Synthesis of Os_3W Alkylidyne and Alkylidene Clusters by Solid-state Pyrolysis; Direct C–O Bond Cleavage of Co-ordinated Ketenyl Ligand†

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The heterometallic tetranuclear ketenyl compound $[Os_3(CO)_{10}(\mu\text{-}H)\{C(O)CH_2W(CO)_3(\eta\text{-}C_5Me_5)\}]$ **1** possessing a pendant $W(\eta\text{-}C_5Me_5)(CO)_3$ substituent is prepared by condensation of $[Os_3(CO)_{10}(NCMe)_2]$ with the aldehyde complex $[W(\eta\text{-}C_5Me_5)(CO)_3(CH_2CHO)]$. Pyrolysis of **1** in the solid state at 185 °C afforded four tetrahedral compounds $[WOs_3(\eta\text{-}C_5Me_5)(CO)_9(\mu\text{-}O)(\mu_3\text{-}CMe)]$ **2**, $[WOs_3(\eta\text{-}C_5Me_5)(CO)_9(\mu\text{-}O)(\mu\text{-}H)(\mu\text{-}CHMe)]$ **5**, $[WOs_3(\eta\text{-}C_5Me_5)(CO)_{11}(\mu_3\text{-}CMe)]$ **3** and $[WOs_3(\eta\text{-}C_5Me_5)(CO)_{11}(\mu_3\text{-}CH)]$ **4**, demonstrating a unique example of C–O bond scission for the ligated ketene fragment. Since treatment of **2** with H_2 in toluene also afforded **5** in moderate yield, it is highly probable that the latter is produced *via* reaction with trace amounts of H_2 generated from the decomposition of **1**. The molecular structures of **2** and **4** have been determined by single-crystal X-ray analysis.

The chemistry of organic ketene molecules as well as of organometallic ketenyl complexes has been investigated extensively,[1] since ketenes are important reagents in organic synthesis and ligated ketenes can serve as intermediates in hydrocarbon chain growth in CO-reduction reactions.[2] Di- and tri-nuclear ketene complexes have been synthesised by coupling of methylene and carbon monoxide: several research groups have demonstrated that ligated methylene can link with CO to give ketene[3] and that the resulting ketene fragments undergo isomerization to afford a formylmethylene ligand[4] and dehydration to afford a ligated acetylide fragment.[5] Further treatment of ketene complexes with alcohol led to formation of acetate,[6] while reaction with dihydrogen gives aldehydes,[7] reactions with electrophiles, such as H^+ or Me^+, give acyl and vinyl ligands,[8] and with diazomethane affords an oxalyl ligand.[9]

In this paper, we describe the preparation of a ketenyl complex $[Os_3(CO)_{10}(\mu\text{-}H)\{C(O)CH_2W(CO)_3(\eta\text{-}C_5Me_5)\}]$ **1** *via* reaction of the aldehyde complex $[W(\eta\text{-}C_5Me_5)(CO)_3(CH_2CHO)]$ with $[Os_3(CO)_{10}(NCMe)_2]$. As one of our research goals is to generate heterometallic clusters,[10] we studied the solid-state pyrolysis of **1** in an attempt to generate direct W–Os bonding between the Os_3 triangle and the $W(\eta\text{-}C_5Me_5)(CO)_3$ fragment through thermally induced CO elimination. Several tetrahedral clusters containing oxo, alkylidyne and alkylidene functional groups were isolated, producing strong evidence for cleavage of the ketenyl C–O bond. Related C–O bond scission has been observed for the triply bridging acyl ligand of the rhomboidal clusters $[MOs_3(\eta\text{-}C_5Me_5)(CO)_{11}\{\mu_3\text{-}\eta^2\text{-}C(O)CH_2C_6H_4Me\text{-}p\}]$ (M = W or Mo).[11]

Experimental

General.—Infrared spectra were recorded on a Bomen M-100 FT-IR spectrometer, ^1H and ^{13}C NMR spectra on a Bruker AM-400, Varian Gemini-300 or Varian Unity-400 instrument. Chemical shifts are quoted with respect to internal $SiMe_4$ (^1H and ^{13}C). Mass spectra were obtained on a JEOL-HX110 instrument operating in fast atom bombardment (FAB) mode. All reactions were performed under a nitrogen atmosphere using deoxygenated solvents dried with an appropriate reagent. The progress of reactions was monitored by thin-layer chromatography (TLC) (5735 Kieselgel 60 F_{254}, E. Merck) and the products were separated on commercially available preparative thin-layer chromatographic plates (Kieselgel 60 F_{254}, E. Merck). The aldehyde complexes $[W(\eta\text{-}C_5Me_5)(CO)_3(CH_2CHO)]$ were prepared from the reactions between the $[W(\eta\text{-}C_5Me_5)(CO)_3]^-$ anion and freshly distilled chloroacetaldehyde at 0 °C. Elemental analyses were performed at the NSC Regional Instrumentation Center at National Cheng Kung University, Tainan, Taiwan.

