Synthesis of the Tetranuclear Mixed-metal Carbido Clusters $[WRu_3L(CO)_{11}(\mu_4\text{-}C)(\mu\text{-}H)]$ *via* Methoxymethylidyne Clusters $[WRu_3L(CO)_{11}(\mu_3\text{-}COMe)]$ ($L = \eta\text{-}C_5H_5$ or $\eta\text{-}C_5Me_5$). Crystal Structures of $[WRu_3(\eta\text{-}C_5Me_5)(CO)_{11}(\mu_3\text{-}COMe)]$ and $[WRu_3(\eta\text{-}C_5H_5)(CO)_{11}(\mu_4\text{-}C)(\mu\text{-}H)]$†

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Treatment of the complex $[Ru_3(CO)_{10}(\mu\text{-}COMe)H]$ with a slight excess of $[WL(CO)_3H]$ ($L = \eta\text{-}C_5H_5$ or $\eta\text{-}C_5Me_5$) in refluxing toluene solution (45 min) produces a methoxymethylidyne complex $[WRu_3L(CO)_{11}(\mu_3\text{-}COMe)]$ [$L = \eta\text{-}C_5H_5$, (**4a**); or $\eta\text{-}C_5Me_5$, (**4b**)]. Hydrogenation of (**4a**) and (**4b**) in toluene induces scission of the C–O bond, giving a unique carbido cluster $[WRu_3L(CO)_{11}(\mu_4\text{-}C)(\mu\text{-}H)]$ [$L = \eta\text{-}C_5H_5$, (**3a**); or $\eta\text{-}C_5Me_5$, (**3b**)]. The crystal structures of complexes (**4b**) and (**3a**) have been determined. Crystal data for (**4b**); space group $P2_1/c$, $a = 8.993(2)$, $b = 14.565(3)$, $c = 21.090(3)$ Å, $\beta = 90.66(2)°$, $Z = 4$, $R = 0.029$, and $R' = 0.030$. Crystal data for (**3a**): space group $Pca2_1$, $a = 19.685(3)$, $b = 7.855(3)$, $c = 14.054(3)$ Å, $Z = 4$, $R = 0.033$, and $R' = 0.037$.

We have recently described the synthesis and crystal structure of heterometallic butterfly clusters with an unusual quadruply bonded CO ligand, $[WRu_3L(CO)_{11}(\mu_4\text{-}\eta^2\text{-}CO)(\mu\text{-}H)]$ [$L = \eta\text{-}C_5H_5$, (**1**); $\eta\text{-}C_5Me_5$, (**2**)].[1] The ^1H n.m.r. spectra of compounds (**1**) and (**2**) showed three hydride signals in solution, indicating that the η^2-CO ligand undergoes rapid exchange with the terminal CO ligands. After establishing that the coordinated CO ligands can undergo reorientation from terminal to π bonding, we were interested to demonstrate whether the η^2-CO ligand can undergo cleavage to yield a carbido cluster as found in the Fe_4 system.[2] In the course of these studies we have carried out the hydrogenation of both complexes (**1**) and (**2**). Unfortunately, this reaction failed to cleave the C–O bond but induced elimination of one CO ligand, giving tetrahedral trihydride clusters $[WRu_3L(CO)_{11}(\mu\text{-}H)_3]$.[3] We report here the preparation of the intended carbido clusters $[WRu_3L(CO)_{11}(\mu_4\text{-}C)(\mu\text{-}H)]$ [$L = \eta\text{-}C_5H_5$, (**3a**); $\eta\text{-}C_5Me_5$, (**3b**)] by hydrogenation of the related mixed-metal methoxymethylidyne clusters $[WRu_3L(CO)_{11}(\mu_3\text{-}COMe)]$ (**4a**) and (**4b**). Consistent with our observation, earlier results have documented the successful preparation of the heterometallic methoxymethylidyne clusters from the novel reaction of the tri-iron complex $[Fe_3(CO)_{10}(\mu\text{-}COMe)H]$ with $[Co(\eta\text{-}C_5H_5)(CO)_2]$ and with $[\{Ni(\eta\text{-}C_5H_5)(CO)\}_2]$ *via* metal–metal exchange.[4] A related study on the formation of the carbido-cluster $[Os_3Pt_2(CO)_9(\mu\text{-}OMe)(\mu_5\text{-}C)H\{P(C_6H_{11})_3\}_2]$ from the reaction of triosmium cluster $[Os_3(CO)_{10}(\mu\text{-}COMe)H]$ with $[Pt(C_2H_4)_2\{P(C_6H_{11})_3\}]$ has also been reported.[5]

