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Synthesis, Characterization, and Reactivity of W_2Ru_3 Clusters That Contain Oxo and Carbido Ligands, Obtained by Direct C−O Bond Activation

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Treatment of $CpWRu_3(CO)_{12}(\mu\text{-H})$ with $CpW(CO)_3H$ in refluxing heptane afforded the cluster compound $Cp_2W_2Ru_3(CO)_{13}$ (**1**). Single-crystal X-ray analysis indicates a trigonal-bipyramidal cluster arrangement with both W atoms located at the equatorial positions. Pyrolysis of **1** in refluxing toluene gave the oxo−carbido cluster $CpW(O)CpWRu_3(\mu_5\text{-C})(CO)_{11}$ (**2a**) in moderate yield, whereas the condensation of $LWRu_3(CO)_{12}(\mu\text{-H})$ and $L'W(CO)_3H$ ($L = L' = Cp^*$; L, $L' = Cp$, Cp^* or Cp^*, Cp) afforded the derivatives $LW(O)L'WRu_3(\mu_5\text{-C})(CO)_{11}$ (**2b**, $L = L' = Cp^*$; **2c**, $L = Cp$; $L' = Cp^*$) exclusively. A combination of spectroscopic and structural data suggests that the complexes **2** adopt a wingtip-bridged butterfly structure and possess a terminal oxo and an interstitial carbide ligand. Thus, the transformation from **1** to **2** illustrates an example of metal-assisted cleavage of the carbonyl C−O bond. Mechanistic considerations based on the result of ^{17}O labeling studies are discussed. Furthermore, extensive heating of **2b**,**c** in toluene leads via elimination of two CO ligands to the formation of the new cluster complexes $LL'W_2(\mu\text{-O})Ru_3(\mu_5\text{-C})(CO)_9$ (**3b**, $L = L' = Cp^*$; **3c**, $L = Cp$; $L' = Cp^*$), in which a distorted-square-pyramidal core structure has been confirmed by single-crystal X-ray analysis. Treatment of **3** with CO gives regeneration of the complexes **2** in high yield.

The chemistry of carbido cluster compounds has developed in recent years to constitute a distinct research domain.[1] For the carbido clusters comprised of metals in low oxidation states, it has been established that the interstitial carbide atoms can be derived from the activation of C−X bonds (X = H, SMe, OMe, Cl),[2] the scission of coordinated isonitrile[3] and acetylide ligands,[4] and the proton-induced reduction of CO ligands[5] or from disproportionation of the CO ligands.[6] Of particular interest is the last reaction, involving the CO disproportionation

$$2CO \rightarrow C + CO_2$$

which has provided many valuable insights into the activation of CO on metal surfaces.[7] However, there are a few examples in the literature in which the oxo and carbido ligands are originating from a single CO ligand through direct activation of the C−O bond and are retained in the coordination sphere of the resulting metal complexes. These examples include the work of Wolczanski on CO dissociation by the tantalum complex $(silox)_3Ta$ or across the M≡M bond of tungsten siloxide complexes (silox = $^tBu_3SiO$).[8] In addition, Chisholm and co-workers have reported the reductive cleavage of CO using tungsten alkoxide clusters to afford formation of oxo−carbido alkoxide complexes,[9] while Johnson and Braga have documented the synthesis of the carbido

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cluster $Ru_6C(CO)_{15}(C_{16}H_{16}\text{-}\mu_2\text{-}O)$ by direct heating,[10] in which the departing oxo ligand is unexpectedly trapped by the [2,2]paracyclophane ligand. Finally, the oxo and carbido ligands in the low-nuclearity cluster $Cp_2Mo_2Ru_4(\mu\text{-}O)(\mu_6\text{-}C)(CO)_{12}$ has been assumed to arise from the direct cleavage of the C−O bond during cluster formation.[11]

In this paper, we report the synthesis and characterization of heterometallic carbonyl clusters $Cp_2W_2Ru_3(CO)_{13}$ (**1**) and the two different types of oxo−carbido cluster complexes $LW(O)L'WRu_3(\mu_5\text{-}C)(CO)_{11}$ (**2a**, L = L′ = Cp; **2b**, L = L′ = Cp*; **2c**, L = Cp; L′ = Cp*) and $LL'W_2(\mu\text{-}O)Ru_3(\mu_5\text{-}C)(CO)_9$ (**3b**, L = L′ = Cp*; **3c**, L = Cp; L′ = Cp*). Moreover, formation of the oxo and carbido ligand fragments during assembling of cluster complexes **2** represents a unique example involving direct scission of the C−O bond, which supplements the cluster-assisted scission of the alkyne C−C triple bond that was previously documented in the literature.[12] Portions of this work have been reported as a preliminary communication.[13]

Experimental Section

General Information and Materials. Infrared spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer. ^1H and ^{13}C NMR spectra were recorded on Bruker AM-400 and AMX-300 instruments; chemical shifts are quoted with respect to the internal standard tetramethylsilane (^1H and ^{13}C NMR). The Bruker AMX-300 instrument was used to obtain the ^{17}O NMR spectra. Mass spectra were obtained on a JEOL-HX110 instrument operating in fast atom bombardment (FAB) mode. All reactions were performed under a nitrogen atmosphere and, using deoxygenated solvents dried with an appropriate reagent. The progress of reactions was monitored by analytical thin-layer chromatography (5735 Kieselgel 60 F_{254}, Merck), and the products were separated on commercially available preparative thin-layer chromatographic plates (Kieselgel 60 F_{254}, Merck). The complexes $CpWRu_3(CO)_{12}(\mu\text{-}H)$ and $Cp^*WRu_3(CO)_{12}(\mu\text{-}H)$ were prepared from the reaction of $[LW(CO)_3][PPh_4]$ (L = Cp and Cp*) with $Ru_3(CO)_{12}$ in refluxing THF solution, followed by addition of 1.2 equiv of trifluoroacetic acid in CH_2Cl_2 solution at room temperature. Elemental analyses were performed at the NSC Regional Instrumentation Center at National Cheng Kung University, Tainan, Taiwan.

