Novel Butterfly Tungsten–Osmium Carbido Cluster Complexes from the Reaction of Os₃(CO)₁₀(NCMe)₂ with CpW(CO)₃(CH₂SMe)

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Received January 31, 1995

Condensation of the triosmium acetonitrile complex Os₃(CO)₁₀(NCMe)₂ with the sulfido complex CpW(CO)₃(CH₂SMe) in refluxing THF solution produced three sulfur-containing compounds $Os_3(CO)_{10}(\mu-H)(\mu-SMe)$ (1), $Os_3(CO)_{11}$ $[S(Me) CH_2W(CO)_3Cp]$ (2) and $CpWOs_3(CO)_{12}(\mu-CH_2)(\mu-SMe)$ (3). Clusters 2 and 3 were products involving a 1:1 combination of starting materials and were characterized by X-ray diffraction studies. Crystals of 2 belongs to monoclinic space group P $2_1/c$ with a = 8.418(2), b = 11.912(2), c = 28.288(4) Å, $\beta = 97.64(2)^{\circ}$, Z = 4; $R_F = 0.048$, $R_W = 0.044$. Crystal dara for 3: space group P $2_1/c$, a = 18.156(4), b = 9.255(6), c = 15.347(4) Å, $\beta = 103.49(2)^{\circ}$, Z = 4; $R_F = 0.047$, $R_W = 0.045$. Upon thermolysis in toluene, the methylene cluster 3 released CO and induced C-H bond activation to afford two tetrametallic carbido clusters with formula $CpWOs_3(CO)_9(\mu_4-C)(\mu-H)_2(\mu-SMe)$ (4) and CpWOs₃(CO)₁₁(μ_4 -C)(μ -SMe) (5) as the principle products. The first complex possesses a butterfly framework encapsulating a μ_{4} -C ligand and a μ -SMe ligand linking a W-Os edge, whereas the second product adopts a puckered, cyclic arrangement of WOs₃ metal atoms with μ -SMe ligand located on a nonbonding Os–Os vector. Complex 4 crystallizes in monoclinic space group P $2_1/c$ with a = 15.633(4) Å, b = 8.699(3) Å, c = 15.422(4) Å, $\beta = 93.12(2)^{\circ}$, Z = 4, R = 0.036, $R_W = 0.034$ for 2780 observed reflections. Crystal data for 5: space group *P mma*, a = 14.542(3), b = 13.710(6), c = 11.758(3) Å, Z = 4, $R_F = 0.038$, $R_{W} = 0.037$ for 1826 observed reflections. A variable temperature ¹H NMR study was also presented to demonstrate the solution fluxionality of 5.

KEY WORDS: Osmium; tungsten; thiolato; methylene; carbide; heterometallic clusters.

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INTRODUCTION

The chemistry of mixed-metal cluster complexes has been the subject of intensive research for many years [1], due to the potential of these systems in studying the bonding and reactivity of organic ligands by varying the electronic and steric properties of transition-metal elements. With the objective to find a systematic method for the preparation of heterometallic cluster complexes, our research group has examined the direct condensation of group 6 hydride, acetylide and aldehyde complexes, $LW(CO)_3H$, $LW(CO)_3(CCPh)$, and $LW(CO)_3(CH_2CHO)$, L = Cp and Cp^* , and group 8 cluster compounds, such as $Os_3(O)_{10}(NCMe)_2$ [2], $Ru_3(O)_{12}$ [3], $Ru_3(CO)_{10}(\mu-H)(\mu-COMe)$ [4], $Ru_3(CO)_{10}(\mu_3-NPh)$ [5], and $Ru_3(CO)_{10}(\mu-H)(\mu-PPh_2)$ [6]. As a result, we obtained a series of heterometallic cluster compounds containing a variety of hydrocarbyl fragments and ligands which possess oxygen, nitrogen, or phosphorus substituents. In order to further extend these cluster assembling reactions to cluster compounds with sulfur-containing hydrocarbon ligands, we have carried out the reactions of osmium thiolato complex $Os_3(CO)_{10}(\mu-H)$ $(\mu$ -SMe) with CpW(CO)₃H [7] and the reaction of Os₃(CO)₁₀(NCMe)₂ with $CpW(CO)_3(CH_2SMe)$. In this report, we describe the spectroscopic and structural characterization of two WOs₃ thiolate clusters obtained from the second reaction, and the X-ray structures of two heterometallic carbido complexes prepared from the subsequent thermolysis of the cluster $CpWOs_3(CO)_{12}(\mu-CH_2)(\mu-SMe)$ through a consecutive sequence of double C-H bond activation and formation of carbide ligand.