Reaction of $[Os_3(CO)_{10}(NCMe)_2]$ *with* $[W(\eta\text{-}C_5Me_5)(CO)_3(CH_2CHO)]$.—A toluene solution (35 cm^3) of $[Os_3(CO)_{10}(NCMe)_2]$ (625 mg, 0.67 mmol) and $[W(\eta\text{-}C_5Me_5)(CO)_3(CH_2CHO)]$ (423 mg, 0.95 mmol) was heated at reflux under nitrogen for 30 min. The solution turned from light yellow to orange. After evaporation of the solvent *in vacuo*, the residue was separated by TLC [silica gel, dichloromethane–hexane (1:2)], giving 320 mg of yellow $[Os_3(CO)_{10}(\mu\text{-}H)\{C(O)CH_2W(CO)_3(\eta\text{-}C_5Me_5)\}]$ **1** (0.246 mmol, 37%). Complex **1** was purified by recrystallization from a layered solution of dichloromethane–hexane at room temperature.

Spectral data for **1**: mass spectrum (FAB, ^{192}Os, ^{184}W), *m/z* 1302 (M^+); IR (C_6H_{12}): ν(CO) 2103w, 2063vs, 2052s, 2034vw, 2017vs, 2005s, 1991m, 1982vw, 1974w, 1930m and 1923m cm^{-1}. NMR ($CDCl_3$, 294 K): ^1H, δ 2.61 [d, 1 H, ^2J(H–H) = 5.1], 2.16 [d, 1 H, ^2J(H–H) = 5.1 Hz], 1.95 (s, 15 H) and −14.6 (s, 1 H); ^{13}C, δ 267.3 (CH_2CO), 230.7 [*J*(W–C) = 128], 224.2 [*J*(W–C) = 146], 222.1 [*J*(W–C) = 156 Hz], 184.6, 182.4, 178.8, 176.6, 176.4, 175.9, 175.8, 175.5, 175.2, 175.0 (CO); 104.3 (5 C, C_5Me_5), 29.0 (CH_2) and 10.6 (5 C, Me) (Found: C, 22.95; H, 1.45. $C_{25}H_{18}O_{14}Os_3W$ requires C, 23.15; H, 1.40%).

Solid-state Pyrolysis of Complex **1**. Complex **1** (213 mg, 0.164 mmol) was placed in a 5 mm NMR tube under N_2 and the tube was inserted into a pre-heated oil-bath at 195 °C for 10 min. Under these conditions, complex **1** melted, released carbon monoxide gas and turned black. The residue was extracted with dichloromethane and separated by TLC [silica gel, dichloromethane–hexane (1:3)], giving 20 mg of orange $[WOs_3(\eta\text{-}C_5Me_5)(CO)_9(\mu\text{-}O)(\mu\text{-}H)(\mu\text{-}CHMe)]$ **5** (0.017 mmol, 10%), 5.8 mg of orange $[WOs_3(\eta\text{-}C_5Me_5)(CO)_{11}(\mu_3\text{-}CMe)]$ **3** (0.005 mmol, 3%), 5.6 mg of red $[WOs_3(\eta\text{-}C_5Me_5)(CO)_{11}(\mu_3\text{-}CH)]$ **4** (0.005 mmol, 3%) and 16 mg of dark brown

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Experimental data for the X-ray diffraction studies of complexes **2** and **4**

Compound	**2**	**4**
Formula	$C_{21}H_{18}O_{10}Os_3W$	$C_{22}H_{16}O_{11}Os_3W$
M	1184.8	1210.8
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	9.524(3)	11.368(2)
b/Å	10.110(2)	16.590(3)
c/Å	15.550(4)	16.614(5)
α/°	75.09(2)	63.06(2)
β/°	77.06(2)	83.31(2)
γ/°	63.74(2)	71.41(2)
U/Å^3	1287(1)	2646(1)
Z	2	4
D_c/g cm^{-3}	3.057	3.039
F(000)	1052	2152
Crystal size/mm	0.34 × 0.16 × 0.10	0.32 × 0.22 × 0.19
h, *k*, *l* ranges	−10 to 11, −11 to 11, 0–18	−13 to 13, −17 to 19, 0–19
μ/mm^{-1}	19.39	18.75
Transmission factors	0.0542, 0.371	0.116, 0.615
No. of unique data	4558	8971
No. of parameters	317	668
Maximum Δ/σ ratio	0.001	0.002
R, *R'*	0.039; 0.043	0.053; 0.056
Weighting scheme, *w*	$[\sigma^2(F) + 0.0022F^2]^{-1}$	$[\sigma^2(F) + 0.0039F^2]^{-1}$
Goodness of fit	1.00	1.13
Residual electron density/e Å^{-3}	1.96, −2.34	2.39, −3.02

[WOs$_3$(η-C$_5$Me$_5$)(CO)$_9$(μ-O)(μ$_3$-CMe)] **2** (0.014 mmol, 9%) in the order of their elution. The first three complexes required repeated preparative TLC for complete separation and most of the starting material turns to an intractable solid which stayed at the base of the TLC plates. Crystals of **2** and **4** suitable for X-ray diffraction were obtained from a layered mixture of CH$_2$Cl$_2$–heptane at room temperature.