For preparation of the ^{17}O-enriched complexes, $Ru_3(CO)_{12}$ was first reacted with 46 atom % of $^{12}C^{17}O$ gas (Isotec Inc., 20 mL) in a sealed reaction vessel (30 mL) at 120 °C for 2 days. The resulting $Ru_3(CO)_{12}$ sample was reacted with $[LW(CO)_3][PPh_4]$ (L = Cp and Cp*) and with trifluoroacetic acid to afford the ^{17}O-enriched complexes $CpWRu_3(CO)_{12}(\mu\text{-}H)$ and $Cp^*WRu_3(CO)_{12}(\mu\text{-}H)$, which in turn were used for preparation of the desired oxo−carbido clusters.

Reaction of $CpWRu_3(CO)_{12}(\mu\text{-}H)$ with $CpW(CO)_3H$. A heptane solution (70 mL) of $CpWRu_3(CO)_{12}(\mu\text{-}H)$ (400 mg, 0.45 mmol) and $CpW(CO)_3H$ (601 mg, 1.80 mmol) was heated to reflux and heating was continued for 1.5 h, during which time the color turned from orange to dark red. After evaporation of the solvent in vacuo, the residue was separated by thin-layer chromatography. Development with a 1:1 mixture of dichloromethane and hexane produced three major bands, which were removed from the TLC plates to yield 15 mg of unreactive $CpWRu_3(CO)_{12}(\mu\text{-}H)$ (0.017 mmol, 3.8%), 126 mg of $CpWRu_3(CO)_{11}(\mu\text{-}H)_3$ (0.146 mmol, 32%), and 150 mg of the dark brown cluster $Cp_2W_2Ru_3(CO)_{13}$ (**1**; 0.129 mmol, 29%).

Spectral data for **1**: MS (FAB, ^{102}Ru, ^{184}W) m/z 1168 (M^+); IR (C_6H_{12}) ν(CO) 2073 (w), 2053 (vs), 2018 (m), 2005 (m), 1986 (s), 1961 (vw), 1912 (vw), 1859 (vw, br), 1838 (vw, br) cm^{-1}; ^1H NMR ($CDCl_3$, 294 K) δ 5.51 (s, 5H), 5.48 (s, 5H); ^{13}C NMR (toluene-d_8, 294 K) δ 230.6 (2C, J_{WC} = 148 Hz), 228.2 (2C, J_{WC} = 145 Hz), 204.4 (3C), 193.4 (2C, br), 191.5 (2C, br), 189.5 (2C, br), 94.5 (C_5H_5), 90.4 (C_5H_5). Anal. Calcd for $C_{23}H_{10}O_{13}Ru_3W_2\cdot CH_2Cl_2$: C, 23.06; H, 0.97. Found: C, 23.30; H, 1.02.

Pyrolysis of 1. A toluene solution (50 mL) of **1** (110 mg, 0.094 mmol) was refluxed for 1 h under nitrogen, during which time the color turned from orange to dark red. After evaporation of the solvent in vacuo, the residue was separated by thin-layer chromatography. Development with a 1:1 mixture of dichloromethane and hexane produced three major bands, which were removed from the TLC plates to afford 50 mg of unreactive **1** (0.043 mmol, 46%) and 12 mg of $CpW(O)CpWRu_3(\mu_5\text{-}C)(CO)_{11}$ (**2a**; 0.011 mmol, 12%).

Spectral data for **2a**: MS (FAB, ^{102}Ru, ^{184}W) m/z 1140 (M^+); IR (C_6H_{12}) ν(CO), 2068 (m), 2037 (vs), 2026 (m, sh), 1999 (s), 1983 (w), 1966 (w) 1951 (vw), 1920 (vw) cm^{-1}; ^1H NMR ($CDCl_3$, 294 K) δ 6.09 (s, 5H), 4.76 (s, 5H); ^{13}C NMR ($CDCl_3$, 294 K) δ 440.8 (μ_5-C, J_{WC} = 87 Hz), 207.1 (2CO, J_{WC} = 157 Hz), 200.3 (6CO), 197.1 (3CO), 102.5 (C_5H_5), 87.8 (C_5H_5). Anal. Calcd for $C_{22}H_{10}O_{12}Ru_3W_2$: C, 23.24; H, 0.89. Found: C, 23.35; H, 1.05.

Reaction of $Cp^*WRu_3(CO)_{12}(\mu\text{-}H)$ with $Cp^*W(CO)_3H$. A heptane solution (25 mL) of $Cp^*WRu_3(CO)_{12}(\mu\text{-}H)$ (34 mg, 0.035 mmol) and $Cp^*W(CO)_3H$ (47 mg, 0.116 mmol) was heated to reflux, and heating was continued for 1.5 h under nitrogen, during which time the color turned from orange to dark red. After evaporation of the solvent in vacuo, the residue was separated by thin-layer chromatography. Development with a 1:2 mixture of dichloromethane and hexane produced three major bands, which were removed from the TLC plates by extraction to afford 1.3 mg of unreactive $Cp^*WRu_3(CO)_{12}(\mu\text{-}H)$ (0.001 mmol, 3%), 14 mg of $Cp^*WRu_3(CO)_{11}(\mu\text{-}H)_3$ (0.015 mmol, 43%), and 11.1 mg of the black cluster $Cp^*_2W_2(O)Ru_3(\mu_5\text{-}C)(CO)_{11}$ (**2b**; 0.009 mmol, 26%).