EXPERIMENTAL PROCEDURE

General Information and Materials. Infrared spectra were recorded on a Perkin Elmer 2000 FT-IR spectrometer. ¹H and ¹³C NMR spectra were recorded on a Bruker AM-400, a Varian Gemini-300 or a Varian Unity-400 instrument. Chemical shifts are quoted with respect to internal standard tetramethylsilane (¹H and ¹³C NMR). Mass spectra were obtained on a JEOL-HX110 instrument operating in the fast atom bombardment (FAB) mode. CpW(CO)₃(CH₂SMe) was prepared from the reaction between [CpW(CO)₃][Na] and MeSCH₂Cl according to the literature method [8]. 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 (5735 Kieselgel 60 F₂₅₄, E. Merck) and the products were separated on commercially available preparative thin-layer

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chromatographic plates (Kieselgel 60 F_{254} , E. Merck). Elemental analyses were performed at the NSC Regional Instrumentation Center at National Cheng Kung University, Tainan, Taiwan.

Reaction of $Os_3(CO)_{10}(NCMe)$, and $CpW(CO)_2(\eta^2-CH_2SMe)$. A THF solution (30 mL) of Os₃(CO)₁₀(NCMe)₂ (212 mg, 0.228 mmol) and $CpW(CO)_3(CH_2SMe)$ (100 mg, 0.273 mmol) was heated to reflux for 2 hours, during which the color changed from orange to red-orange. After cooling the solution to room temperature, the solvent was evaporated and the residue was separated by thin layer chromatography (dichloromethane: hexane = 1:3), giving 84 mg of light-vellow $Os_3(CO)_{10}(\mu-H)(\mu-SMe)$ (1, 0.094 mmol, 41%), 49 mg of yellow-orange $Os_3(O)_{11}[S(Me)CH_2W(CO)_3Cp]$ (2, 0.039 mmol, 19%) and 22 mg of orange-red CpWOs₃(CO)₁₂(μ -CH₂)(μ -SMe) (**3**, 0.018 mmol, 8%). Single crystals of 2 and 3 suitable for X-ray analysis were obtained from a layered solution of dichloromethane-heptane at room temperature.

Spectral data for 1: MS (FAB, ¹⁹²Os), m/z 904 (M⁺). IR(C₆H₁₂): v(CO), 2108(m), 2066(vs), 2058(vs), 2034(w), 2023(vs), 2018(vs), 1998(vs), 1989(vs), 1963(s), 1955(vw) cm⁻¹; ¹H NMR (CDCl₃, 294 K): δ 2.43 (s, 3 H), -17.16 (s, 1 H); ¹³C NMR (CDCl₃, 294 K): CO, δ 180.8, 180.2, 176.3 (2C), 173.7 (2C), 170.7 (2C), 169.2 (2C); δ 38.7 (SCH₃). Anal. Calcd for C₁₁H₄O₁₀S₁Os₃: C, 14.60; H, 0.45 Found: C, 14.76; H, 0.47.

Spectral data for **2**: MS (FAB, ¹⁹²Os, ¹⁸⁴W), m/z 1278 (M⁺). IR(C₆H₁₂): ν (CO), 2105(vw), 2068(vw), 2051(s), 2031(s), 2017(vs), 1999(w), 1988(w), 1975(w), 1959(w), 1950(m), 1941(w), 1932(w) cm⁻¹; ¹H NMR (CDCl₃, 294 K): δ 5.52 (s, 5 H), 2.98 (s, 2 H), 2.81 (s, 3 H), ¹³C NMR (CD₂Cl₂, 230 K): CO, δ 225.6 (J_{W-C} = 143 Hz), 217.3 (2C, J_{W-C} = 154 Hz), 194.7 (d, J_{C-C} = 36.5 Hz), 185.5 (d, J_{C-C} = 36.5 Hz), 185.5 (2C), 183.5 (2C), 177.0, 176.3, 171.8, 171.3, 170.8; δ 92.3 (C₅H₅), 34.1 (CH₃), 3.5 (CH₂, J_{W-C} = 47 Hz). Anal. Calcd for C₂₁H₁₀O₁₄S₁Os₃W₁: C, 19.82; H, 0.79 Found: C, 19.66; H, 0.77.