Experimental

General Information and Materials.—Infrared spectra were recorded on a Perkin-Elmer 580 spectrometer or a Bomen M-100 FT-IR spectrometer, ^1H and ^{13}C n.m.r. spectra on a Bruker AM-400 (400.13 MHz) or a Varian Gemini-300 (300 MHz) instrument, and mass spectra on a JEOL-HX110 spectrometer operating in fast atom bombardment (f.a.b.) mode. All reactions were performed under a nitrogen atmosphere using deoxygenated solvents dried with an appropriate reagent. The progress of reactions was monitored by analytical thin-layer chromatography (Kieselgel 60 F_{254}, E. Merck) and the products were separated on preparative t.l.c. plates. Elemental analyses were performed at the NSC Regional Instrument Center at National Cheng Kung University, Tainan, Taiwan. The triruthenium cluster $[Ru_3(CO)_{10}(\mu\text{-}COMe)H]$[6] and the tungsten hydride complexes $[W(\eta\text{-}C_5H_5)(CO)_3H]$ and $[W(\eta\text{-}C_5Me_5)(CO)_3H]$[7] were prepared according to the published procedures. The selectively ^{13}C-enriched $[Ru_3(CO)_{10}(\mu\text{-}{*}COMe)H]$ was obtained by stirring a toluene solution of the ^{13}C-enriched $[Ru_3({*}CO)_{10}(\mu\text{-}{*}COMe)H]$ under a regular CO atmosphere [30 lbf in^{-2} (*ca.* 2.07×10^5 Pa), 100 °C, 16 h].

Preparation of $[WRu_3(\eta\text{-}C_5H_5)(CO)_{11}(\mu_3\text{-}COMe)]$ (**4a**).—A toluene solution (60 cm^3) of a mixture of $[Ru_3(CO)_{10}(\mu\text{-}COMe)H]$ (200 mg, 0.32 mmol) and $[W(\eta\text{-}C_5H_5)(CO)_3H]$ (135 mg, 0.40 mmol) was heated to reflux over a period of 65 min. After evaporation of the solvent *in vacuo* the residue was separated by t.l.c. [silica gel, dichloromethane–hexane (2:3)], giving red-brown methylidyne complex $[WRu_3(\eta\text{-}C_5H_5)(CO)_{11}(\mu_3\text{-}COMe)]$ (**4a**) (144 mg, 0.16 mmol; 50%) and the yellow carbido complex $[WRu_3(\eta\text{-}C_5H_5)(CO)_{11}(\mu_4\text{-}C)(\mu\text{-}H)]$ (**3a**) (10 mg, 0.011 mmol; 3.6%). The preparation of ^{13}C-enriched samples of (**4a**) was performed under similar conditions. Spectral data for (**4a**): mass (f.a.b., ^{102}Ru, ^{184}W), *m/z* 906 (M^+); i.r. (CH_2Cl_2), ν(CO) 2 075m, 2 033vs, 2 002s, 1 979m, 1 882vw, and 1 832vw (br) cm^{-1}; ^1H n.m.r. ($CDCl_3$, 294 K), δ 5.50 (s, 5 H) and 4.29 (s, 3 H); ^{13}C n.m.r. (CD_2Cl_2, 200 K), δ 349.3 ($COCH_3$, $J_{CW} = 113$, 1 C), 226.3 ($J_{CW} = 161$ Hz, W–CO, 2 C), 198.6 (Ru–CO, 6 C), 194.6 (Ru–CO, 3 C), and 93.8 (C_5H_5) (Found: C, 23.95; H, 0.80. Calc. for $C_{18}H_8O_{12}Ru_3W$: C, 23.95; H, 0.90%).

Preparation of $[WRu_3(\eta\text{-}C_5Me_5)(CO)_{11}(\mu_3\text{-}COMe)]$ (**4b**).—A toluene solution (45 cm^3) of a mixture of $[Ru_3(CO)_{10}(\mu\text{-}COMe)H]$ (195 mg, 0.31 mmol) and $[W(\eta\text{-}C_5Me_5)(CO)_3H]$ (160 mg, 0.40 mmol) was heated at reflux under nitrogen over 60 min. After evaporation of the solvent *in vacuo*, the residue was separated by t.l.c. [silica gel, dichloromethane–hexane (1:2)],

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Non-S.I. unit employed: atm = 101 325 Pa.

Table 1. Experimental data for the *X*-ray diffraction studies of complexes (**4b**) and (**3a**)

	Complex (**4b**)	Complex (**3a**)
Formula	$C_{23}H_{17}O_{12}Ru_3W$	$C_{17}H_6O_{11}Ru_3W$
M	972.43	873.30
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$Pca2_1$
a/Å	8.993(2)	19.685(3)
b/Å	14.565(3)	7.855(3)
c/Å	21.090(3)	14.054(3)
β/°	90.66(2)	
U/Å^3	2 762.3(9)	2 173(1)
Z	4	4
λ/Å	0.709 30	0.709 30
F(000)	1 831.64	1 607.76
D_c/g cm^{-3}		2.669
μ/mm^{-1}	5.88	7.45
No of unique data	4 858	2 596
No. with $I > 2\sigma(I)$	3 929	2 326
No. of atoms and parameters refined	57, 353	37, 289
R	0.029	0.033
R'	0.030	0.037
Goodness of fit	2.16	3.30