Spectral data for **2b**: MS (FAB, ^{102}Ru, ^{184}W) m/z 1275 (M^+); IR (C_6H_{12}) ν(CO) 2059 (s), 2022 (vs), 2006 (m), 1990 (s), 1955 (w), 1934 (w), 1802 (vw, br) cm^{-1}; IR (KBr) ν(W≡O) 928 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 294 K) δ 2.14 (s, 15H), 1.72 (s, 15H); ^{13}C NMR (CD_2Cl_2, 200 K) δ 441.5 (μ_5-C, J_{WC} = 88 and 101 Hz), 223.0 (2CO, br), 212.0 (2CO, J_{WC} = 161 Hz), 205.8 (2CO, br), 201.4 (2CO), 199.6 (2CO, br), 192.2 (1CO), 117.1 (C_5Me_5), 102.3 (C_5Me_5), 11.6 (C_5Me_5), 9.7 (C_5Me_5); ^{17}O NMR ($CDCl_3$, 297 K) δ 832.9 (1O, W≡O, br), 388.1 (6O, br), 377.3 (2CO), 355.7 (3CO). Anal. Calcd for $C_{32}H_{30}O_{12}Ru_3W_2$: C, 30.09; H, 2.37. Found: C, 30.03; H, 2.47.

Reaction of $Cp^*WRu_3(CO)_{12}(\mu\text{-}H)$ with $CpW(CO)_3H$. A heptane solution (50 mL) of $Cp^*WRu_3(CO)_{12}(\mu\text{-}H)$ (72.3 mg, 0.075 mmol) and $CpW(CO)_3H$ (99 mg, 0.296 mmol) was heated at reflux for 100 min under nitrogen, during which time the color turned from orange to dark red. After evaporation of the solvent in vacuo, the residue was separated by thin-layer chromatography using a 1:2 mixture of dichloromethane and hexane, giving 30.8 mg of $Cp^*WRu_3(CO)_{11}(\mu\text{-}H)_3$ (0.033 mmol, 44%) and 33.6 mg of the black cluster $CpW(O)Cp^*WRu_3(\mu_5\text{-}C)(CO)_{11}$ (**2c**; 0.028 mmol, 37%).

Reaction of $CpWRu_3(CO)_{12}(\mu\text{-}H)$ with $Cp^*W(CO)_3H$. A heptane solution (50 mL) of $CpWRu_3(CO)_{12}H$ (100 mg, 0.112 mmol) and $Cp^*W(CO)_3H$ (183 mg, 0.453 mmol) was heated at reflux for 1.5 h under nitrogen, during which time the color turned from orange to dark red. After evaporation of the solvent in vacuo, the residue was separated by thin-layer

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Table 1. X-ray Structural Data of Complexes 1, 2c, and 3c[a]

	1	**2c**	**3c**
formula	$C_{23}H_{10}O_{13}Ru_4W_2\cdot CH_2Cl_2$	$C_{27}H_{20}O_{12}Ru_3W_2$	$C_{25}H_{20}O_{10}Ru_3W_2$
mol wt	1250.15	1206.34	1151.33
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a (Å)	12.802(3)	19.518(2)	11.051(2)
b (Å)	14.575(3)	16.327(2)	15.523(1)
c (Å)	16.752(4)	20.679(2)	17.092(2)
α (deg)	73.05(2)		
β (deg)	81.55(2)	105.838(7)	91.89(2)
γ (deg)	83.40(2)		
V (Å^3)	2949(1)	6339(2)	2930.4(7)
Z	4	8	4
D_c (g/cm^3)	2.816	2.528	2.610
F(000)	2272	4406	2095
2θ(max) (deg)	45.0	50.0	50.0
hkl ranges	−13 to +13, 0−15, −16 to +18	−23 to +22, 0−19, 0−24	−13 to +13, 0−18, 0−20
cryst size, mm	0.10 × 0.15 × 0.20	0.22 × 0.25 × 0.60	0.20 × 0.20 × 0.25
μ(Mo Kα), cm^{-1}	94.76	83.66	95.38
transmissn: max, min	1.000, 0.489	1.000, 0.800	1.000, 0.749
no. of data in refinement	5934 with $I > 2\sigma(I)$	8140 with $I > 2\sigma(I)$	4225 with $I > 2\sigma(I)$
no. of atoms and params	112, 764	128, 794	60, 362
weight modifier, g	0.000 05		
max Δ/σ ratio	0.022	0.0086	0.0108
R_F; R_w	0.034; 0.032	0.033; 0.030	0.032; 0.033
GOF	1.88	1.88	2.76
D map, max/min, e/Å^3	2.33/−1.68	1.13/−1.10	1.00/−1.40

[a] Features common to all determinations: λ(Mo Kα) = 0.7107 Å; minimize function $\Sigma(w|F_o - F_c|^2)$, weighting scheme: $w^{-1} = \sigma^2(F_o) + |g|F_o^2$; GOF $= [\Sigma w|F_o - F_c|^2/(N_o - N_v)]^{1/2}$ (N_o = number of observations; N_v = number of variables).

