ph (**5**)], with hydrogen chloride and trifluoroacetic acid. The reactions of the previously unstudied homonuclear complexes $[\mathrm{MM'}(\mu\text{-HCCMe})(\mathrm{CO})_4\text{-}(\eta^5\text{-C}_5\mathrm{H}_5)_2]$ [MM' = $\mathrm{W_2}$ (**1**); $\mathrm{Mo_2}$ (**3**)] with HCl and $[\mathrm{W_2}(\mu\text{-HCCPh})(\mathrm{CO})_4(\eta^5\text{-C}_5\mathrm{H}_5)]$ (**4**) with $\mathrm{CF_3COOH}$ have also been investigated.

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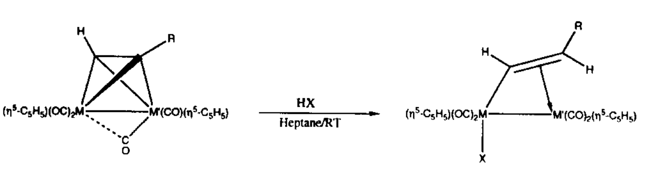
2. Results and discussion

(a) Reaction of HCl with [MM′(μ-HCCMe)(CO)$_4$(η^5-C$_5$H$_5$)$_2$] [MM′ = W$_2$ (1); WMo (2); Mo$_2$ (3)] and [WMo(μ-HCCPh)(CO)$_4$(η^5-C$_5$H$_5$)$_2$] (5)

A range of 1-propyne-bridged complexes, [MM′(μ-HCCMe)(CO)$_4$(η^5-C$_5$H$_5$)$_2$] [MM′ = W$_2$ (**1**); WMo (**2**); Mo$_2$ (**3**)] were treated with hydrogen chloride in heptane. The products, obtained in 65%–67% yield, were the complexes [MM′Cl(μ-HC=CHMe)(CO)$_4$(η^5-C$_5$H$_5$)$_2$] [MM′ = W$_2$ (**6**); WMo (**7a**); Mo$_2$ (**8**)] resulting from oxidative addition of HCl. Hydrogen chloride was also added to [WMo(μ-HCCPh)(CO)$_4$(η^5-C$_5$H$_5$)$_2$] (**5**) to give [WMoCl(μ-HC=CHPh)(η^5-C$_5$H$_5$)$_2$] (**9a**) in 63% yield. Complexes **6**, **7a**, **8** and **9a** have been characterised spectroscopically and by elemental analysis (see Table 1 and Experimental details). The molecular structure of **9a** has also been determined by an X-ray diffraction study.

The ordering of W and Mo in the chemical formulae will, throughout this account, indicate the orientation of the organic bridging ligand. That is, when the α-carbon of the alkenyl ligand is σ-bonded to W rather than to Mo, then W will precede Mo in the ordering of the formula and vice versa (see also chart in Scheme 1).



Complex	M	M′	R
1	W	W	Me
2	W	Mo	Me
3	Mo	Mo	Me
4	W	W	Ph
5	W	Mo	Ph

Complex	M	M′	R	X
6	W	W	Me	Cl
7a	W	Mo	Me	Cl
7b	W	Mo	Me	CF$_3$COO
8	Mo	Mo	Me	Cl
9a	W	Mo	Ph	Cl
9b	W	Mo	Ph	CF$_3$COO
10	W	W	Ph	CF$_3$COO

Scheme 1. Products from the reactions of **1–5** with HCl and CF$_3$COOH.

The IR spectra of **6**, **7a**, **8** and **9a** each show either three or four absorption bands in the terminal carbonyl region which are characteristic of this type of alkenyl complex [6]. The electron impact (EI) mass spectra do not show a molecular ion peak for any of the four compounds. There are, however, fragment ion peaks due to the loss of a Cl ligand and up to two CO ligands from the molecular ion.

The ^{1}H NMR spectra of **6**, **7a** and **8** show a series of peaks which are very similar for each of the three complexes. The signal arising from the α-proton (μ-