Spectral data for 3: MS (FAB, ¹⁹²Os, ¹⁸⁴W), m/z 1222 (M⁺). IR(C₆H₁₂): ν (CO), 2109(w), 2063(s), 2029(vs), 2023(vs), 2008(vs), 1982(w), 1948(w), cm⁻¹; ¹H NMR (CDCl₃, 294 K): δ 5.47 (s, 5 H), 3.84 (d, 1 H, ²J_{H-H} = 4.0 Hz), 3.41 (d, 1 H, ²J_{H-H} = 4.0 Hz), 2.19 (s, 3 H); ¹³C NMR (CDCl₃, 294 K): CO, δ 222.0 (J_{W-C} = 141 Hz), 215.2 (J_{W-C} = 106 Hz), 187.2, 185.1, 183.8 (4C), 174.1 (2C), 167.8 (2C, br); δ 88.9 (C₅H₅), 34.7 (CH₂, J_{W-C} = 36 Hz), 27.9 (CH₃). Anal. Calcd for C₁₉H₁₀O₁₂S₁Os₃W₁: C, 18.76; H, 0.83 Found: C, 18.94; H, 0.85.

Thermolysis of 3. A toluene solution (15 mL) of 3 (25 mg, 0.021 mmol) was heated to reflux for 1.5 hours, during which the color

changed from red-orange to orange-brown. After allowing the solution to cool to room temperature, the solvent was evaporated and the residue was separated by thin layer chromatography (dichloromethane:hexane = 1:2), giving 7 mg of green CpWOs₃(CO)₉(μ_4 -C)(μ -H)₂(μ -SMe) (4, 0.006 mmol, 30%) and 9 mg of orange CpWOs₃(CO)₁₁(μ_4 -C)(μ -SMe) (5, 0.007 mmol, 37%). Single-crystals of 4 suitable for X-ray analysis were obtained from a layered solution of dichloromethane-heptane at room temperature, whereas crystals of 5 was obtained from a mixture of chloroform-heptane.

Spectral data for 4: MS (FAB, ¹⁹²Os, ¹⁸⁴W), m/z 1138 (M⁺). IR(C₆H₁₂): v(CO), 2087(s), 2057(vs), 2044(w), 2034(vs), 2012(vs), 2007 (*s*, sh), 1988(s), 1974(w), 1876(m) cm⁻¹; ¹H NMR (CDCl₃, 294 K): δ 5.46 (*s*, 5 H), 2.76 (*s*, 3 H), -17.04 (*s*, 1 H), -24.14 (*s*, 1 H); ¹³C NMR (CDCl₃, 294 K): CO, δ 220.4 (J_{W-C} =179 Hz), 181.3, 179.8, 176.6, 173.9, 172.6, 169.4, 165.8, 165.6; δ 305.4 (μ_4 -C), 91.3 (C₅H₅), 36.2 (CH₃). Anal. Calcd for C₁₆H₁₀O₉S₁Os₃W₁: C, 16.97; H, 0.89. Found: C, 16.80; H, 0.91.

Spectral data for 5: MS (FAB, ¹⁹²Os, ¹⁸⁴W), m/z 1192 (M⁺). IR(C₆H₁₂): ν (CO), 2084(vw), 2060(vs), 2053(m, sh), 2042(vs), 2033(w), 2017(m), 2000(vs), 1976(w), 1963(m), 1929(vw), 1917(w), 1877(vw), 1868(vw) cm⁻¹. ¹H NMR (CD₂Cl₂, 218 K): C₅H₅: δ 5.81, 5.47, 5.40; CH₃: δ 1.91, 1.89, 1.83. ¹³C NMR (CD₂Cl₂, 230 K): μ_4 -C: δ 329.9, 329.7, 316.1; W-CO: δ 224.0 (J_{W-C} = 161 Hz), 219.4 (J_{W-C} = 161 Hz), 208.0 (J_{W-C} = 162 Hz); C₅H₅: δ 92.5, 91.7, 86.9; CH₃: δ 33.7, 32.6, 31.5. Anal. Calcd for C₁₈H₈O₁₁S₁Os₃W₁: C, 18.22; H, 0.68. Found: C, 18.13; H, 0.66.