Spectral data for **2**: mass spectrum (FAB, ^{192}Os, ^{184}W), *m*/*z* 1120 (*M*$^+$); IR (C$_6$H$_{12}$): ν(CO) 2073s, 2038vs, 2022vs, 2005vw, 1989m, 1983s, 1962s, 1951w and 1943m cm^{-1}. NMR (CD$_2$Cl$_2$, 294 K): ^{1}H, δ 3.60 (s, 3 H) and 2.18 (s, 15 H); ^{13}C, δ 196.7, 190.5, 183.1, 183.0 (3 C, br), 180.4, 179.4, 167.5 (CO); 225.4 [*J*(W–C) = 115 Hz, *C*Me], 114.8 (*C*$_5$Me$_5$), 43.8 (C*Me*) and 12.8 (5 C, C$_5$*Me*$_5$) (Found: C, 21.35; H, 1.55. C$_{21}$H$_{18}$O$_{10}$Os$_3$W requires C, 21.30; H, 1.55%). Spectral data for **3**: mass spectrum (FAB, ^{192}Os, ^{184}W), *m*/*z* 1230 (*M*$^+$); IR (C$_6$H$_{12}$): ν(CO) 2075m, 2034vs, 2027vs, 2003m, 1986w, 1980w, 1974m, 1965w, 1950w and 1824 (br), vw cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 294 K): δ 3.70 (s, 3 H) and 2.08 (s, 15 H) (Found: C, 22.35; H, 1.50. C$_{23}$H$_{18}$O$_{11}$Os$_3$W requires C, 22.55; H, 1.50%). Spectral data for **4**: mass spectrum (FAB, ^{192}Os, ^{184}W), *m*/*z* 1216 (*M*$^+$); IR (C$_6$H$_{12}$): ν(CO) 2078m, 2038vs, 2033vs, 2003m, 1993w, 1983w, 1977w, 1968w, 1922 (br), vw and 1819 (br), vw cm^{-1}. NMR (CD$_2$Cl$_2$, 294 K): ^{1}H, δ 18.76 (s, 1 H) and 2.09 (s, 15 H); ^{13}C, δ 219.2 [*J*(C–W) = 154, 2 C], 181.6 (3 C), 180.7 (6 C) (CO); 282.6 [*J*(C–W) = 76 Hz, CH], 104.5 (*C*$_5$Me$_5$) and 11.1 (5 C, Me) (Found: C, 21.50; H, 1.35. C$_{22}$H$_{16}$O$_{11}$Os$_3$W requires C, 21.80; H, 1.35%). Spectral data for **5**: mass spectrum (FAB, ^{192}Os, ^{184}W), *m*/*z* 1192 (*M*$^+$); IR (C$_6$H$_{12}$): ν(CO) 2084m, 2056vs, 2017vs, 2008m, 2002w (sh), 1992w, 1986w, 1949w and 1928w cm^{-1}. NMR (294 K): ^{1}H (CDCl$_3$), δ 4.78 [q, 1 H, ^3J(H–H) = 7.6], 2.77 [d, 3 H, ^3J(H–H) = 7.6 Hz], 2.05 (s, 15 H) and −18.11 (s, 1 H); ^{13}C (CD$_2$Cl$_2$), δ 192.8, 187.0, 185.4, 183.9, 175.9, 174.1, 173.1, 171.2, 170.5 (CO); 128.9 [*J*(C–W) = 97 Hz, *C*HMe], 112.9 (*C*$_5$Me$_5$), 37.9 (1 C, Me) and 11.9 (5 C, Me) (Found: C, 21.30; H, 1.75. C$_{21}$H$_{20}$O$_{10}$Os$_3$W requires C, 21.25; H, 1.70%).

Hydrogenation of Complex **2**.—A toluene solution (20 cm^3) of complex **2** (18 mg, 0.016 mmol) was heated at reflux under hydrogen for 2 h. The solution turned from brown to orange. After evaporation of the solvent *in vacuo*, the residue was separated by TLC [silica gel, dichloromethane–hexane (1:2)], giving 8.6 mg of [WOs$_3$(η-C$_5$Me$_5$)(CO)$_9$(μ-O)(μ-H)(μ-CHMe)] **5** (0.007 mmol, 45%). Complex **5** was recrystallized from CH$_2$Cl$_2$–heptane.