Table 1
IR and ^{1}H NMR data for the new complexes studied

Compound	IR ν(CO) (cm^{-1}) [a]	^{1}H NMR (δ) [b]
6	2008 (s); 1936 (vs); 1870 (m)	7.89 [d, ^3J(HH) = 11.1, ^2J(HW) = 5.0, 1H, C*H*=CHMe]; 5.41 [s, 5H, Cp]; 5.35 [s, 5H, Cp]; 3.81 [dq, ^3J(HMe) = 5.9, 1H, CH=C*H*Me]; 1.99 [d, 3H, Me]
7a	2006 (s); 1940 (vs); 1874 (m)	8.31 [d, ^3J(HH) = 12.0, ^2J(HW) = 6.5, 1H, C*H*=CHMe]; 5.34 [s, 5H, Cp]; 5.26 [s, 5H, Cp]; 4.00 [dq, ^3J(HMe) = 6.0, 1H, CH=C*H*Me]; 1.92 [d, 3H, Me]
7b	2014 (s); 1945 (s); 1880 (m); 1698 (w)	7.90 [d, ^3J(HH) = 11.9, ^2J(HW) = 7.0, 1H, C*H*=CHMe]; 5.39 [s, 5H, Cp]; 5.08 [s, 5H, Cp]; 4.05 [dq, ^3J(HMe) = 6.0, 1H, CH=C*H*Me]; 1.95 [d, 3H, Me]
8	2056 (m); 2019 (vs); 1949 (s); 1880 (m)	8.94 [d, ^3J(HH) = 11.7, 1H, C*H*=CHMe]; 5.31 [s, 5H, Cp]; 5.27 [s, 5H, Cp]; 4.09 [dq, ^3J(HMe) = 5.9, 1H, CH=C*H*Me]; 1.87 [d, 3H, Me]
9a	2011 (s); 1941 (vs); 1882 (m)	9.22 [d, ^3J(HH) = 12.7, ^{2}(HW) = 7.6, 1H, CH=CHPh]; 8.5–7.0 [m, 5H, Ph]; 5.40 [s, 5H, Cp]; 5.04 [s, 5H, Cp]; 4.81 [d, 1H, CH=C*H*Ph]
9b	2063 (m); 2014 (s); 1947 (s); 1885 (w); 1668 (w)	8.82 [d, ^3J(HH) = 12.7, ^{2}(HW) = 7.8, 1H, C*H*=CHPh]; 7.5–7.2 [m, 5H, Ph]; 5.48 [s, 5H, Cp]; 4.91 [s, 5H, Cp]; 4.84 [d, 1H, CH=C*H*Ph]
10	2060 (m); 2013 (s); 1952 (s); 1903 (m); 1697 (w)	8.43 [d, ^3J(HH) = 11.9, ^{2}(HW) = 6.8, 1H, C*H*=CHPh]; 7.5–7.1 [m, 5H, Ph]; 5.46 [s, 5H, Cp]; 5.04 [s, 5H, Cp]; 4.67 [d, 1H, CH=C*H*Ph]

[a] Recorded in CH$_2$Cl$_2$ solution.

[b] ^{1}H chemical shifts (δ) in ppm relative to SiMe$_4$ (0.0 ppm), coupling constants in Hz in CDCl$_3$ at 293 K.

$H_\alpha C{=}CH_\beta Me$) is, in each case, a doublet coupled to the β-proton and appearing at δ 7.89 ppm [$^3J(H_\alpha H_\beta)$ = 11.7 Hz] (**6**), δ 8.31 ppm [$^3J(H_\alpha H_\beta)$ = 12.0 Hz] (**7a**) and δ 8.94 ppm [$^3J(H_\alpha H_\beta)$ = 11.7 Hz] (**8**). The signal due to the β-proton itself appears as a pseudo sextet which is actually an overlapping doublet of quartets, caused by the β-proton coupling to the methyl protons with a coupling constant half that of the coupling to the α-proton [$^3J(H_\beta Me)$ = 5.9 Hz (**6**), 6.0 Hz (**7a**), 5.9 Hz (**8**)]. There are also signals arising from the cyclopentadienyl protons and, in each case, a doublet due to the methyl group coupling to the β-proton at δ 1.99 ppm (**6**); δ 1.92 ppm (**7a**) and δ 1.87 ppm (**8**). In the ^1H NMR spectrum of **9a**, the α-proton appears as a doublet [$^3J(H_\alpha H_\beta)$ = 12.7 Hz] at δ 9.22 ppm and the β-proton appears as a doublet at δ 4.81 ppm. Resolvable ^{183}W satellites are seen on the α-proton signals of **6**, **7a** and **9a**. The magnitude of the coupling of ^{183}W to H_α is in the range 5.0–7.6 Hz.

From the above data, complexes **6**, **7a**, **8** and **9a** can be suggested to have structures with alkenyl bridging ligands. The data do not, however, provide information as to whether the Cl ligand in **7a** and **9a** is on the molybdenum or tungsten atom. In addition, there is the possibility that in solution the alkenyl ligand is fluxional, so that at 293 K the observed ^1H NMR spectra are the average of those for the two possible isomers, one in which the Cl and α-carbon atoms are σ-bonded to the molybdenum and the other in which they are σ-bonded to the tungsten atom. However, even at 202 K, the ^1H NMR spectrum of **9a** in dichloromethane provides no evidence for the existence of more than one isomer.

Suitable crystals of **9a** for a single-crystal X-ray diffraction study were grown from dichloromethane solution by slow diffusion of hexane at 273 K. The molecular structure of **9a** is shown in Fig. 1 and selected bond lengths and bond angles are presented in Table 2. The crystal structure contains two independent but structurally equivalent dimer molecules per asymmetric unit. Because of this, the average values of the most relevant structural parameters will be used throughout the following discussion.