X-Ray Crystallography. Diffraction measurements for all complexes were carried out on a Nonius CAD-4 diffractometer. All reflections were corrected for Lorentz, polarization, and absorption effects. Data reduction and refinement were performed using the NRCC-SDP-VAX packages. Empirical absorption corrections were applied by using Ψ scan data. Anisotropic thermal parameters were introduced for all nonhydrogen atoms. The hydrogen atoms were assumed to attach at the idealized position. The hydrogen atom positions were included in the structure factor calculations but not refined in the final least squares cycles. The combined data collection and refinement parameters are summarized in Table I. Atomic positional parameters for 2, 3, 4, and 5 are presented in Tables II–V, whereas selected bond angles and lengths are listed in Tables VI–IX, respectively.

Lattice parameters of **2** were determined from 25 randomly selected high angle reflections with 2θ angles in the range $18.8-24.8^{\circ}$. The minimum and maximum transmission factors were 0.35 and 1.00, respectively. Full matrix least-squares refinement with 50 atoms and 362 parameters gave

	2	£	4	vi
Formula Mol wr	C ₂₁ H ₁₀ O ₁₄ SOs ₃ W	C ₁₉ H ₁₀ O ₁₂ SOs ₃ W	C ₁₆ H ₁₀ O ₉ SOs ₃ W	C ₁₈ H ₈ O ₁₁ SOs ₃ W
Crystal system	monoclinic	n210.79 monoclinic	monoclinic	cthorhombic
Space group	$P 2_1/c$	P 21/c	P 2,/c	P nma
a (Å)	8.418(2)	18.156(4)	15.633(4)	14.542(3)
$b(\mathbf{\hat{A}})$	11.912(2)	9.255(6)	8.699(3)	13.710(6)
c (Å)	28.288(4)	15.347(4)	15.422(4)	11.758(3)
β (°)	97.64(2)	103.49(2)	93.12(2)	
$U(\mathbf{A}^3)$	2811(1)	2507(2)	2215(1)	2344(1)
Ζ	4	4	4	4
D_c (g/cm ³)	3.007	3.223	3.370	3.363
F(000)	2263	2151	1983	2095
Crystal size, mm	$0.30 \times 0.40 \times 0.50$	$0.25 \times 0.40 \times 0.50$	$0.03 \times 0.08 \times 0.60$	$0.05 \times 0.30 \times 0.45$
h, k, l ranges	-98,012,030	- 1919,09,016	- 19 19, 0 10, 0 28	0 17, 0 16, 0 13
$\mu (\mathrm{mm}^{-1})$	17.83	19.98	22.60	21.37
No. of unique data $(2\theta_{\text{max}})$	$3646(45^{\circ})$	$4188(50^{\circ})$	3891 (50°)	2158 (50°)
No. of data with $I > 2\sigma(I)$	2582	3187	2780	1826
No. of parameters	362	326	272	167
Maximum A/σ ratio	0.034	0.100	0.027	0.057
$R; R_{W}$	0.048; 0.044	0.047; 0.045	0.036; 0.034	0.038; 0.037
G.O.F.	1.67	2.54	1.50	2.71

Table I. Experimental Data for the X-Ray Diffraction Studies of Complexes 2, 3, 4, and 5