Table 2. Atomic co-ordinates for complex (**4b**)

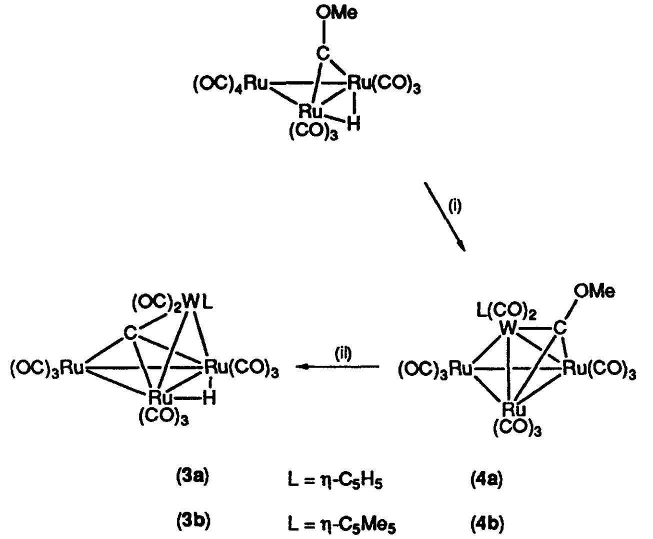
Atom	*x*	*y*	*z*
W	0.230 51(4)	0.269 865(24)	0.073 514(13)
Ru(1)	0.457 84(7)	0.259 61(5)	0.173 11(3)
Ru(2)	0.170 56(8)	0.186 91(5)	0.194 71(3)
Ru(3)	0.220 96(8)	0.374 24(5)	0.196 12(3)
C(1)	0.022 1(10)	0.288 3(7)	0.096 0(4)
C(2)	0.275 1(10)	0.401 8(7)	0.083 0(4)
C(3)	0.558 8(10)	0.364 8(7)	0.142 8(4)
C(4)	0.519 1(9)	0.276 1(6)	0.259 2(4)
C(5)	0.620 2(10)	0.178 5(7)	0.154 9(4)
C(6)	0.247 4(10)	0.147 7(7)	0.274 1(4)
C(7)	0.085 1(11)	0.074 5(8)	0.169 1(4)
C(8)	−0.010 7(10)	0.234 0(8)	0.230 1(4)
C(9)	0.032 3(13)	0.433 6(8)	0.195 1(4)
C(10)	0.321 2(12)	0.486 3(8)	0.199 6(4)
C(11)	0.226 4(10)	0.360 1(6)	0.284 9(4)
C(12)	0.171 9(10)	0.312 4(7)	−0.029 5(4)
C(13)	0.109 4(9)	0.225 8(7)	−0.021 0(3)
C(14)	0.221 7(10)	0.161 7(6)	−0.009 8(3)
C(15)	0.359 8(10)	0.208 3(6)	−0.013 4(3)
C(16)	0.331 6(9)	0.302 7(6)	−0.026 0(3)
C(17)	0.093 2(11)	0.398 9(8)	−0.049 6(4)
C(18)	−0.051 9(11)	0.201 3(9)	−0.033 0(4)
C(19)	0.198 8(12)	0.060 0(7)	−0.010 4(4)
C(20)	0.512 5(11)	0.167 3(7)	−0.013 6(4)
C(21)	0.448 4(11)	0.371 3(7)	−0.042 0(4)
C(22)	0.330 6(9)	0.166 7(6)	0.125 0(3)
C(23)	0.416 4(12)	0.010 7(7)	0.148 6(4)
O(1)	−0.108 1(7)	0.302 9(6)	0.099 2(3)
O(2)	0.301 4(8)	0.477 7(5)	0.066 4(3)
O(3)	0.620 7(8)	0.424 6(6)	0.122 8(4)
O(4)	0.555 4(7)	0.284 5(5)	0.310 7(3)
O(5)	0.718 8(7)	0.133 9(6)	0.143 4(3)
O(6)	0.294 0(8)	0.123 4(6)	0.321 3(3)
O(7)	0.030 4(9)	0.007 9(6)	0.153 0(3)
O(8)	−0.121 0(8)	0.253 3(7)	0.251 2(3)
O(9)	−0.079 3(9)	0.468 7(7)	0.195 2(4)
O(10)	0.377 3(11)	0.555 9(6)	0.204 0(3)
O(11)	0.227 6(9)	0.354 0(5)	0.337 9(3)
O(12)	0.380 3(7)	0.081 7(4)	0.103 63(24)

Table 3. Atomic co-ordinates for complex (**3a**)