X-Ray Crystallography.—Diffraction measurements of **2** and **4** were carried out on a Siemens R3m/V diffractometer. Lattice parameters of **2** were determined from 15 randomly selected high-angle reflections with 2θ angles in the range 13.64–27.44°, whereas the corresponding cell dimensions of **4** were determined from 14 reflections, with 2θ angles in the range 10.08–27.95°. The space group $P\bar{1}$ was assumed for both cluster complexes and confirmed by successful refinement. The structures were solved by direct methods and all non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of methyl groups were placed in idealized positions and were included in the structure-factor calculation. Scattering factors were taken from ref. 12. All calculations were performed on a DEC MicroVAXII computer system using the SHELXTL PLUS programs.[13] Selected data collection and refinement parameters of complexes **2** and **4** are given in Table 1. Atomic positional parameters are given in Tables 2 and 3, selected bond lengths are given in the legends of Figs. 1 and 2, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The tetranuclear ketenyl compound [Os$_3$(CO)$_{10}$(μ-H){C(O)-CH$_2$W(CO)$_3$(η-C$_5$Me$_5$)}] **1** possessing a pendant W(η-C$_5$Me$_5$)(CO)$_3$ substituent is readily obtained by condensation of [Os$_3$(CO)$_{10}$(NCMe)$_2$] with the Group 6 mononuclear aldehyde reagent [W(η-C$_5$Me$_5$)(CO)$_3$(CH$_2$CHO)] in refluxing toluene (30 min). Compound **1** has been fully characterized by spectroscopic methods. The key feature is provided by the ^{1}H NMR data which shows two diastereotopic methylene protons at δ 2.61 and 2.16 with ^2J(H–H) = 5.1 Hz and a hydride signal at δ −14.16. This observation indicates that this organometallic aldehyde reagent has reacted with [Os$_3$(CO)$_{10}$(NCMe)$_2$] in a

Table 2 Atomic coordinates (× 10^4) for complex **2**

Atom	*x*	*y*	*z*
Os(1)	411(1)	11 066(1)	8 351(1)
Os(2)	972(1)	11 069(1)	6 485(1)
Os(3)	3 566(1)	9 963(1)	7 396(1)
W	1 797(1)	8 407(1)	7 854(1)
O(1)	−613(15)	14 328(12)	7 397(8)
O(2)	−2 921(14)	11 786(15)	9 377(8)
O(3)	2 073(18)	11 739(17)	9 555(9)
O(4)	−2 217(17)	13 271(16)	5 869(9)
O(5)	2 403(19)	13 320(15)	5 564(10)
O(6)	1 940(15)	9 614(13)	4 858(7)
O(7)	5 405(17)	8 204(19)	8 965(9)
O(8)	6 244(18)	8 486(19)	6 037(12)
O(9)	4 187(18)	12 755(17)	7 231(12)
O(10)	1 279(11)	8 735(10)	9 015(6)
C(1)	−194(18)	13 044(19)	7 716(10)
C(2)	−1 696(18)	11 500(17)	8 998(9)
C(3)	1 515(22)	11 448(19)	9 097(11)
C(4)	−1 036(18)	12 424(17)	6 094(11)
C(5)	1 969(23)	12 439(18)	5 880(11)
C(6)	1 628(17)	10 131(15)	5 473(9)
C(7)	4 697(17)	8 879(19)	8 392(12)
C(8)	5 187(21)	9 053(22)	6 548(12)
C(9)	3 940(19)	11 736(20)	7 240(14)
C(10)	2 721(23)	5 792(16)	8 472(10)
C(11)	3 883(19)	5 923(15)	7 749(10)
C(12)	3 174(18)	6 390(16)	6 959(10)
C(13)	1 570(18)	6 623(15)	7 161(10)
C(14)	1 269(16)	6 259(15)	8 127(10)
C(15)	5 598(22)	5 319(20)	7 829(14)
C(16)	542(21)	6 968(17)	6 480(10)
C(17)	4 090(22)	6 390(19)	6 021(11)
C(18)	−214(15)	9 947(14)	7 474(9)
C(19)	−1 914(18)	10 084(18)	7 508(12)
C(20)	−251(19)	6 237(19)	8 656(9)
C(21)	2 865(22)	5 283(18)	9 445(11)

manner similar to its organic counterparts,[14] giving a cluster compound *via* activation of the aldehyde C–H bond and co-ordination of the aldehyde CO fragment to the unique Os–Os edge bridged by a hydride ligand. The bonding mode of the resulting ketenyl fragment, CH_2CO, resembles that found in the parent triosmium acyl complexes $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OCR)]$ (R = Me or Ph).[15]

Compound **1** is stable in refluxing toluene solution; treatment of **1** with equimolar, freshly sublimed Me_3NO in acetonitrile followed by heating in toluene solution led to only decomposition. However, when a solid sample of **1** was heated under nitrogen at 185–195 °C for 10 min, four tetranuclear complexes $[WOs_3(\eta\text{-}C_5Me_5)(CO)_9(\mu\text{-}O)(\mu_3\text{-}CMe)]$ **2**, $[WOs_3(\eta\text{-}C_5Me_5)(CO)_{11}(\mu_3\text{-}CMe)]$ **3**, $[WOs_3(\eta\text{-}C_5Me_5)(CO)_{11}(\mu_3\text{-}CH)]$ **4** and $[WOs_3(\eta\text{-}C_5Me_5)(CO)_9(\mu\text{-}O)(\mu\text{-}H)(\mu\text{-}CHMe)]$ **5** were obtained in 9, 3, 3 and 10% yields, respectively. Interestingly, two of these products possess a triply bridging alkylidyne ligand, formally derived by direct C–O bond cleavage of the co-ordinated ketenyl functional group followed by hydride migration to the CH_2 fragment.