Table 2. Selected Bond Distances (Å) and Angles (deg) of 1 (Esd's in Parentheses)

W(1)−W(2)	2.941(1)	W(1)−Ru(1)	2.885(1)
W(1)−Ru(2)	2.880(1)	W(1)−Ru(3)	2.875(1)
W(2)−Ru(1)	2.913(1)	W(2)−Ru(2)	2.843(1)
W(2)−Ru(3)	2.905(1)	Ru(1)−Ru(2)	2.765(2)
Ru(2)−Ru(3)	2.785(2)		
∠W(1)−C(1)−O(1)	159.0(10)	∠W(1)−C(2)−O(2)	158.9(11)
∠W(2)−C(3)−O(3)	163.6(10)	∠W(2)−C(4)−O(4)	164.0(11)

chromatography using a 2:3 mixture of dichloromethane and hexane, giving 2.6 mg of unreactive $CpWRu_3(CO)_{12}(\mu\text{-}H)$ (0.003 mmol, 2.7%), 14.4 mg of $CpWRu_3(CO)_{11}(\mu\text{-}H)_3$ (0.017 mmol, 15%), and 51.5 mg of the black pentanuclear cluster $CpW(O)Cp^*WRu_3(\mu_5\text{-}C)(CO)_{11}$ (**2c**; 0.043 mmol, 38%).

Spectral data for **2c**: MS (FAB, ^{102}Ru, ^{184}W) m/z 1210 (M^+); IR (C_6H_{12}) ν(CO) 2062 (m), 2028 (vs), 1992 (s), 1961 (w), 1940 (vw) cm^{-1}; IR (KBr) ν(W≡O) 935 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 294 K) δ 6.14 (s, 5H), 1.82 (s, 15H); ^{13}C NMR ($CDCl_3$, 294 K) δ 442.7 (μ_5-C, J_{WC} = 88 and 101 Hz), 211.2 (2CO, J_{WC} = 159 Hz), 202.4 (6CO, br), 196.8 (3CO, br), 103.2 (C_5H_5), 102.7 (C_5Me_5), 10.4 (C_5Me_5). Anal. Calcd for $C_{27}H_{20}O_{12}Ru_3W_2$: C, 26.86; H, 1.67. Found: C, 26.60; H, 1.73.

Thermolysis of 2b. A toluene solution (25 mL) of **2b** (18 mg, 0.014 mmol) was heated at reflux for 1 h under nitrogen. After evaporation of the solvent in vacuo, the residue was separated by thin-layer chromatography using a 2:3 mixture of dichloromethane and hexane, giving 12 mg of $Cp^*_2W_2(\mu\text{-}O)Ru_3(\mu_5\text{-}C)(CO)_9$ (**3b**; 0.01 mmol, 70%) as a dark brown solid.

Spectral data for **3b**: MS (FAB, ^{102}Ru, ^{184}W) m/z 1222 (M^+); IR (C_6H_{12}) ν(CO) 2049 (m), 2019 (vs), 2010 (m), 1980 (s), 1972 (w), 1955 (w), 1943 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 294 K) δ 2.31 (s, 15H), 1.92 (s, 15H); ^{13}C NMR ($CDCl_3$, 294 K) CO, δ 210.2 (2CO, br), 205.9 (3CO), 203.0 (2CO, br), 201.0 (2CO, br); δ 412.5 (μ_5-C, J_{WC} = 105 and 56 Hz), 115.0 ($C_5\mathrm{Me}_5$), 111.2 ($C_5\mathrm{Me}_5$), 14.0 (C_5Me_5), 13.2 (C_5Me_5). Anal. Calcd for $C_{30}H_{30}O_{10}Ru_3W_2$: C, 29.5; H, 2.48. Found: C, 29.62; H, 2.67.

Treatment of 3b with CO. A toluene solution (20 mL) of **3b** (20 mg, 0.016 mmol) was refluxed under CO at 1 atm for 1 h. After evaporation of the solvent in vacuo, the residue was separated by thin-layer chromatography, giving 15 mg of **2b** (0.012 mmol, 78%).

Thermolysis of 2c. A toluene solution (35 mL) of **2c** (60 mg, 0.05 mmol) was heated at reflux for 1 h under nitrogen. After evaporation of the solvent in vacuo, the residue was separated by thin-layer chromatography using a 2:3 mixture of dichloromethane and hexane, giving 12 mg of unreacted starting material (19%) and 19 mg of dark brown $Cp^*CpW_2(\mu\text{-}O)Ru_3(\mu_5\text{-}C)(CO)_9$ (**3c**; 0.017 mmol, 41%).

Spectral data for **3c**: MS (FAB, ^{102}Ru, ^{184}W) m/z 1290 (M^+); IR (C_6H_{12}) ν(CO) 2053 (m), 2024 (vs), 2013 (m), 1984 (s), 1972 (vw), 1960 (w), 1951 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 294 K) δ 5.56 (s, 5H), 2.33 (s, 15H); ^{17}O NMR ($CDCl_3$, 223 K) δ 589.9 (br, μ-O), 374.8 (br, 2CO), 369.3 (3CO), 362.0 (2CO), 347.0 (2CO). Anal. Calcd for $C_{25}H_{20}O_{10}Ru_3W_2$: C, 26.08; H, 1.75; Found: C, 26.25; H, 1.68.

Treatment of 3c with CO. A toluene solution (20 mL) of **3c** (26 mg, 0.022 mmol) was refluxed under CO at 1 atm for 1 h. After evaporation of the solvent in vacuo, the residue was separated by thin-layer chromatography, giving 19 mg of dark brown **2c** (0.015 mmol, 67%).

X-ray Crystallography. The X-ray diffraction measurements were carried out on a Nonius CAD-4 diffractometer. Lattice parameters were determined from 25 randomly selected high-angle reflections. Three standard reflections were monitored every 3600 s. No significant change in intensities, due to crystal decay, was observed over the course of all data collection. Intensities of the diffraction signals were corrected for Lorentz, polarization, and absorption effects (ι scans). The structure was determined using the NRCC-SDP-VAX package. All the non-hydrogen atoms were refined with anisotropic temperature factors, and the hydrogen atoms were placed at idealized positions with $U_H = U_C + 0.1$. The crystallographic refinement parameters of complexes **1**, **2c**, and **3c** are given in Table 1, while their selective bond distances and angles are presented in Tables 2−4, respectively.