Table 2
Selected bond distances (Å) and angles (°) in complex [WMoCl(μ-CH=CHPh)$(CO)_4(\eta^5-C_5H_5)_2$] (**9a**) for the two independent molecules 1 and 2

	Molecule 1	Molecule 2
Bond distance		
W(11)–Mo(11)	3.083(2)	3.086(2)
W(11)–C(11)	2.018(17)	1.996(18)
W(11)–C(15)	2.126(15)	2.144(14)
Mo(11)–C(13)	1.962(19)	1.955(19)
Mo(11)–C(15)	2.228(14)	2.269(15)
W(11)–Cl(11)	2.504(5)	2.512(5)
W(11)–C(12)	2.007(17)	1.984(15)
Mo(11)–C(14)	1.947(20)	1.947(17)
Mo(11)–C(16)	2.437(16)	2.394(15)
C(15)–C(16)	1.371(21)	1.414(20)
Bond angle		
Mo(11)–W(11)–Cl(11)	83.4(1)	84.4(1)
Cl(11)–W(11)–C(11)	82.6(5)	84.7(6)
Cl(11)–W(11)–C(11)	150.2(6)	153.0(6)
Mo(11)–W(11)–C(15)	46.3(4)	47.3(4)
C(11)–W(11)–C(15)	131.7(6)	128.0(7)
W(11)–Mo(11)–C(14)	79.1(6)	80.8(6)
W(11)–Mo(11)–C(15)	43.6(4)	44.0(4)
C(14)–Mo(11)–C(15)	120.4(7)	120.4(7)
C(13)–Mo(11)–C(16)	73.3(7)	71.3(7)
C(15)–Mo(11)–C(16)	33.8(5)	35.2(5)
Mo(11)–W(11)–C(11)	86.4(5)	81.6(5)
Mo(11)–W(11)–C(12)	69.3(5)	69.4(5)
C(11)–W(11)–C(12)	84.1(7)	84.8(7)
Cl(11)–W(11)–C(15)	83.0(4)	81.8(4)
C(12)–W(11)–C(15)	86.3(6)	85.2(5)
W(11)–Mo(11)–C(13)	112.7(6)	118.5(6)
C(13)–Mo(11)–C(14)	79.0(8)	78.4(8)
C(13)–Mo(11)–C(15)	105.1(7)	106.0(7)
W(11)–Mo(11)–C(16)	68.4(4)	69.1(3)
C(14)–Mo(11)–C(16)	123.6(7)	117.8(7)
W(11)–C(11)–O(11)	177.4(15)	174.9(16)
Mo(11)–C(13)–O(13)	173.6(17)	177.2(18)
W(11)–C(15)–Mo(11)	90.1(5)	88.7(5)
Mo(11)–C(15)–C(16)	81.5(9)	77.2(9)
W(11)–C(12)–O(12)	167.8(17)	166.9(16)
Mo(11)–C(14)–O(14)	172.5(17)	171.2(18)
W(11)–C(15)–C(16)	127.0(12)	123.9(10)
Mo(11)–C(16)0C(15)	64.7(8)	67.6(8)

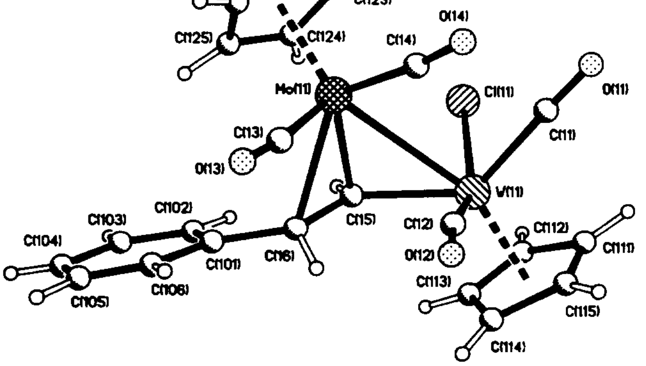


Fig. 1. Molecular structure of [WMoCl(μ-HC=CHPh)(CO)(η^5-$C_5H_5)_2$], **9a**, including the atom numbering scheme.

In complex **9a**, the two metal centres, Mo and W, each carry two carbonyl groups and one cyclopentadienyl ligand. In addition, the W atom is bonded to a chloride ligand. The two metal atoms are also bridged by an alkenyl group which is σ-bonded to W and π-bonded to Mo.

The Mo–W bond length [3.085(2) Å] in **9a** is in the middle of the range of reported Mo–W single bond lengths (see Table 3) and appreciably longer than the

Mo–W double bond length [2.772(3) Å] in [WMoCl$_2$(μ-Ph$_2$PC=CHPh)(μ-PPh$_2$)(η^5-C$_5$H$_5$)$_2$] [11].

The cyclopentadienyl ligands in **9a** adopt a transoid configuration and the carbonyl groups are staggered with respect to the corresponding carbonyl groups on the other metal atom. The Mo–C(CO) bond lengths [av. 1.953(19) Å] are slightly shorter than the W–C(CO) bond lengths [av. 2.002(17) Å]. The arrangement of these ligands is comparable to that observed in [Mo$_2$(CF$_3$COO)(μ-HC=CH$_2$)(CO)$_4$(η^5-C$_5$H$_5$)$_2$] [6a] except that in the Mo$_2$ complex one of the carbonyl groups adopts a semi-bridging position.