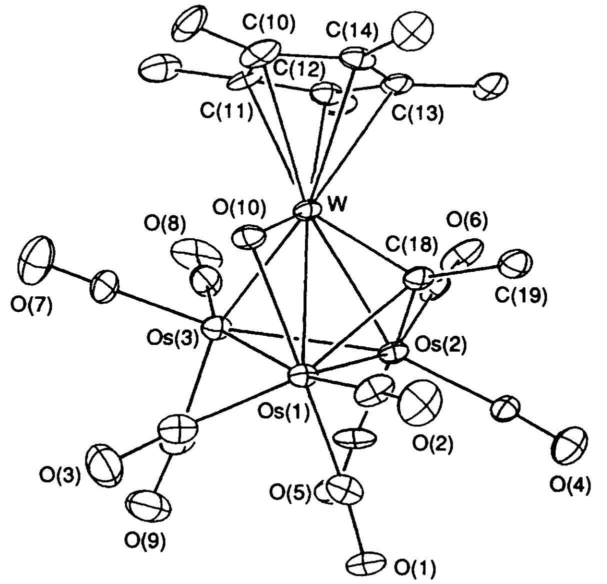


Fig. 1 Molecular structure of $[WOs_3(\eta\text{-}C_5Me_5)(CO)_9(\mu\text{-}O)(\mu_3\text{-}CMe)]$ **2**. Bond lengths (Å): Os(1)–Os(2) 2.830(1), Os(2)–Os(3) 2.769(1), Os(1)–Os(3) 2.893(1), Os(1)–W 2.653(1), Os(2)–W 2.885(1), Os(3)–W 2.655(1), W–O(10) 1.84(1), Os(1)–O(10) 2.17(1), Os(1)–C(18) 2.29(2), W–C(18) 1.96(1), Os(2)–C(18) 2.09(1), C(18)–C(19) 1.55(2)

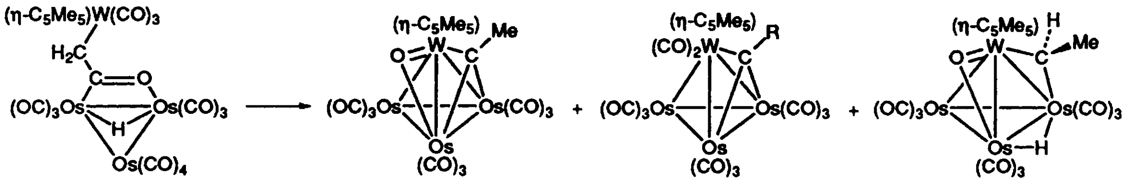
Characterization of Complex **2**.—The IR spectrum of **2** in solution indicates the absence of bridging CO ligands and shows CO stretching bands in the range 2073–1943 cm^{-1}. The ^1H NMR spectrum of **2** exhibits a methyl signal at δ 3.60 and a C_5Me_5 resonance at δ 2.18 in the expected ratio 1:5. The ^{13}C NMR signals of the α and β carbons of the ethylidyne fragment occur at δ 225.4 [*J*(W–C) = 115 Hz] and 43.8, respectively; the Os–CO resonances appear at δ 196.7, 190.5, 183.1, 183.0 (3 C), 180.4, 179.4 and 167.5. These spectral data are fully consistent with the X-ray crystal structure (Fig. 1), showing the tetrahedral core with three CO ligands on each Os atom, an edge-bridging oxo and a triply bridging ethylidyne ligand. The bridging oxo ligand, which spans the W–Os(1) bond with distances W–O(10) 1.838(9) and Os(1)–O(10) 2.170(8) Å, is involved in a W=O→Os bridge as proposed by Churchill and co-workers.[16] The ethylidyne ligand caps a WOs_2 face of the WOs_3 tetrahedral core with distances Os(1)–C(18) 2.291(17), W–C(18) 1.959(11) and Os(2)–C(18) 2.094(14) Å. This architecture resembles that of the structurally characterized WOs_3 compound $[WOs_3(\eta\text{-}C_5H_5)(CO)_9(\mu\text{-}O)(\mu_3\text{-}CCH_2C_6H_4Me\text{-}p)]$[17] and its phosphine substituted derivative $[WOs_3(\eta\text{-}C_5H_5)(CO)_8(PPh_2Me)(\mu\text{-}O)(\mu_3\text{-}CCH_2C_6H_4Me\text{-}p)]$.[18]