Results

The dark brown cluster complex $Cp_2W_2Ru_3(CO)_{13}$ (**1**) was obtained in a modest amount from a direct reaction involving the heterometallic cluster $CpWRu_3(CO)_{12}(\mu\text{-}H)$ and an excess of $CpW(CO)_3H$ in refluxing heptane.

Table 3. Selected Bond Distances (Å) and Angles (deg) of 2c (Esd's in Parentheses)

W(1)–Ru(1)	2.902(1)	W(1)–Ru(2)	2.872(1)
W(2)–Ru(1)	3.025(1)	W(2)–Ru(2)	3.020(1)
W(2)–Ru(3)	2.842(1)	Ru(1)–Ru(3)	2.801(1)
Ru(2)–Ru(3)	2.836(2)	W(1)–O(12)	1.692(8)
W(1)–C(12)	2.051(10)	W(2)–C(12)	2.099(10)
Ru(1)–C(12)	2.068(9)	Ru(2)–C(12)	1.991(10)
Ru(3)–C(12)	2.191(10)		
∠W(1)–C(1)–O(1)	129.3(10)	∠Ru(2)–C(1)–O(1)	146.6(11)
∠W(1)–C(12)–W(2)	148.4(5)	∠W(1)–C(12)–Ru(3)	128.5(5)
∠W(2)–C(12)–Ru(3)	82.9(4)	∠Ru(1)–C(12)–Ru(2)	164.0(5)
∠O(12)–W(1)–C(12)	102.9(4)		

Table 4. Selected Bond Distances (Å) and Angles (deg) of 3c (Esd's in Parentheses)

W(1)–W(2)	2.6741(7)	W(1)–Ru(1)	2.919(1)
W(1)–Ru(3)	2.914(1)	W(2)–Ru(1)	2.706(1)
W(2)–Ru(2)	2.944(1)	W(2)–Ru(3)	2.693(1)
Ru(1)–Ru(2)	2.833(1)	Ru(2)–Ru(3)	2.847(2)
W(1)–O(10)	1.892(7)	W(2)–O(10)	1.921(7)
W(1)–C(10)	1.877(11)	W(2)–C(10)	2.186(10)
Ru(1)–C(10)	2.191(11)	Ru(2)–C(10)	2.005(11)
Ru(3)–C(10)	2.137(11)		
∠W(1)–O(10)–W(2)	89.1(3)	∠W(1)–C(10)–Ru(2)	170.9(6)
∠Ru(1)–C(10)–Ru(3)	152.2(5)		

After that, the products were separated by thin-layer chromatography and purified by recrystallization from a mixture of CH_2Cl_2 and CH_3OH at room temperature. The spectroscopic analysis confirmed that complex **1** is structurally identical with the partially characterized cluster complex $Cp_2W_2Ru_3(CO)_{13}$, a product was first synthesized in low yield from a photolysis reaction between $[CpW(CO)_3]_2$ and $Ru_3(CO)_9BH_5$.[14] In addition, the trihydride cluster product $Cp^*WRu_3(CO)_{11}(\mu\text{-}H)_3$ was produced in small amounts due to a result of hydrogenation of $CpWRu_3(CO)_{12}(\mu\text{-}H)$,[15] where the hydrogen may be produced by decomposition of the second hydride complex $CpW(CO)_3H$.

In our case, a single-crystal X-ray diffraction study of **1** revealed that the asymmetric unit contains one CH_2Cl_2 solvate molecule and two crystallographically distinct but structurally similar molecules. A perspective view of one such molecule is indicated in Figure 1, which clearly exhibits a distorted-trigonal-bipyramidal metal framework with three terminal CO ligands attached to each of the Ru atoms and two semibridging CO groups coordinated on each of the W atoms, with the W–CO angles being in the range 159–164(1)°. Moreover, the apical sites of the TBP framework are occupied by two $Ru(CO)_3$ fragments, while the $CpW(CO)_2$ fragments are located at the equatorial sites. The unique W(1)–W(2) bond (2.941(1) Å) is considerably longer than the W–Ru distances (2.843(1)–2.913(1) Å) and the Ru–Ru distances (2.765(2) and 2.785(2) Å); the latter are the shortest metal–metal bonds of the whole molecule. Similar variations of metal–metal bond distances have been observed in the closely related pentametallic TBP cluster $Cp_2Mo_2Os_3(CO)_{12}(\mu\text{-}H)_2$,[16] in which the distance Mo–Mo = 3.028(1) Å is also found to be much shorter than the Os–Os distances of 2.834–2.844(1) Å. As the radius of the W (or Mo) ion in a +1 oxidation state is comparable to that of the Ru (or Os) atom, this variation of M–M distances implies that the interligand repulsion around the W centers may be much greater than that of the Ru atoms, which leads to the uneven expansion of the framework in the close proximity of the W atoms.