The W(11)–Cl(11) bond length [2.508(5) Å] is significantly longer than the W–Cl bond length in [WMoCl$_2$(μ-Ph$_2$PC=HPh)(μ-PPh$_2$)(η^5-C$_5$H$_5$)$_2$] [2.450(7) Å] [11]. It may be that this chloride ligand is not very strongly bound to W, since **9a** undergoes conversion fairly easily to [MoW(μ-HCCPh)(CO)$_4$(η^5-C$_5$H$_5$)$_2$] (**5**) in solution by loss of HCl, although **6**, **7a** and **8**, in which the alkenyl substituent is Me rather than Ph, do not undergo reconversion under these conditions.

The μ-alkenyl ligand carries a phenyl substituent on the β-carbon which is *cis* to the H atom on the α-carbon. This μ-alkenyl ligand is σ-bonded to W and π-bonded to Mo. The W(11)–C(15) bond length [2.135(15) Å] is shorter than the W–C$_\alpha$ bond length [2.173(6) Å] observed for [WNi(CF$_3$COO)(μ-MeC=CHMe)(CO)$_4$(η^5-C$_5$H$_5$)$_2$] [7] and is comparable to the Mo–C$_\alpha$ bond length [2.123(3) Å] in [Mo$_2$(CF$_3$COO)(μ-HC=CH$_2$)(CO)$_4$(η^5-C$_5$H$_5$)$_2$] [6a]. The C(15)–C(16) bond distance [1.393(20) Å] is typical of values observed for coordinated alkenyl groups. The C=C double bond lengths in [Mo$_2$(CF$_3$COO)(μ-HC=CH$_2$)(CO)$_4$(η^5-C$_5$H$_5$)$_2$] [6a] and [WNi(CF$_3$COO)(μ-MeC=CHMe)(CO)$_4$(η^5-C$_5$H$_5$)$_2$] [7] are 1.394(5) Å and 1.393(9) Å, respectively.

In the reaction of [MoW(μ-HCCPh)(CO)$_4$(η^5-C$_5$H$_5$)$_2$] (**5**) with HCl to produce **9a**, the W atom is formally oxidised from a (+1) to a (+3) oxidation state while the Mo atom remains in a (+1) oxidation state. This can be rationalised on the basis that W as a third row transition metal is more stable in high oxidation states than Mo.

(b) Reactions of CF$_3$COOH with [WMo(μ-HCCMe)(CO)$_4$(η^5-C$_5$H$_5$)$_2$] (2) and [MM′(μ-HCCPh)(CO)$_4$(η^5-C$_5$H$_5$)] [MM′ = W$_2$ (4); WMo (5)]

Addition of trifluoroacetic acid to the phenylacetylene-bridged complexes [MM′(μ-HCCPh)(CO)$_4$(η^5-C$_5$H$_5$)$_2$] [MM′ = W$_2$ (**4**); WMo (**5**)] gave [MM′(CF$_3$COO)(μ-HC=CHPh)(CO)$_4$(η^5-C$_5$H$_5$)$_2$] [MM′ = W$_2$ (**10**); WMo (**9b**)] in yields of 95% and 86%, respectively. Complex [WMo(μ-HCCMe)(CO)$_4$(η^5-C$_5$H$_5$)$_2$] (**2**) was also treated with CF$_3$COOH to give [WMo(CF$_3$COO)(μ-HC=CHMe)(CO)$_4$(η^5-C$_5$H$_5$)$_2$] (**7b**) in 71% yield. Complexes **7b**, **9b** and **10** have been characterised spectroscopically and by elemental analysis (see Table 1 and Experimental details).

The IR spectra of **7b**, **9b** and **10** each show three or four bands in the terminal carbonyl region and also peaks due to the C=O stretch of the CF$_3$COO group in the region 1668–1698 cm^{-1}. EI mass spectrometry of each complex shows a molecular ion peak and a peak due to the loss of a CF$_3$COOH molecule. A ^{19}F-{^{1}H} NMR spectrum at 293 K of **10** confirms the presence of a CF$_3$COO group, with a single peak being seen at δ 87.6 ppm [relative to C$_6$F$_6$ = 0.0 ppm].

In the ^{1}H NMR spectra of **7b**, a doublet resonance at δ 7.90 ppm is observed for the α-proton which couples to the β-proton [^3J(H$_\alpha$H$_\beta$) = 11.9 Hz]. The β-proton signal appears as a pseudo sextet at δ 4.05 ppm [^3J(H$_\alpha$Me) = 6.0 Hz] and the doublet due to the methyl group appears at δ 1.95 ppm. The spectra of **9b** and **10** consist of doublet resonances at δ 8.82 ppm [^3J(H$_\alpha$H$_\beta$) = 12.7 Hz] (**9b**) and δ 8.43 ppm [^3J(H$_\alpha$H$_\beta$) = 11.9 Hz] (**10**) for the α-protons and δ 4.84 ppm (**9b**) and δ 4.67 ppm (**10**) for the β-protons. The α-proton signals for **7b**, **9b** and **10** all have resolvable ^{183}W satellites of ca. J = 7 Hz.