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	x	y	2	<i>B</i> (eq) ^{<i>a</i>}
Osl	0.83645(12)	0.70043(10)	0.15290(3)	2.72(4)
Os2	1.01813(13)	0.85300(10)	0.10413(3)	3.29(5)
Os3	0.85147(13)	0.67031(10)	0.05206(3)	3.43(5)
W	0.61407(12)	0.25076(10)	0.16180(3)	2.75(4)
S	0.6501(7)	0.5491(6)	0.15608(19)	3.0(3)
Cl	1.018(3)	0.6031(24)	0.1676(7)	3.6(12)
C2	0.868(3)	0.7481(25)	0.2168(7)	3.9(13)
C3	0.666(3)	0.8016(22)	0.1418(8)	3.5(12)
C4	1.071(3)	0.937(3)	0.1614(8)	4.9(15)
C5	0.838(3)	0.9471(25)	0.0852(8)	4.7(16)
C6	1.129(3)	0.930(3)	0.0599(9)	5.7(17)
C7	1.203(3)	0.749(3)	0.1197(8)	4.5(14)
C8	0.649(4)	0.751(3)	0.0438(8)	6.1(17)
C9	0.906(3)	0.7198(25)	-0.0072(8)	4.8(15)
C10	0.741(3)	0.537(3)	0.0321(8)	5.0(15)
C11	1.029(4)	0.578(3)	0.0660(9)	6.1(18)
C12	0.635(3)	0.294(3)	0.2298(8)	4.9(15)
C13	0.674(3)	0.1071(24)	0.1947(8)	4.1(14)
C14	0.823(3)	0.2168(21)	0.1471(6)	2.9(12)
C15	0.755(3)	0.4196(21)	0.1617(7)	2.7(11)
C16	0.573(3)	0.5590(23)	0.2106(8)	3.8(13)
C17	0.346(3)	0.199(3)	0.1453(9)	6.2(18)
C18	0.428(4)	0.152(3)	0.1107(11)	6.7(18)
C19	0.490(3)	0.235(3)	0.0826(8)	5.3(16)
C20	0.440(3)	0.331(3)	0.0998(9)	5.3(16)
C21	0.356(3)	0.318(3)	0.1381(9)	5.3(16)
O1	1.1202(1)	0.5449(20)	0.1801(6)	6.3(11)
O2	0.890(3)	0.7773(23)	0.2554(5)	8.2(15)
O3	0.5635(21)	0.8685(17)	0.1381(6)	5.0(11)
O4	1.102(3)	0.9902(20)	0.1953(6)	7.1(12)
O5	0.7273(24)	1.0013(19)	0.0702(6)	6.5(12)
O6	1.2010(23)	0.9780(24)	0.0325(6)	8.2(15)
07	1.3152(21)	0.6978(19)	0.1285(8)	8.1(13)
O8	0.5290(25)	0.7944(23)	0.0367(7)	8.8(14)
O9	0.958(3)	0.754(3)	-0.0404(7)	12.3(20)
O10	0.669(4)	0.456(3)	0.0207(8)	12.2(21)
O11	1.140(3)	0.5154(23)	0.0739(7)	9.6(15)
O12	0.644(3)	0.3136(19)	0.2699(6)	7.5(14)
O13	0.7031(23)	0.0251(17)	0.2153(5)	5.4(11)
014	0.9547(20)	0.1958(19)	0.1357(6)	5.8(11)

Table II. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients for 2

" B (eq) is the mean of the principal axes of the thermal ellipsoid.

	х	y,	<i>z</i>	<i>B</i> (eq)"
Osl	0.23176(4)	0.99308(9)	0.21657(6)	1.95(3)
Os2	0.31884(5)	0.90279(10)	0.38760(6)	2.42(4)
Os3	0.39323(5)	0.95938(10)	0.24765(6)	2.50(4)
W	0.10361(5)	1.18007(10)	0.16254(6)	2.37(4)
S	0.2334(3)	1.2563(6)	0.2319(4)	2.47(24)
Cl	0.1975(10)	0.8062(22)	0.2032(14)	2.4(9)
C2	0.2506(9)	0.9877(22)	0.1048(17)	3.4(11)
C3	0.3215(11)	1.109(3)	0.4183(13)	3.1(10)
C4	0.2393(12)	0.8751(25)	0.4440(17)	3.8(12)
C5	0.3167(12)	0.692(3)	0.3529(17)	4.4(12)
C6	0.4074(13)	0.861(3)	0.4785(18)	4.5(13)
C7	0.3657(12)	0.763(3)	0.2006(17)	4.2(13)
C8	0.4879(11)	0.9091(25)	0.3186(17)	3.8(12)
C9	0.4243(13)	1.003(3)	0.1415(16)	4.3(12)
C10	0.4069(11)	1.1585(23)	0.2918(15)	3.0(10)
C11	0.0661(12)	0.984(3)	0.1120(14)	3.3(11)
C12	0.1273(9)	1.1917(22)	0.0460(15)	2.7(10)
C13	0.2742(11)	1.3472(25)	0.1511(16)	3.8(11)
C14	0.1476(11)	1.0472(25)	0.2831(14)	3.0(10)
C15	0.0234(14)	1.268(4)	0.2500(19)	7.1(18)
C16	0.0696(14)	1.378(3)	0.2381(20)	6.0(15)
C17	0.0540(11)	1.4076(24)	0.1459(18)	3.9(13)
C18	-0.0022(12)	1.310(3)	0.1041(17)	5.2(13)
C19	-0.0196(13)	1.225(3)	0.1705(20)	5.8(16)
01	0,1708(8)	0.6890(16)	0.1972(12)	4.4(9)
O2	0.2579(9)	0.9715(18)	0.0296(11)	4.8(9)
O3	0.3231(10)	1.2232(18)	0.4454(11)	5.2(10)
O4	0.1911(9)	0.8580(24)	0.4831(12)	6.8(12)
O5	0.3136(11)	0.5771(17)	0.3384(14)	6.9(13)
O6	0.4585(8)	0.8357(19)	0.5354(12)	5.3(9)
O7	0.3540(11)	0.6554(18)	0.1666(13)	6.5(12)
O8	0.5440(8)	0.8699(19)	0.3668(13)	5.5(10)
O9	0.4464(11)	1.0332(21)	0.0795(13)	6.7(12)
O10	0.4182(8)	1.2774(16)	0.3158(11)	3.9(8)
O11	0.0416(8)	0.8801(17)	0.0805(11)	4.8(8)
O12	0.1367(9)	1.2087(22)	-0.0269(11)	5.7(10)