Atom	*x*	*y*	*z*
W	0.012 62(3)	0.191 97(8)	0.250 00
Ru(1)	0.204 30(7)	0.091 18(20)	0.301 36(13)
Ru(2)	0.123 08(7)	0.374 18(18)	0.347 42(12)
Ru(3)	0.142 64(8)	0.280 43(21)	0.155 47(12)
C(1)	0.001 3(9)	0.080(3)	0.375 1(14)
C(2)	0.026 0(10)	−0.038(3)	0.185 8(13)
C(3)	0.219 1(9)	−0.109(3)	0.227 9(14)
C(4)	0.299 4(11)	0.163(3)	0.307 6(19)
C(5)	0.199 3(10)	−0.022(3)	0.419 4(16)
C(6)	0.209 0(11)	0.475 4(25)	0.383 4(14)
C(7)	0.101 9(10)	0.298(3)	0.471 9(13)
C(8)	0.064 3(11)	0.568 6(24)	0.356 4(14)
C(9)	0.096 7(11)	0.427(3)	0.067 0(13)
C(10)	0.147 4(10)	0.097(3)	0.068 1(13)
C(11)	0.230 3(12)	0.360(3)	0.127 5(15)
C(12)	−0.073 6(10)	0.395(3)	0.276 1(12)
C(13)	−0.104 4(9)	0.234(3)	0.266 5(21)
C(14)	−0.095 8(11)	0.163(3)	0.173 9(19)
C(15)	−0.057 2(11)	0.278(3)	0.122 6(15)
C(16)	−0.043 1(10)	0.431(3)	0.184 2(16)
C(17)	0.108 6(8)	0.140 1(23)	0.274 9(11)
O(1)	−0.006 8(8)	0.005 9(21)	0.443 7(10)
O(2)	0.032 2(8)	−0.166 8(17)	0.155 3(12)
O(3)	0.226 4(8)	−0.228 7(20)	0.189 1(13)
O(4)	0.352 8(7)	0.221 1(21)	0.314 5(15)
O(5)	0.193 7(9)	−0.089 8(23)	0.490 5(12)
O(6)	0.257 0(9)	0.538 2(19)	0.400 7(13)
O(7)	0.093 2(9)	0.242 6(18)	0.545 1(10)
O(8)	0.033 6(9)	0.684 1(21)	0.364 1(13)
O(9)	0.069 6(9)	0.522 4(24)	0.016 5(11)
O(10)	0.150 3(8)	−0.013 8(24)	0.015 6(11)
O(11)	0.285 5(9)	0.411 5(24)	0.115 4(12)

providing red-brown methoxymethylidyne complex [WRu$_3$(η-C$_5$Me$_5$)(CO)$_{11}$(μ$_3$-COMe)] (**4b**) (61 mg, 0.062 mmol) and unreacted starting material [Ru$_3$(CO)$_{10}$(μ-COMe)H] (77 mg, 0.12 mmol). The yield of (**4b**) calculated on the basis of the consumption of [Ru$_3$(CO)$_{10}$(μ-COMe)H] is 33%. Crystals of (**4b**) suitable for *X*-ray diffraction were obtained by recrystallization from dichloromethane–methanol solution at room temperature. Spectral data for (**4b**): mass (f.a.b., ^{102}Ru, ^{184}W), *m*/*z* 976 (M^+); i.r. (C$_6$H$_{12}$), ν(CO) 2 075s, 2 032vs, 2 003s, 1 975m, 1 881vw, and 1 807vw (br) cm^{-1}; ^{1}H n.m.r. (CDCl$_3$, 294 K), δ 4.35 (s, 3 H) and 1.98 (s, 15 H); ^{13}C n.m.r. (CD$_2$Cl$_2$, 294 K), δ 351.4 (*C*OCH$_3$, br), 230.5 (J_{CW} = 158 Hz, W–CO, 2 C), 198.5 (Ru–CO, 6 C), 193.6 (Ru–CO, 3 C), 104.9 (*C*$_5$Me$_5$, 5 C), 73.6 (CO*C*H$_3$, 1 C), and 10.1 (CH$_3$, 5 C) (Found: C, 28.25; H, 1.80. Calc. for C$_{23}$H$_{18}$O$_{12}$Ru$_3$W; C, 28.40; H, 1.85%).

Hydrogenation of [WRu$_3$(η-C$_5$H$_5$)(CO)$_{11}$(μ$_3$-COMe)].—A toluene solution (30 cm^3) of the complex (34 mg, 0.038 mmol) was heated at reflux under 1 atm of hydrogen. After 25 min the solvent was evaporated under vacuum and the residue separated on a preparative t.l.c. plate [dichloromethane–hexane (2:3)], providing some unreacted starting material (**4a**) (8.5 mg, 0.009 mmol, 25%) and the carbido complex [WRu$_3$(η-C$_5$H$_5$)(CO)$_{11}$(μ$_4$-C)(μ-H)] (**3a**) (11 mg, 0.013 mmol; 33%). Yellow single crystals of (**3a**) suitable for diffraction study were obtained by recrystallization from a layered solution of dichloromethane–hexane at room temperature. The preparation of ^{13}C-enriched samples of (**3a**) was performed under similar conditions. Spectral data for (**3a**): mass (f.a.b., ^{102}Ru, ^{184}W), *m*/*z* 876 (M^+); i.r. (CH$_2$Cl$_2$), ν(CO) 2 084m, 2 053vs, 2 039s, 2 020s, 1 997m, 1 966w, and 1 922vw cm^{-1}; ^{1}H n.m.r. (CDCl$_3$, 294 K), δ 5.27 (s, 5 H), and −22.33 (s, 1 H); ^{13}C n.m.r. (C$_4$D$_8$O, 294 K), δ 380.8 (1 C, J_{WC} = 80), 210.7 (W–CO, J_{WC} = 169, 2 C), 201.2 (Ru–CO, 2 C), 200.8 (Ru–CO, br, 3 C), 198.9 (Ru–CO, 2 C),