In the light of the above data, the trifluoroacetate

Table 3
Lengths of tungsten–molybdenum single bonds in dinuclear organometallic complexes

Complex	W–Mo bond length (Å)	Ref.
[WMo(μ-SMe)(CO)$_7$(η^5-C$_5$H$_5$)]	3.131(1)	[12]
[WMo(C$_4$H$_6$O)(CO)$_5$(η^5-C$_5$H$_5$)$_2$]	3.239(4)	[13]
[WMo{μ-C(C$_6$H$_4$Me-4)C(Me)C(Me)}(η-MeC$_2$Me)$_2$(CO)$_3$(η^5-C$_5$H$_5$)]	2.971(2)	[14]
[WMo{μ-C(C$_6$H$_4$Me-4)C(=CH$_2$)C(H)MeC(O)}(CO)$_6$(η^5-C$_5$H$_5$)]	3.131(1)	[14]
[WMoCl(μ-HC=CHPh)(CO)$_4$(η^5-C$_5$H$_5$)$_2$] (**9a**)	3.085(2)	this work
[WMo{μ-C(^{t}Bu)CC(=C(H)C$_6$H$_4$Me-4)}(CO)$_4$(η^5-7,8-C$_2$B$_9$H$_{11}$)(η^5-C$_5$H$_5$)]	3.031(2)	[15]
[WMo(μ-C$_4$Me$_4$){σ,η^5-CH(C$_6$H$_4$Me-4)C$_2$B$_9$H$_8$Me$_2$}(η^7-C$_7$H$_7$)]	2.922(1)	[16]
[WMo{μ-C(C$_6$H$_4$(OMe-1))C(O)Me}(η^5-C$_5$H$_5$)$_2$]	2.935(1)	[17]
[WMo(μ-CS)(CO)$_4${HB(pz)$_3$}(η^5-C$_9$H$_7$)]	3.3102(4)	[18]
[WMo(μ-PPh$_2$)(CO)$_7$(η^5-C$_5$H$_5$)]	3.2054(16)	[19]

complexes **7b**, **9b** and **10** may be assigned structures similar to those of the chloro-containing complexes **6**, **7a**, **8** and **9a** (Scheme 1). The CF_3COO group could conceivably be present as a counterion. X-Ray structural data for the related complexes $[Mo_2(CF_3COO)(\mu\text{-}HC{=}CH_2)(CO)_4(\eta^5\text{-}C_5H_5)_2]$ [6a] and $[WNi(CF_3COO)(\mu\text{-}MeC{=}CHMe)(CO)_4(\eta^5\text{-}C_5H_5)_2]$ [7], however, indicate that the trifluoroacetate group is coordinated to one of the metal centres, and thus a similar ligand environment is proposed for **7b**, **9b** and **10**.

Several points are worth highlighting about the formation of the bridging alkenyl complexes **6–10** from the protonation of **1–5**:

(i) Although net oxidative addition of the acids HCl and CF_3COOH to both tungsten (**1** and **4**) and molybdenum (**3**) alkyne-bridged homobimetallics occurs readily at room temperature to form the alkenyl-bridged complexes (**6**, **8** and **10**), protonation of the tungsten–molybdenum alkyne-bridged complexes (**2** and **5**) gives in each case only the isomer having the alkenyl ligands π-bound to the molybdenum atom and σ-bonded to tungsten.

(ii) In all the products obtained, anti-Markovnikov addition of a proton to the alkyne groups in **1–5** has occurred. The $J(H_\alpha H_\beta)$ couplings for **6–10** of between 11.1–12.7 Hz are consistent with the α- and β-protons being *trans* to one another with a resultant (E)-configuration of the alkenyl group. In the case of **9a**, the X-ray structure analysis shows that this stereochemistry exists also in the solid state.

(iii) Conversion of the bridging alkyne complexes to the alkenyl species has been postulated to proceed via initial protonation of the metal–metal bond followed by migration of the proton to a bridging alkyne carbon and coordination of the conjugate base [7]. A similar pathway is postulated here for the formation of complexes **6–10**.

3. Experimental details

All reactions were carried out under a nitrogen atmosphere by use of standard Schlenk techniques. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use.

Infrared absorption spectra were recorded in CH_2Cl_2 solution in 0.5 mm NaCl cells using a Perkin–Elmer 983 spectrometer or a Perkin-Elmer 1710 Fourier-transform spectrometer. Electron impact (EI) mass spectra were obtained on a Kratos MS-902 spectrometer with Fomblin as reference.

^1H, ^{19}F and ^{13}C NMR spectra were recorded on Bruker WM-250 or AM-400 spectrometers at 293 K using the solvent resonance or C_6F_6 as references. Microanalyses were performed by the Microanalytical Department, University of Cambridge.