Characterization of Complexes **3** *and* **4**.—The second heterometallic cluster isolated is the ethylidyne complex **3**. The FAB mass spectrum indicates an ion at *m*/*z* 1230, corresponding to the presence of one ethylidyne and 11 CO ligands. The ^1H NMR spectrum exhibits a methyl signal at δ 3.70 and a C_5Me_5 resonance at δ 2.08. The IR spectrum shows a CO stretching band at 1824 cm^{-1}, which indicated the presence of bridging CO ligands, together with CO stretches due to terminal CO ligands. Based on the above spectroscopic data we assign a formulation $[WOs_3(\eta\text{-}C_5Me_5)(CO)_{11}(\mu_3\text{-}CMe)]$ for this complex (Scheme 1). The related alkylidyne clusters $[WOs_3(\eta\text{-}C_5H_5)(CO)_{11}(\mu_3\text{-}CR)]$ (R = C_6H_4Me-*p* or C_5H_{11}), have been prepared from condensation of $[W(\eta\text{-}C_5H_5)(CO)_2(\equiv CC_6H_4Me\text{-}p)]$ and $[Os_3(CO)_{10}(NCMe)_2]$[19] and from hydrogenation of the acetylide cluster $[WOs_3(\eta\text{-}C_5H_5)(CO)_{11}(C\equiv CBu^n)]$,[20] whereas the related WRu_3 methoxymethylidyne cluster was isolated from reactions of $[WL(CO)_3H]$ with $[Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OMe)]$ (L = C_5H_5 or C_5Me_5).[21]

In addition to the ethylidyne cluster **3**, we isolated a methylidyne analogue, **4**. The pattern of the CO stretching bands in IR spectrum indicates that the gross molecular geometry of **4** resembles that of complex **3**. The ^{13}C NMR spectrum exhibits a methylidyne carbon signal at δ 282.6 with ^1J(C–W) = 76 Hz, whereas the CO signals occur at δ 219.2 [*J*(C–W) = 154 Hz], 181.6 and 180.7 in the ratio 2:3:6, suggesting that all CO ligands are highly fluxional and that the molecule possesses a time-average plane of symmetry. The methylidyne hydrogen appears at δ 18.76 in the ^1H NMR spectrum. This chemical shift value is at lower field than for the corresponding trinuclear methylidyne complexes $[Fe_3(CO)_{10}(\mu_3\text{-}CH)]^-$ (δ 12.24),[22] $[Fe_2Co(CO)_{10}(\mu_3\text{-}CH)]$ (δ

Table 3 Atomic coordinates (× 10^4) for complex **4**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1A)	3657(1)	6181(1)	1429(1)	C(8A)	2475(25)	9213(18)	−810(17)
Os(2A)	1768(1)	7821(1)	1357(1)	C(9A)	4850(25)	8075(18)	−758(22)
Os(3A)	3434(1)	7960(1)	−51(1)	C(10A)	5812(25)	7030(19)	1026(15)
Os(1B)	1068(1)	3722(1)	3889(1)	C(11A)	3877(23)	8898(17)	696(14)
Os(2B)	3035(1)	2439(1)	3429(1)	C(12A)	6098(22)	7759(20)	2155(16)
Os(3B)	1733(1)	1751(1)	5015(1)	C(13A)	5967(27)	6849(17)	2826(20)
W(1A)	4390(1)	7582(1)	1691(1)	C(14A)	4902(20)	6957(17)	3261(15)
W(1B)	441(1)	2495(1)	3281(1)	C(15A)	4228(24)	7990(19)	2876(16)
O(1A)	1817(20)	5544(15)	866(16)	C(16A)	4988(19)	8448(13)	2307(14)
O(2A)	4522(25)	4431(18)	3144(17)	C(17A)	7188(22)	7995(18)	1713(19)
O(3A)	5768(20)	5421(15)	408(13)	C(18A)	6966(29)	5934(24)	2984(25)
O(4A)	−7(20)	7779(17)	143(16)	C(19A)	4407(36)	6273(25)	4133(18)
O(5A)	−20(20)	7470(19)	2928(13)	C(20A)	3067(25)	8448(24)	3249(18)
O(6A)	903(21)	9942(14)	757(18)	C(21A)	4797(32)	9475(20)	1936(24)
O(7A)	2610(25)	7041(17)	−991(16)	C(22A)	3093(21)	6849(15)	2301(14)
O(8A)	1880(22)	9946(16)	−1309(16)	C(1B)	2161(29)	3992(21)	4502(19)
O(9A)	5658(17)	8191(16)	−1225(13)	C(2B)	485(31)	4989(24)	2974(24)
O(10A)	6683(17)	6750(14)	747(14)	C(3B)	−218(23)	3815(22)	4729(22)
O(11A)	3699(22)	9707(13)	264(13)	C(4B)	4257(23)	2221(18)	4276(15)
O(1B)	2833(26)	4185(23)	4771(19)	C(5B)	3859(23)	3084(18)	2336(20)
O(2B)	59(25)	5792(15)	2460(15)	C(6B)	3707(21)	1243(17)	3462(18)
O(3B)	−1012(24)	3910(21)	5190(15)	C(7B)	2558(31)	1989(29)	5778(17)
O(4B)	4970(19)	2182(17)	4714(13)	C(8B)	2833(21)	527(19)	5404(22)
O(5B)	4363(21)	3463(16)	1734(14)	C(9B)	530(27)	1345(18)	5874(24)
O(6B)	4096(22)	539(15)	3387(19)	C(10B)	−842(22)	2541(22)	4241(20)
O(7B)	2852(38)	2183(24)	6280(18)	C(11B)	1142(23)	1128(17)	4023(16)
O(8B)	3555(21)	−216(16)	5571(15)	C(12B)	−913(25)	2076(17)	2692(16)
O(9B)	−193(23)	1075(17)	6421(13)	C(13B)	−1479(21)	3075(19)	2483(20)
O(10B)	−1639(20)	2538(20)	4636(15)	C(14B)	−666(20)	3584(17)	1845(16)
O(11B)	1381(21)	283(14)	4268(15)	C(15B)	318(24)	2902(19)	1712(15)
C(1A)	2468(25)	5785(18)	1089(19)	C(16B)	144(22)	1972(17)	2257(16)
C(2A)	4172(26)	5076(19)	2511(17)	C(17B)	−1560(25)	1351(18)	3281(18)
C(3A)	4958(24)	5722(20)	781(20)	C(18B)	−2718(21)	3500(20)	2691(18)
C(4A)	681(27)	7775(23)	607(19)	C(19B)	−1030(25)	4648(17)	1386(17)
C(5A)	681(28)	7611(22)	2304(23)	C(20B)	1289(23)	3126(20)	1015(16)
C(6A)	1173(22)	9172(21)	938(19)	C(21B)	1023(28)	1036(21)	2176(19)
C(7A)	2871(29)	7370(26)	−591(20)	C(22B)	1464(21)	3496(18)	2704(17)