Scheme. (*i*) $[WL(CO)_3H]$; (*ii*) H_2

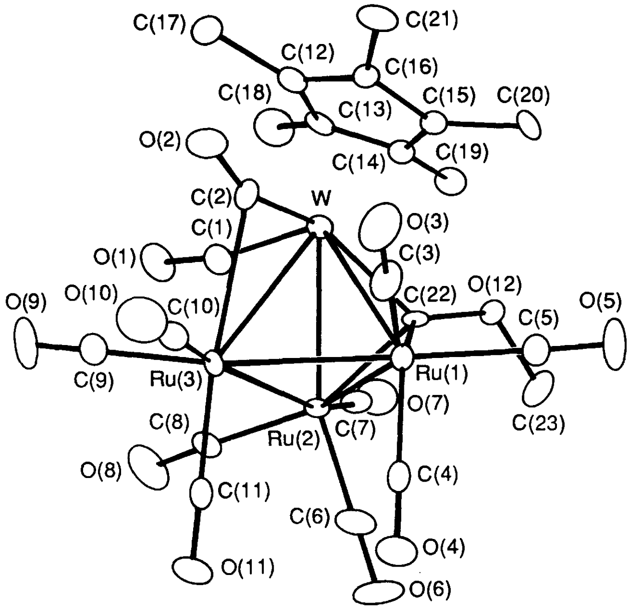


Figure 1. ORTEP diagram of the complex $[WRu_3(\eta\text{-}C_5Me_5)(CO)_{11}(\mu_3\text{-}COMe)]$ (**4b**). Bond lengths (Å): W–Ru(1) 2.918 0(9), W–Ru(2) 2.883 8(8), W–Ru(3) 3.001 6(8), Ru(1)–Ru(2) 2.834(1), Ru(1)–Ru(3) 2.754(1), Ru(2)–Ru(3) 2.766(1), W–C(22) 2.054(8), Ru(1)–C(22) 2.036(8), Ru(2)–C(22) 2.090(8), and C(22)–O(12) 1.39(1). Bond angles (°): W–C(1)–O(1) 168.9(7), W–C(2)–O(2) 157.1(7), Ru(3)–C(2)–O(2) 118.6(6), W–C(22)–O(12) 128.3(5), Ru(1)–C(22)–O(12) 124.8(6), Ru(2)–C(22)–O(12) 125.3(5), and C(22)–O(12)–C(23) 119.8 (6)

192.0 (Ru–CO, J_{CH} = 13 Hz, 2 C), and 90.6 (C_5H_5) (Found: C, 23.35; H, 0.70. Calc. for $C_{17}H_6O_{11}Ru_3W$: C, 23.40; H, 0.70%].

Hydrogenation of $[WRu_3(\eta\text{-}C_5Me_5)(CO)_{11}(\mu_3\text{-}COMe)]$.—A toluene solution (20 cm^3) of the complex (24 mg, 0.025 mmol) was heated at reflux under 1 atm of hydrogen. After 25 min the solvent was evaporated under vacuum and the residue separated on a preparative t.l.c. plate [dichloromethane–hexane (1:2)], providing some unreacted starting material (**4b**) (8 mg, 0.008 mmol; 32%) and the orange carbido complex $[WRu_3(\eta\text{-}C_5Me_5)(CO)_{11}(\mu_4\text{-}C)(\mu\text{-}H)]$ (**3b**) (2.8 mg, 0.003 mmol; 12%). Spectral data for (**3b**): mass (f.a.b., ^{102}Ru, ^{184}W), m/z 946 (M^+); i.r. (C_6H_{12}), ν(CO) 2 085m, 2 056vs, 2 048vs, 2 037m, 2 010s, 1 972w, 1 922w, and 1 870vw cm^{-1}; ^1H n.m.r. ($CDCl_3$, 294 K), δ 2.06 (s, 15 H), and −22.07 (s, 1 H) (Found: C, 27.70; H, 1.60. Calc. for $C_{22}H_{16}O_{11}Ru_3W$: C, 28.00; H, 1.70%).