All reagents were obtained from commercial suppliers and used without further purification. The syntheses of $[MM'(\mu\text{-}HCCMe)(CO)_4(\eta^5\text{-}C_5H_5)_2]$ [$MM' = W_2$ (**1**); WMo (**2**); Mo_2 (**3**)] and $[MM'(\mu\text{-}HCCPh)(CO)_4(\eta^5\text{-}C_5H_5)_2]$ [$MM' = W_2$ (**4**); WMo (**5**)] have been described previously [10,11,20].

3.1. Reaction of $[MM'(\mu\text{-}HCCMe)(CO)_4(\eta^5\text{-}C_5H_5)_2]$ [$MM' = W_2$ (1); WMo (2); Mo_2 (3)] and $[WMo(\mu\text{-}HCCPh)(CO)_4(\eta^5\text{-}C_5H_5)_2]$ (5) with HCl

(a) Complex $[W_2(\mu\text{-}HCCMe)(CO)_4(\eta^5\text{-}C_5H_5)_2]$ (**1**) (0.090 g, 0.14 mmol) was dissolved in heptane (50 ml) and HCl gas bubbled through the solution at room temperature for 20 min. The solvent was removed under reduced pressure, the residue redissolved in ice cold pentane, and the solution filtered to remove starting material. The residue from filtration was then redissolved in CH_2Cl_2 and the solution filtered through a Celite plug to remove decomposition products. The solid recovered from the filtrate was recrystallised from the minimum amount of CH_2Cl_2 layered with hexane to yield orange $[W_2Cl(\mu\text{-}HC{=}CHMe)(CO)_4(\eta^5\text{-}C_5H_5)_2]$ (**6**) (0.062 g, 65%) (Anal. Found: C, 29.61; H, 2.20%. $C_{17}H_{15}ClO_4W_2$ requires: C, 29.71; H, 2.20%); EI mass spectrum, no molecular ion (M^+) peak, m/z 651 ($M^+ - Cl$) and $M^+ - Cl - 3CO$.

(b) Complex $[WMo(\mu\text{-}HCCMe)(CO)_4(\eta^5\text{-}C_5H_5)_2]$ (**2**) (0.220 g, 0.39 mmol) was dissolved in heptane (100 ml) and treated as in (a) above to give orange $[WMoCl(\mu\text{-}HC{=}CHMe)(CO)_4(\eta^5\text{-}C_5H_5)_2]$, (**7a**) (0.151 g, 65%) (Anal. Found: C, 33.80; H, 2.48%. $C_{17}H_{15}ClMoO_4W$ requires: C, 34.11; H, 2.52%); EI mass spectrum, no molecular ion (M^+) peak, m/z 563 ($M^+ - Cl$) and $M^+ - Cl - nCO$ ($n = 1,2$); ^{13}C NMR (^1H composite pulse decoupled, $CDCl_3$) δ: 236.9 (s, Mo=CO); 235.7 (s, Mo=CO); 223.5 (s, W=CO); 220.6 (s, W=CO); 147.9 (s, HC=CHMe); 94.2 (s, Cp); 91.3 (s, Cp); 86.8 (s, HC=CHMe); 28.8 (s, Me) ppm.

(c) Complex $[Mo_2(\mu\text{-}HCCMe)(CO)_4(\eta^5\text{-}C_5H_5)_2]$ (**3**) (0.230 g, 0.41 mmol) was dissolved in heptane (100 ml) and treated as in (a) above to give orange $[Mo_2Cl(\mu\text{-}HC{=}CHMe)(CO)_4(\eta^5\text{-}C_5H_5)_2]$ (**8**) (0.130 g, 67%) (Anal. Found: C, 39.71; H, 2.90%. $C_{17}H_{15}ClMo_2O_4$ requires: C, 39.99; H, 2.96%); EI mass spectrum, no molecular ion (M^+) peak, m/z 475 ($M^+ - Cl$).

(d) Complex $[WMo(\mu\text{-}HCCPh)(CO)_4(\eta^5\text{-}C_5H_5)_2]$ (**5**) (0.100 g, 0.16 mmol) was dissolved in heptane (100 ml) and treated as in (a) above to give orange $[WMoCl(\mu\text{-}HC{=}CHPh)(CO)_4(\eta^5\text{-}C_5H_5)_2]$ (**9a**) (0.067 g, 63%) (Anal. Found: C, 39.81; H, 2.49%. $C_{22}H_{17}ClMoO_4W$ requires: C, 40.00; H, 2.59%); EI mass spectrum, no molecular ion (M^+) peak, m/z 625 ($M^+ - Cl$) and $M^+ - Cl - nCO$ ($n = 2,4$).