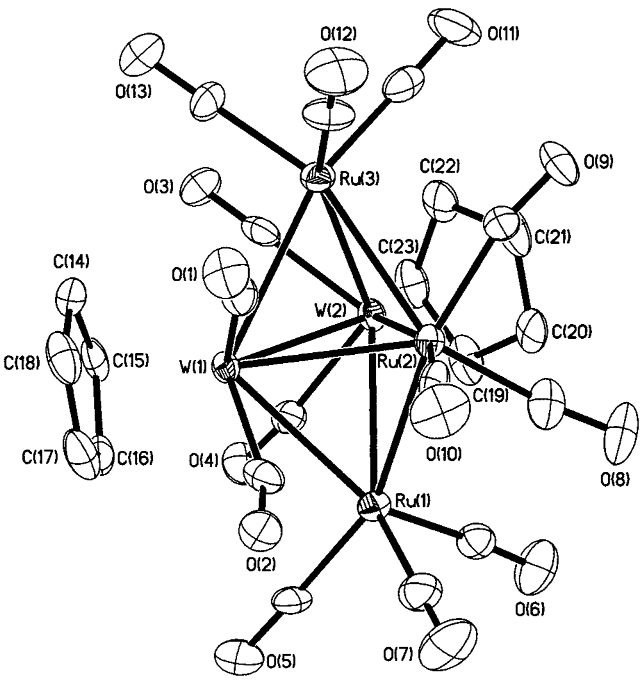
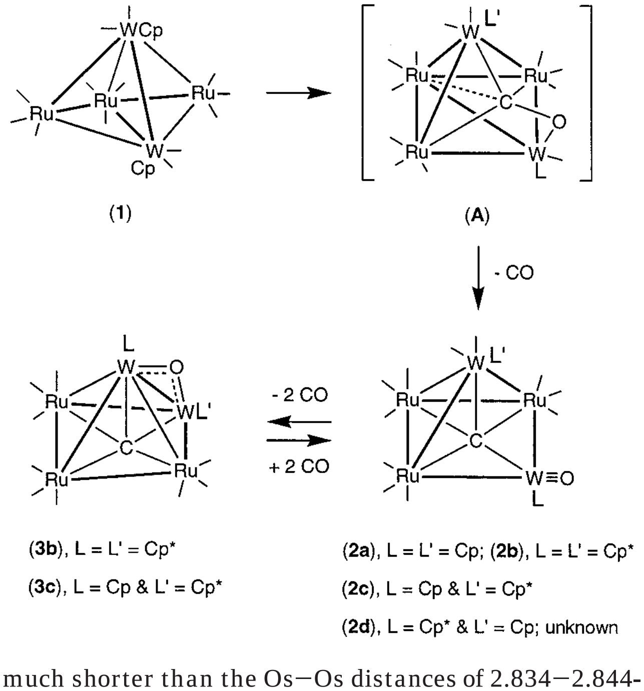


Figure 1. Molecular structure and atomic labeling scheme of $Cp_2W_2Ru_3(CO)_{13}$ (**1**) with thermal ellipsoids shown at the 30% probability level.

Scheme 1



In a remarkable further development we discovered that complex **1** slowly eliminated one CO in refluxing toluene solution (30 min) to afford the oxo–carbido complex $CpW(O)CpWRu_3(\mu_5\text{-}C)(CO)_{11}$ (**2a**) in 22% yield, based on the amount of starting material **1** depleted during reaction (Scheme 1). The two additional oxo–

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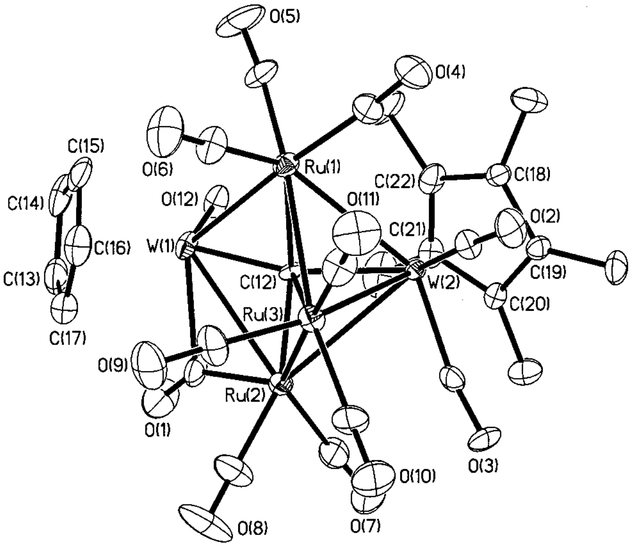

Figure 2. Molecular structure and atomic labeling scheme of $CpW(O)CpWRu_3(\mu_5\text{-}C)(CO)_{11}$ (**2c**) with thermal ellipsoids shown at the 30% probability level.

carbido derivative complexes $LW(O)L'WRu_3(\mu_5\text{-}C)(CO)_{11}$ (**2b**, L = L′ = Cp*, 26%; **2c**, L = Cp and L′ = Cp*, 37%) were obtained from the direct treatment of $LWRu_3(CO)_{12}H$ and $L'W(CO)_3H$ (L = L′ = Cp*; L ≠ L′ = Cp, Cp*) through the consecutive elimination of H_2 and three CO ligands. Interestingly, no trigonal-bipyramidal carbonyl complex with formula $LL'W_2Ru_3(CO)_{13}$ (L ≠ Cp or L′ ≠ Cp) was observed for the latter reactions, suggesting that the ancillary ligand on the W atom has played a pivotal rule in determining the stability and final composition of the products.

The X-ray diffraction study on the oxo−carbido cluster **2c** disclosed that it adopts a wingtip-bridged butterfly arrangement, which is formally derived from the trigonal bipyramid in **1** by scission of two equatorial metal−metal bonds (Figure 2). All 11 out of the 12 CO ligands adopt a terminal bonding mode; the only exception is the carbonyl ligand C(1)O(1), which spans the W(1)−Ru(2) edge with bond angles ∠W(1)−C(1)−O(1) = 129(1)° and ∠Ru(2)−C(1)−O(1) = 147(1)°. The carbido atom is linked to all five transition-metal atoms with distances in the range 1.991(10)−2.099(10) Å, and the oxo ligand is coordinated to the CpW fragment at the bridgehead position, pointing toward the $Cp^*W(CO)_2$ fragment. If we consider that the oxo ligand serves as a 4-electron donor, this system then shows a total of 76 cluster valence electrons, which is consistent with many other carbido clusters adopting this skeletal geometry.[17] Moreover, as this donor ability invokes a W≡O triple-bond bonding interaction, the very short distance W(2)−O(1) = 1.697(5) Å is observed, which is in good agreement with that observed in other oxo-containing metal cluster complexes.[18]