1 **2** R = Me **3** R = H **4** **5**

Scheme 1

12.72)[23] and $[Os_3H(CO)_{10}(\mu_3\text{-CH})]$ (δ 14.16)[24] and the tetranuclear complex $[Ru_2Pt_2(\eta\text{-}C_5H_5)_2(CO)_3(PR_3)_2(\mu\text{-H})(\mu_4\text{-CH})]$ (δ 14.89–14.87).[25] We attribute this exceptional downfield shift partially to the electron deficiency of the methylidyne hydrogen and to the deshielding effect of the C_5Me_5 ring, as the methylidyne proton is very close to the C_5Me_5 ring. This postulate is further confirmed by the single-crystal X-ray analysis. As indicated in Fig. 2, the molecular structure of **4** shows the expected tetrahedral core arrangement. Each Os atom of the molecule possesses three mutually orthogonal terminal CO ligands, whereas one CO ligand on the W atom adopts an edge-bridging mode with the Os(3)–C(11) distance [2.55(3) Å] being slightly shorter than the terminal Os(3)–C(10) [2.97(3) Å]. The methylidyne ligand is located on a WOs_2 triangle and the shortest non-bonding contact between the methylidyne carbon and the methyl groups of the C_5Me_5 ligand (3.15–3.17 Å) are substantially shorter than the sum of the van der Waals radii (3.65–3.7 Å) between a methyl group and carbon atom.[26] Finally, it is of interest that complex **4** possesses an identical formulation with the butterfly carbide complexes $[WRu_3L(CO)_{11}(\mu_4\text{-C})(\mu\text{-H})]$ (L = C_5H_5 or C_5Me_5).[21] Apparently, the tetrahedral arrangement in **4** is relatively more stable than the hypothetical butterfly core, thus preventing oxidative addition at the methylidyne C–H bond and formation of the analogous WOs_3 hydridocarbide cluster. The mixed-metal clusters $[WOs_3L(CO)_{12}(\mu\text{-H})]$ (L = C_5H_5 or C_5Me_5) also display the same preference for the tetrahedral arrangement over the butterfly geometry as observed in the WRu_3 analogues $[WRu_3L(CO)_{12}(\mu\text{-H})]$.[27]

Characterization of Complex **5**.—The ethylidene compound $[WOs_3(\eta\text{-}C_5Me_5)(CO)_9(\mu\text{-O})(\mu\text{-H})(\mu\text{-CHMe})]$ **5** is the only non-alkylidyne cluster isolated from the solid-state pyrolysis. Alternatively, complex **5** can be prepared in 45% yield through hydrogenation of **2** in refluxing toluene. The structural identification was easily achieved by spectroscopic methods.