X-Ray Crystallography.—Diffraction measurements were carried out on a Nonius CAD-4 fully automated four-circle diffractometer (λ = 0.709 30 Å). Unit cells were determined and refined from 25 randomly selected reflections, with 2θ in the range of 2.5—50°, obtained by using the CAD-4 automatic search, centre, index, and least-squares routines. All data reduction and structural refinement were performed using the NRCC-SDP-VAX packages. The structures were solved by the Patterson method and refined by least-squares recycle; all non-hydrogen atoms were refined with anisotropic thermal parameters. The data-collection and refinement parameters for complexes (**4b**) and (**3a**) are given in Table 1, atomic positional parameters in Tables 2 and 3, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results and Discussion

Treatment of the triruthenium complex $[Ru_3(CO)_{10}(\mu\text{-}COMe)H]$ with a slight excess of $[W(\eta\text{-}C_5H_5)(CO)_3H]$ in refluxing toluene for 45 min yielded a red-orange methoxymethylidyne cluster (**4a**) (50%) in addition to a trace amount of the yellow carbido cluster (**3a**) (3.6%). The respective pentamethylcyclopentadienyl methoxymethylidyne cluster (**4b**) was also prepared from the reaction with $[W(\eta\text{-}C_5Me_5)(CO)_3H]$ (110 °C, 60 min, 33%) under similar conditions (Scheme).

These heterometallic cluster complexes were initially characterized from spectroscopic data and by microanalysis. The ^1H n.m.r. spectra of both (**4a**) and (**4b**) show the absence of a hydride signal in the high-field region, indicating that the two hydrides from the starting materials were removed as a dihydrogen molecule. The i.r. ν(CO) spectra are similar to those of the WOs_3 complexes $[WOs_3(\eta\text{-}C_5H_5)(CO)_{11}(\mu_3\text{-}CR)]$ (R = C_6H_4Me-*p* or n-C_5H_{11}),[8] suggesting that their structures consist of a tetrahedral arrangement with a triply bridging methylidyne fragment. Furthermore, the ^{13}C n.m.r. signal of the methylidyne α-carbon of (**4a**) and (**4b**) appears at δ 349.3 and 351.4, respectively. The chemical shifts observed are very different from that (δ 264.7) reported for the WOs_3 analogue $[WOs_3(\eta\text{-}C_5H_5)(CO)_{11}(\mu_3\text{-}CC_6H_4Me\text{-}p)]$. We propose that the downfield shift is due to the deshielding effect of the electronegative oxygen atom. Such an observation has been well documented in the literature for complexes possessing the triply and doubly bridging methoxymethylidyne ligand.[4a,6]

The *X*-ray diffraction study of complex (**4b**) was carried out to confirm the structural assignment. The ORTEP diagram of (**4b**) and bond lengths and angles are shown in Figure 1. The tungsten and three ruthenium atoms form an essentially tetrahedral arrangement which is associated with 60 outer valence electrons. The methoxymethylidyne fragment is capped with a WRu_2 triangular face while its methyl substituent is tilted towards the Ru(1)–Ru(2) bond. Other structural features, such as the arrangement of the CO and C_5Me_5 ligands, are very similar to those of the structurally characterized $[WOs_3(\eta\text{-}C_5H_5)(CO)_{11}(\mu_3\text{-}CC_6H_4Me\text{-}p)]$.

The chemistry of these methoxymethylidyne complexes is particularly noteworthy. As indicated from the isolation of the trace amount of the carbido complex (**3a**) during the direct condensation of $[Ru_3(CO)_{10}(\mu\text{-}COMe)H]$ and $[W(\eta\text{-}C_5H_5)(CO)_3H]$, we decide to investigate the hydrogenation reaction of complexes (**4a**) and (**4b**). Hydrogenation of the trinuclear

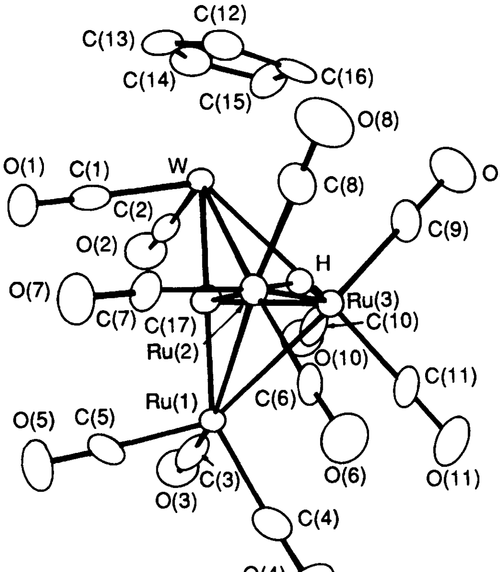


Figure 2. ORTEP diagram of the complex $[WRu_3(\eta\text{-}C_5H_5)(CO)_{11}(\mu_4\text{-}C)(\mu\text{-}H)]$ (**3a**). Bond lengths (Å): W–Ru(2) 2.941(2), W–Ru(3) 2.966(2), Ru(1)–Ru(2) 2.814(2), Ru(1)–Ru(3) 2.808(2), Ru(2)–Ru(3) 2.823(2), W–C(17) 1.99(2), Ru(2)–C(17) 2.12(2), Ru(1)–C(17) 1.96(2), and Ru(3)–C(17) 2.12(2). Bond angles (°): W–C(17)–Ru(1) 179(1), Ru(2)–C(17)–Ru(3) 83.5(6), Ru(2)–Ru(3)–C(9) 113.5(6), Ru(2)–Ru(3)–C(11) 103.8(7), Ru(3)–Ru(2)–C(8) 110.6(5), and Ru(3)–Ru(2)–C(6) 103.7(6)