Table 4
Atomic coordinates ($\times 10^4$) for complex [WMoCl(μ-HC=CHPh)-(CO)$_4$(η^5-C$_5$H$_5$)$_2$] (**9a**)

Atom	x	y	z
W(11)	6335(1)	2199(1)	1471(1)
Mo(11)	7890(1)	408(1)	1454(1)
Cl(11)	5521(4)	1479(5)	631(2)
C(11)	5189(13)	1327(13)	1806(7)
Q(11)	4528(10)	873(10)	1996(6)
C(12)	7183(13)	2049(14)	2168(7)
Q(12)	7577(11)	2117(12)	2562(6)
C(13)	9057(15)	426(14)	2024(8)
Q(13)	9743(13)	345(12)	2351(6)
C(14)	6990(15)	120(14)	2069(8)
Q(14)	6526(13)	−142(13)	2436(7)
C(15)	7898(12)	1896(10)	1111(6)
C(16)	8953(13)	1905(12)	1351(7)
C(101)	10082(13)	1834(11)	1102(6)
C(102)	10151(16)	1925(14)	563(8)
C(103)	11211(16)	1855(14)	330(8)
C(104)	12191(17)	1700(14)	663(8)
C(105)	12090(16)	1624(14)	1196(8)
C(106)	11089(13)	1676(12)	1398(7)
C(111)	4918(19)	3370(16)	1502(9)
C(112)	5536(21)	3549(15)	1009(10)
C(113)	6621(18)	3753(15)	1138(9)
C(114)	6730(20)	3771(14)	1673(10)
C(115)	5672(23)	3502(16)	1901(10)
C(121)	8695(29)	−991(22)	1166(18)
C(122)	7604(41)	−1172(16)	1199(17)
C(123)	6991(26)	−665(25)	828(17)
C(124)	7781(27)	−131(17)	547(10)
C(125)	8826(21)	−381(19)	777(13)
W(21)	1428(1)	5675(1)	1358(1)
Mo(21)	2917(1)	7512(1)	1386(1)
Cl(21)	681(4)	6344(4)	489(2)
C(21)	330(15)	6583(14)	1682(8)
O(21)	−343(11)	7039(10)	1863(6)
C(22)	2267(11)	5783(14)	2050(6)
O(22)	2667(11)	5674(11)	2466(6)
C(23)	4172(17)	7582(14)	1908(7)
O(23)	4885(13)	7655(12)	2223(6)
C(24)	2122(16)	7702(14)	2044(7)
O(24)	1692(15)	7937(13)	2423(7)
C(25)	3015(12)	6017(11)	1015(5)
C(26)	4049(12)	6084(11)	1309(6)
C(201)	5166(15)	6171(13)	1004(7)
C(202)	5273(25)	6075(20)	470(11)
C(203)	6363(29)	6113(23)	258(15)
C(204)	7301(21)	6223(17)	567(10)
C(205)	7219(16)	6243(13)	1080(8)
C(206)	6139(14)	6166(13)	1320(7)
C(211)	1685(18)	4099(13)	1038(9)
C(212)	1818(16)	4116(12)	1617(9)
C(213)	700(16)	4380(13)	1804(8)
C(214)	−23(17)	4535(12)	1339(9)
C(215)	635(17)	4295(13)	892(7)
C(221)	2232(30)	9049(16)	1162(13)
C(222)	3423(30)	9055(17)	1138(14)
C(223)	3729(21)	8409(18)	709(10)
C(224)	2709(22)	8064(18)	488(9)
C(225)	1828(27)	8429(18)	764(11)

3.2. Reaction of [WMo(μ-HCCMe)(CO)$_4$(η^5-C$_5$H$_5$)$_2$] (2) and [MM′(μ-HCCPh)(CO)$_4$(η^5-C$_5$H$_5$)$_2$] [MM′ = W$_2$ (4); WMo (5)] with CF$_3$COOH

(a) Complex [WMo(μ-HCCMe)(CO)$_4$(η^5-C$_5$H$_5$)$_2$] (**2**) (0.125 g, 0.22 mmol) was dissolved in heptane (100 ml), an excess of CF$_3$COOH added and the solution stirred at room temperature for 30 min. The solvent was removed under reduced pressure, the residue redissolved in ice cold pentane and the solution filtered to remove starting material. The residue from the filtration was redissolved in CH$_2$Cl$_2$ and filtered through a Celite plug to remove decomposition products. The solid recovered from the filtrate was recrystallised from the minimum amount of CH$_2$Cl$_2$ layered with hexane to yield orange [WMo(CF$_3$COO)(μ-HC–CHMe)(CO)$_4$(η^5-C$_5$H$_5$)$_2$] (**7b**) (0.105 g, 71%) (Anal. Found: C, 33.50; H, 2.07%. C$_{19}$H$_{15}$F$_3$MoO$_6$W requires: C, 33.75; H, 2.24%); EI mass spectrum, m/z 676 (M$^+$) and M$^+$ − CF$_3$COOH − nCO (n = 2–4). NMR (CDCl$_3$): ^{13}C (^{1}H composite pulse decoupled) δ: 236.6 (s, Mo–CO); 234.9 (s, Mo–CO); 223.9 (s, W–CO); 221.6 (s, W–CO); 162.5 [q, ^2J(CF) = 36.5 Hz, CF$_3$*C*OO]; 147.0 (s, H*C*=CHMe); 113.6 [q, ^1J(CF) = 291 Hz, *C*F$_3$COO]; 92.7 (s, Cp); 91.4 (s, Cp); 85.1 (s, HC=*C*HMe); and 28.8 (s, Me) ppm; ^{19}F (^{1}H composite pulse decoupled) δ: 87.6 (s, CF$_3$COO) ppm.