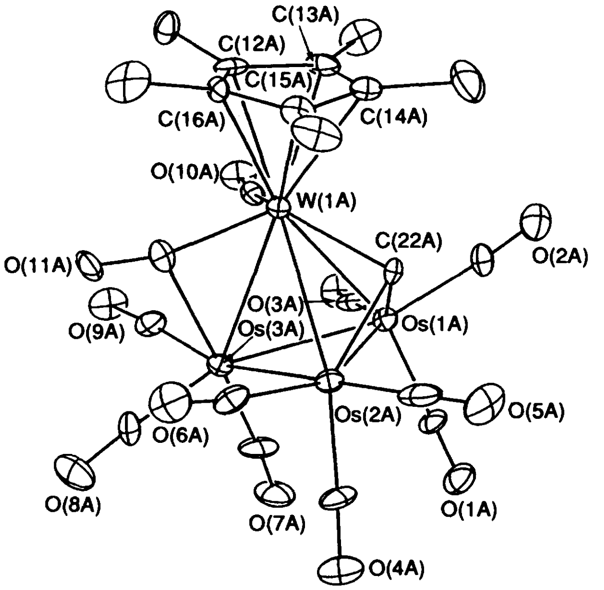
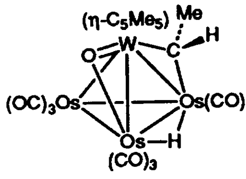


Fig. 2 Molecular structure of $[WOs_3(\eta\text{-}C_5Me_5)(CO)_{11}(\mu_3\text{-}CH)]$ **4**; the first and second set of data are for molecules A and B, respectively. Bond lengths (Å): Os(1)–Os(2) 2.841(2), 2.857(2); Os(1)–Os(3) 2.813(1), 2.824(2); Os(2)–Os(3) 2.806(2), 2.807(2); Os(1)–W(1) 2.920(2), 2.937(2); Os(2)–W(1) 2.963(2), 2.956(2); Os(3)–W(1) 2.934(2), 2.931(2); Os(1)–C(22) 2.13(3), 2.14(3); Os(2)–C(22) 2.01(2), 2.08(2); W(1)–C(22) 2.09(3), 2.13(3)



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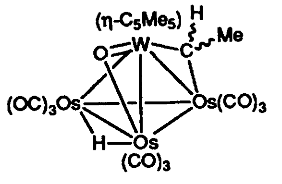

7

The ^1H NMR spectrum shows a doublet at δ 2.77 and a quartet at δ 4.78 [^3J(H-H) = 7.6 Hz] due to the ethylidene fragment, and a bridging hydride at δ −18.11. The ^{13}C NMR spectrum exhibits a signal at δ 128.9 with J(C-W) = 97 Hz, indicating that the ethylidene is linked to the W atom. Finally, since the pattern of the IR CO stretches is similar to that of the alkylidene complex $[WOs_3(\eta\text{-}C_5H_5)(CO)_9(\mu\text{-}O)(\mu\text{-}H)(\mu\text{-}CH\text{-}C_6H_4Me)]$,[28] we propose that **5** adopts an arrangement in which the hydride, oxo and ethylidene ligands span three edges of a WOs_2 triangular face. This assignment is consistent with the result of ^1H nuclear Overhauser effect (NOE) intensity enhancement: irradiation of the methine and the methyl site produces no ($\leqslant 1.5\%$) enhancement and 28% enhancement at the hydride, whereas irradiation of the hydride site affords no intensity enhancement at the methine and 17% enhancement at the methyl site, respectively. These results eliminate the other two possible structures **6** or **7**, one in which the methine hydrogen of the ethylidene is oriented toward the bridging hydride (**6**)[28] and the second in which the hydride, oxo and ethylidene take up a zig-zag alignment (**7**).[29] Steric interactions between the ethylidene and C_5Me_5 ligands seem to be the primary factor in determining the configuration of **5**.

Conclusion

This work provides the first example of conversion of ketene to oxo and ethylidyne fragments *via* a combined process of C–O bond cleavage and hydride migration. Complex **2** is obviously formed by direct C–O bond scission, although we do not have the required evidence of a cross-over experiment to demonstrate that it proceeds *via* an intramolecular process. On the other hand, the simultaneous formation of ethylidene cluster **3** and methylidyne cluster **4** implies that both the bimolecular C–O bond scission and cleavage of the C–C bond between the CO and CH_2 fragments are as important as intramolecular cleavage of the C–O bond. The exact mechanism of the formation of ethylidene cluster **5** is unclear at present. However, because we have verified that complex **2** reacts with H_2 to give the ethylidene cluster **5** in refluxing toluene solution, it is highly possible that the latter may be produced through a reaction with trace amounts of H_2 trapped in the reaction vessel, which is generated from activation of the methyl C–H bond of the C_5Me_5 ligand. This speculation is pertinent to a recent report of the intramolecular C–H activation of $[Re(\eta\text{-}C_5Me_5)(CO)_3]$ under UV irradiation.[30]

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