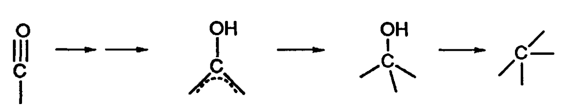
methoxymethylidyne complexes $[Ru_3(CO)_9(\mu_3\text{-}COMe)H_3]$[9] and $[Co_3(CO)_9(\mu_3\text{-}COMe)]$[10] induces destruction of the cluster framework and gives dimethyl ether as the detectable organic product. Heating a toluene solution of (**4a**) under 1 atm of hydrogen produced up to 33% of carbido complex (**3a**) and left about 25% of (**4a**) unreacted in 25 min. Extending the reaction time to 60 min failed to drive the reaction to completion, but generated severe decomposition. We believe that the low conversion into the carbido complex (**3a**) is due both to the uncontrolled destruction of (**4a**) and to the poor thermal stability of the carbido cluster itself. Similarly, hydrogenation of (**4b**) in refluxing toluene generated (**3b**) (25 min, 12%), leaving some unreacted (**4b**) (32%).

Furthermore, hydrogenation of selectively ^{13}C-enriched (**4a**), $[WRu_3(\eta\text{-}C_5H_5)(CO)_{11}(\mu_3\text{-}{*}COMe)]$, produced only selectively ^{13}C-enriched (**3a**), $[WRu_3(\eta\text{-}C_5H_5)(CO)_{11}(\mu_4\text{-}{*}C)(\mu\text{-}H)]$. This labelling study confirms that the carbide ligand is indeed derived from the methylidyne fragment. Based on these experimental observations, we propose that the methoxymethylidyne cluster is the true precursor for the carbido cluster. The stepwise transformation in the synthesis of the carbido clusters is indicated in the Scheme.

The carbido complexes were characterized by spectroscopic methods and by elemental analysis. The ^1H n.m.r. spectrum of (**3a**) indicates the presence of a C_5H_5 signal at δ 5.25 and a hydride signal at δ −22.33, suggesting that the methoxy group is eliminated (as methanol) by the interaction with dihydrogen. The ^{13}C n.m.r. spectrum of a ^{13}C-enriched sample of (**3a**) exhibits a signal at δ 380.8 ($J_{WC} = 80$ Hz) assigned to the carbido-carbon, in addition to five CO signals at δ 210.7 ($J_{WC} = 169$ Hz), 201.2, 200.8 (br), 198.9, and 192.0 ($J_{CH} = 13$ Hz) with an intensity ratio 2:2:3:2:2. The broad CO signal at δ 200.8 is clearly due to the CO ligands of a $Ru(CO)_3$ fragment which undergoes relatively slow, localized three-fold rotation. Furthermore, from the characteristic J_{WC} and J_{CH} coupling, the signals at δ 201.7 and 192.0 are assigned to the W–CO ligands and to the Ru–CO ligands *trans* to the bridging hydride, respectively.

The *X*-ray diffraction study on complex (**3a**) was also carried out to confirm the structure. As indicated in Figure 2, the molecule consists of a WRu_3 butterfly arrangement with the carbide atom C(17) located between the wing-tip atoms W and Ru(1) with W–C(17)–Ru(1) 179(1)° and centred over the hinge Ru(2)–Ru(3) bond with Ru(2)–C(17)–Ru(3) 83.5(6)°. Each ruthenium atom is associated with three terminal CO ligands and the tungsten atom is co-ordinated by two terminal CO ligands and a C_5H_5 ligand. In general, the core arrangement is similar to that of the WRu_3 complexes (**1**) and (**2**) which possess a η^2-CO ligand but differs from that of the anionic Fe_3M carbido clusters which have the heterometal at a hinge site.[11] The parameters associated with the carbide atom resembles those of the related Fe_4 and Ru_4 carbido clusters,[12] showing short M(wing-tip)–C(carbide) distances [av. 1.98(2) Å], long M(hinge)–C(carbide) distances [av. 2.12(2) Å], and a relatively acute dihedral angle [102.55(6)°]. Finally, the bridging hydride is associated with the hinge Ru(2)–Ru(3) bond with two enlarged Ru–Ru–CO angles [110.6(5) and 113.5(6)°].