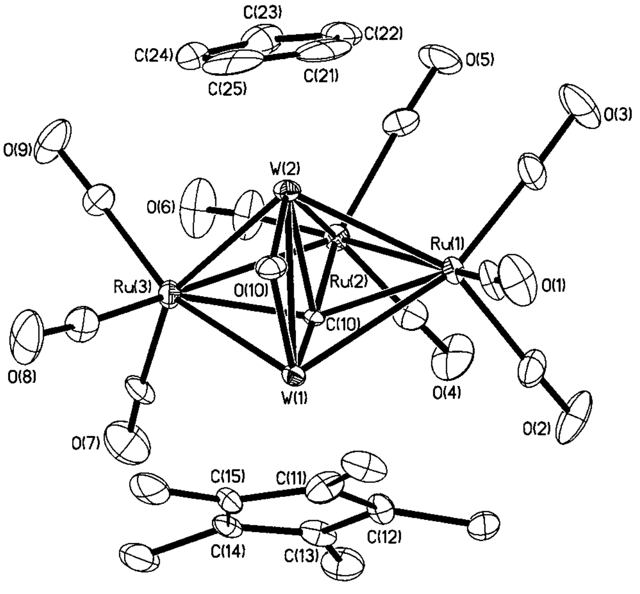

Figure 3. Molecular structure and atomic labeling scheme of $CpCp^*W_2(\mu\text{-}O)Ru_3(\mu_5\text{-}C)(CO)_9$ (**3c**) with thermal ellipsoids shown at the 30% probability level.

Moreover, extensive heating of the oxo−carbido cluster complexes **2b**,**c** in toluene solution gives formation of the new cluster complexes $LL'W_2(\mu\text{-}O)Ru_3(\mu_5\text{-}C)(CO)_9$ (**3b**, L = L′ = Cp*; **3c**, L = Cp, L′ = Cp*) in good yields, the structure of which is schematically depicted in Scheme 1. The identification of these complexes was achieved by a combination of spectroscopic methods and X-ray analysis.

As depicted in Figure 3, the molecular structure of **3c** contains a distorted-square-pyramidal arrangement, which is constituted by two LW fragments and three $Ru(CO)_3$ units, with an interstitial carbido ligand that is analogous to that of its parent **2c**. The carbide C(10) is located 0.28(1) Å below the approximate square plane defined by the four basal metal atoms W(1), Ru(1), Ru(2), and Ru(3) and with the bond angles ∠W(1)−C(10)−Ru(2) = 170.9(6)° and ∠Ru(1)−C(10)−Ru(3) = 152.2(5)°. The W(1)−C(10) distance of 1.877(11) Å is substantially shorter than that of other M−C(carbide) distances, 2.005(11)−2.191(11) Å. The oxo ligand is symmetrically linked to the W−W edge, showing two nearly equal W−O distances of 1.892(7) and 1.921(7) Å and a relatively short W(1)−W(2) distance of 2.6741(7) Å.

The local bond pattern of the W(1)−O(10)−W(2) motif is worthy of comment, as the observed W−O distances (1.892−1.921 Å) are significantly longer than that of the W≡O triple bond observed in **2c** and those of the W=O double bonds reported in the literature (1.709−1.720 Å)[19] but are comparable to that of the W−O single-bond distance of 1.889 Å in the complex $Cp^*W(O)_2(OC_5Me_5)$,[20] indicating the existence of the W−O−W single-bond interaction. Moreover, the W(1)−W(2) distance is substantially shorter than that of the W−W single bond of **1** and the alkyne complex $Cp_2W_2Os(C_2Tol_2)(CO)_7$ (3.016−

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3.158 Å),[21] as well as the other M−M distances within the molecule, particularly the M(basal)−M(basal) distances, which span the range 2.833(1)−2.919(1) Å. This observation is consistent with the unsaturated nature of **3**, shown by the possession of a total of 70 valence electrons, if we assume that the oxo ligand donates only 2 electrons to the cluster framework. In fact, two other M(apical)−M(basal) distances, W(2)−Ru(1) = 2.706(1) Å and W(2)−Ru(3) = 2.693(1) Å, are also found to exhibit such a shortened M−M interaction, indicating that the unsaturation is principally spread over these three M(apical)−M(basal) bonds. The only exception is the fourth M(apical)−M(basal) bond, i.e., the W(2)−Ru(2) vector, which is located at a unique position opposite the oxo atom O(10), thus showing an elongated metal−metal distance of 2.944(1) Å due to a trans-labilization effect imposed by the strong W−O bonding.

On the other hand, we assume that bonding of the oxo ligand is best represented by a structure involving the two resonance hybrids W═O→W and W←O═W, according to the W═O→Os bonding (1.74−1.81 Å) observed in cluster complexes containing the $WOs_3(\mu\text{-}O)$ motif.[22] As the donor capability of the oxo ligand is now increased from 2 to 4, the total valence electrons of the cluster will be increased from 70 to 72; the latter is more reasonable, as the coordinative unsaturation is less severe than that of the first proposed structure with a W−O−W single-bond interaction.