(b) Complex [W$_2$(μ-HCCPh)(CO)$_4$(η^5-C$_5$H$_5$)$_2$)] (**4**) (0.350 g, 0.49 mmol) was dissolved in heptane (150 ml) and treated as in (a) above to give orange [W$_2$(CF$_3$COO)(μ-HC=CHPh)(CO)$_4$(η^5-C$_5$H$_5$)$_2$] (**10**) (0.350 g, 86%) (Anal. Found: C, 34.60; H, 1.98%. C$_{24}$H$_{17}$F$_3$O$_6$W$_2$ requires: C, 34.89; H, 2.07%); EI mass spectrum, m/z 826 (M$_+$) and M$^+$ − nCF$_3$COOH (n = 0–1).

(c) Complex [WMo(μ-HCCPh)(CO)$_4$(η^5-C$_5$H$_5$)$_2$] (**5**) (0.050 g, 0.08 mmol) was dissolved in heptane (35 ml) and treated as in (a) above to give orange [WMo(CF$_3$COO)(μ-HC=CHPh)(CO)$_4$(η^5-C$_5$H$_5$)$_2$] (**9b**) (0.056 g, 95%) (Anal. Found: C, 39.01; H, 2.20%. C$_{24}$H$_{17}$F$_3$MoO$_6$W requires: C, 39.05; H, 2.32%); EI mass spectrum, m/z 738 (M$^+$) and M$^+$ − nCF$_3$COOH (n = 0–1).

3.3. X-Ray crystal structure determination of ***9a***

Suitable single crystals of [WMoCl(μ-HC=CHPh)-(CO)$_4$(η^5-C$_5$H$_5$)$_2$] (**9a**) were grown from a dichloromethane solution by slow diffusion of hexane at 273 K. A single crystal was mounted on a goniometer head using epoxy resin and transferred to a Siemens R3m/V diffractometer.

Crystal data: C$_{22}$H$_{17}$O$_4$ClMoW, M = 660.6, monoclinic, space group $P2_1/n$ (alt. setting of $P2_1/c$, No. 14), a = 11.835(4), b = 13.798(5), c = 25.187(7) Å, β =

91.75(1)°, $V = 4111(2)$ Å^3, $Z = 8$, $D_c = 2.135$ mg m^{-3}, $F(000) = 2512$, μ(Mo Kα) = 6.466 mm^{-1}.

A dark red block-shaped crystal with approximate dimensions 0.25 × 0.30 × 0.40 mm was used. Accurate cell dimensions were obtained from 25 reflections in the range $20 \leq 2\theta \leq 25°$. Intensity data were recorded using graphite monochromated Mo Kα radiation (λ = 0.71069 Å), and an $\omega/2\theta$ scan mode to a maximum 2θ value of 50°. Three standard reflections were monitored every 97 reflections throughout the data collection and showed no significant variation in intensity.

A total of 3145 intensities were measured within the range $-14 \leq h \leq 0$, $-16 \leq k \leq 0$, $-30 \leq l \leq 30$ and averaged to give 7169 unique reflections ($R_{\text{int}} = 0.009$) of which 4497 were judged as significant using the criterion $F_{\text{obs}} > 4\sigma(F_{\text{obs}})$. Corrections for Lorentz and polarisation effects were applied. A semi-empirical absorption correction based on 350 psi-scan data was applied; min. and max. transmission, 0.2339/0.2845. The structure was solved by a combination of direct methods (W and Mo atoms) and Fourier difference techniques. The structure was refined by full-matrix least-squares methods with all non-hydrogen atoms assigned anisotropic displacement parameters [21]. Hydrogen atoms were placed in idealised positions and allowed to ride on the relevant carbon atom with C–H = 0.96 Å; hydrogen atom displacement parameters were set at 0.08 Å^2. In the final cycles of refinement a weighting scheme of the form $\omega^{-1} = \sigma^2(F) + 0.0018F^2$, which gave satisfactory agreement analysis, was introduced. The refinement converged to $R = 0.050$ and $R' = 0.065$, G.O.F. = 1.06. A final Fourier difference synthesis showed electron density ripples of ca. 1.4 e Å^{-3} close to the positions of the tungsten atoms but no other regions of significant electron density. Final atomic coordinates and equivalent isotropic displacement parameters for the non-hydrogen atoms are listed in Table 4.

Tables including hydrogen-atom coordinates, displacement parameters, and full lists of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre. Lists of structure factors are available from the authors.

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