In summary, tetranuclear transition-metal clusters containing an exposed carbido-carbon are convenient models to examine the properties of surface carbides.[13] Their synthesis has been achieved by several different methods; none however involves direct hydrogenation of the methoxymethylidyne group. The successful synthesis of the carbido clusters (**3a**) and (**3b**) illustrates the high activity of the methylidyne C–O linkage. In addition, since the μ_3-OMe fragment is derived from a CO ligand and the methyl group is isoelectronic with a hydrogen atom, the sequence established in equation (1) can be considered as a model for the formation of surface carbides in the Fischer–Tropsch synthesis.[14]



(1)

Finally, a tetranuclear cluster possessing a η^2-COMe group has been observed, $[Fe_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}COMe)H]$.[15] Therefore, formation of a butterfly intermediate with this type of η^2-COMe interaction, followed by elimination of methanol, is a plausible pathway for the transformation from methoxymethylidyne to carbide. Interestingly, the Fe_4 cluster reacts further with strong acid to give methane which originates from the η^2-COMe fragment as indicated by selective ^{13}C-labelling studies. Our experiments reported here are complementary to the chemistry of the above-mentioned Fe_4 cluster and provide unambiguous evidence to support that the mechanism involving a carbido cluster is responsible for the release of methane.

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References

1 Y. Chi, F-J. Wu, B-J. Liu, C-C. Wang, and S-L. Wang, *J. Chem. Soc., Chem. Commun.*, 1989, 873; S-M. Peng, G-H Lee, Y. Chi, C-L. Peng, and L-S. Hwang, *J. Organomet. Chem.*, 1989, **371**, 197.
2 E. M. Holt, K. H. Whitmire, and D. F. Shriver, *J. Organomet. Chem.*, 1981, **213**, 125; K. H. Whitmire and D. F. Shriver, *J. Am. Chem. Soc.*, 1981, **103**, 6754.

3 Y. Chi, C-Y. Cheng, and S-L. Wang, *J. Organomet. Chem.*, 1989, **378**, 45.

4 A. A. Aitchison and L. J. Farrugia, *Organometallics*, (*a*) 1986, **5**, 1103, (*b*) 1987, **6**, 819.

5 L. J. Farrugia, A. D. Miles, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1985, 2437.

6 J. B. Keister, M. W. Payne, and M. J. Muscatella, *Organometallics*, 1983, **2**, 219.

7 G. L. Kubas, H. J. Wasserman, and R. R. Ryan, *Organometallics*, 1985, **4**, 2012; G. J. Kubas, *Inorg. Chem.*, 1983, **22**, 692.

8 L. Busetto, M. Green, B. Hesser, J. A. K. Howard, J. C. Jeffrey, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1983, 519; Y. Chi, G-H. Lee, S-M. Peng, and C-H Wu, *Organometallics*, 1989, **8**, 1574.

9 J. B. Keister, *J. Chem. Soc., Chem. Commun.*, 1979, 214; J. B. Keister, M. W. Payne, and M. J. Muscatella, *Organometallics*, 1983, **2**, 219.

10 G. Fachinetti, R. Lazzaroni, and S. Pucci, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 1063.

11 J. W. Kolis, E. M. Holt, J. A. Hriljac, and D. F. Shriver, *Organometallics* 1984, **3**, 496; J. A. Hriljac, P. N. Swepston, and D. F. Shriver, *ibid.*, 1985, **4**, 158.

12 A. G. Cowie, B. F. G. Johnson, J. Lewis, and P. R. Raithby, *J. Organomet. Chem.*, 1986, **306**, C63; *J. Chem. Soc., Chem. Commun.*, 1984, 1710; J. S. Bradley, G. B. Ansell, M. E. Leonowicz, and E. W. Hill, *J. Am. Chem. Soc.*, 1981, **103**, 4968; J. H. Davis, M. A. Beno, J. M. Williams, M. Tachikawa, and E. L. Muetterties, *Proc. Natl. Acad. Sci. USA*, 1981, **78**, 668; M. A. Beno, J. M. Williams, M. Tachikawa, and E. L. Muetterties, *J. Am. Chem. Soc.*, 1981, **103**, 4542.

13 M. Tachikawa and E. L. Muetterties, *Prog. Inorg. Chem.*, 1981, **28**, 203; J. S. Bradley, *Adv. Organomet. Chem.*, 1983, **22**, 1; B. F. G. Johnson, J. Lewis, W. J. H. Nelson, N. Nicholls, and M. D. Vargas, *J. Organomet. Chem.*, 1983, **249**, 255.

14 C. Masters, *Adv. Organomet. Chem.*, 1979, **17**, 61; P. M. Maitlis, *Pure Appl. Chem.*, 1989, **61**, 1747.

15 K. Whitmire and D. F Shriver, *J. Chem. Soc., Chem. Commun.*, 1980, 780; P. A. Dawson, B. F. G. Johnson, J. Lewis, and P. R. Raithby, *ibid.*, p. 781.

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