Discussion

Preparation of the oxo−carbido cluster complexes **2** and **3** was successfully achieved. The origin of the oxo and carbido ligands in complexes **2** was explored in attempts to clarify the mechanism of their formation. First, we observed no evolution of CO_2 gas for all reactions conducted between $LWRu_3(CO)_{12}(\mu\text{-}H)$ and $L'W(CO)_3H$ by passing the exhaust into a saturated $Ca(OH)_2$ solution. This negative result suggests that the carbide is not produced from the CO disproportionation.[23] Second, the oxo ligand is produced from the ligated carbonyl molecule but not from other oxygen-containing impurities in the system.[24] To identify the source of the oxo ligand, the ^{17}O-enriched oxo−carbido cluster **2b** was prepared by treatment of the ^{17}O-enriched $Cp^*WRu_3(CO)_{12}(\mu\text{-}H)$ with the regular tungsten hydride complex $Cp^*W(CO)_3H$. The ^{17}O NMR spectrum of the resulting product sample shows a broad W≡O signal at δ 832.9 and three CO signals at δ 388.1, 377.3, and 355.7 in an integral ratio of 1:6:2:3. These ^{17}O NMR chemical shift data are comparable to those of the typical W-bound oxo ligands[25] and the CO ligands[26] reported in the literature. Thus, observation of all four ^{17}O NMR signals, particularly of the most downfield one, provides unambiguous support that the oxo ligand is indeed derived from the CO ligands of the cluster complex.

On the basis of the above experimental evidence, one possible reaction path can be proposed to account for the stepwise formation of the oxo−carbido clusters from condensation of the WRu_3 cluster hydride and monometallic tungsten hydrides (Scheme 1). The facile conversion from complex **1** to **2a** and the failure to obtain the mixed derivative **2d** from the reactions between $LWRu_3(CO)_{12}(\mu\text{-}H)$ and $L'W(CO)_3H$ ($L \neq L'$ = Cp, Cp*) indicate that the trigonal-bipyramidal clusters with structures similar to that of **1** are the primary product of the condensation reaction and that the W atoms of the primary product are located at the indistinguishable equatorial sites. After that, the reaction passes an intermediate or transition state (**A**) with a μ_4-η^2-CO or a μ_5-η^2-CO ligand through scission of the W−W bond to reduce the interligand repulsion. The unsaturation provided by a subsequent elimination of a CO ligand on the W atom would then induce the cleavage of this multisite coordinated CO ligand.

Alternatively, we may propose that formation of the transition state with the η^2-CO ligand is induced by a prior CO dissociation on one W atom, and cleavage of the resulting η^2-CO ligand is then induced by simultaneous cleavage of the W−W bond. These two possibilities differ in the timing of the W−W bond cleavage and the elimination of the CO ligand, and neither pathway can be ruled out according to our current experimental data; however, the detection of μ_4-η^2-CO in the closely related WRu_3, WRu_4, WRu_6, and Mo_2Ru_4 systems[27] and the isolation of ruthenium cluster compounds with the μ_6-η^2-CO ligand[28] provide the precedents for our postulation. It is important to note that the C atom being interstitial as well as formation of the stable W≡O multiple bonding are crucial, as they provide the thermodynamic driving forces in stabilizing the product.

Moreover, heating of the complexes **2b**,**c** induced a further loss of two CO ligands and gave formation of the second oxo−carbido cluster complexes **3b**,**c**. The X-ray structural analysis of complex **3c** suggests that the Cp ligand is associated with the W atom at the apical position. This molecular configuration suggests that the transformation from **2** to **3** is not proceeded by simple metal−metal bond formation between two W atoms, as this would give a cluster complex with the CpW fragment located not at the observed apical site, but at a basal site of the square-pyramidal framework. To cope with the observed structural features of **3c**, a slightly more complicated process may be incorporated,

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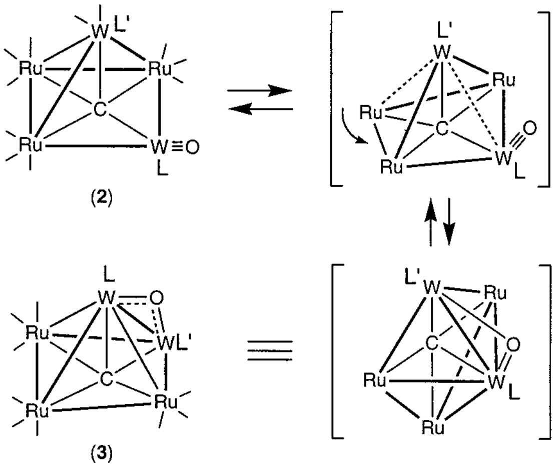
Scheme 2



which contains three additional steps of W−Ru bond cleavage, moving the Ru atom to the opposite side, and regeneration of the new W−Ru bond (Scheme 2). Thus, the transformation from **2** to **3** shows a special case, in which a more complex mechanism has replaced the simplest reaction pathway, to account for the skeletal rearrangement of cluster complexes.

Summary

We have shown that the trigonal-bipyramidal type of cluster **1**, prepared from condensation of the WRu_3 hydride cluster and W hydride, can give formation of oxo−carbido cluster complexes **2** via C−O bond cleavage and that the subsequent conversion from complexes **2** to complexes **3** involves a complex skeletal rearrangement induced by loss of two CO ligands on the W atom and transferring of the terminal oxo ligand into a bridging mode. The latter is also revealed by observation of a much downfield ^{17}O NMR signal at δ 589.9 for the oxo ligand of complex **3c**. Moreover, in contrast to other structurally characterized square-pyramidal cluster complexes that typically contain 74 valence electrons,[29] our complexes **3** are considered to be unsaturated, as they contain a total of 72 valence electrons by assuming that the oxo atom donates 4 electrons. Finally, this skeletal rearrangement is essentially reversible, as treatment of **3** with CO at elevated temperature gives regeneration of the starting wingtip-bridged butterfly complexes **2** in excellent yields.

Acknowledgment. We are grateful to the National Science Council of the Republic of China for financial support (Grant No. NSC 88-2113-M-007-034).

Supporting Information Available: X-ray crystallographic files, in CIF format, for **1**, **2c**, and **3c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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