Table III. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients for 3

" B(eq) is the mean of the principal axes of the thermal ellipsoid.

	x	<i>J</i> ,	2	$B(eq)^a$
Osl	0.31137(4)	0.16672(8)	0.00291(4)	2.75(3)
Os2	0.36242(4)	0.36370(8)	0.14283(4)	3.11(3)
Os3	0.23940(4)	0.46564(8)	0.01739(4)	2.79(3)
W	0.14664(4)	0.20679(8)	0.07186(4)	2.73(3)
S	0.1095(3)	0.3845(6)	-0.04201(24)	3.97(20)
C1	0.2809(12)	0.0757(21)	-0.1075(10)	4.5(9)
C2	0.3287(10)	-0.0196(21)	0.0642(9)	3.9(8)
C3	0.4211(11)	0.1914(21)	-0.0252(11)	4.6(9)
C4	0.3960(10)	0.2157(23)	0.2255(9)	4.3(9)
C5	0.4713(11)	0.4258(22)	0.1150(9)	4.5(9)
C6	0.3495(11)	0.5154(22)	0.2266(9)	4.3(8)
C7	0.2636(10)	0.6130(20)	-0.0657(9)	3.5(7)
C8	0.1881(2)	0.6090(19)	0.0872(9)	4.3(9)
C9	0.1531(9)	0.0198(20)	0.0016(9)	3.3(7)
C10	0.2559(10)	0.2782(19)	0.1103(8)	3.2(7)
C11	0.1163(13)	0.3210(24)	-0.1516(10)	5.7(11)
C12	0.0143(10)	0.2441(22)	0.1208(10)	4.4(9)
C13	0.0693(10)	0.321(3)	0.1752(11)	5.6(10)
C14	0.1224(10)	0.214(3)	0.2166(9)	5.7(11)
C15	0.1013(12)	0.0723(24)	0.1874(10)	5.4(10)
C16	0.0339(10)	0.0919(23)	0.1282(10)	4.5(9)
01	0.2626(8)	0.0304(14)	-0.1745(6)	5.1(7)
O2	0.3386(8)	-0.1343(16)	0.1028(8)	6.1(8)
O3	0.4861(8)	0.1944(21)	-0.0438(9)	8.3(9)
O4	0.4143(8)	0.1214(16)	0.2741(7)	6.0(7)
O5	0.5349(8)	0.4552(18)	0.0971(8)	6.7(8)
O6	0.3363(10)	0.6118(18)	0.2762(7)	7.3(9)
O7	0.2804(9)	0.7034(15)	-0.1175(7)	5.8(7)
O8	0.1585(9)	0.6916(15)	0.1346(7)	6.4(8)
O9	0.1469(7)	-1.1000(17)	-0.0321(8)	5.8(7)

Table IV. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients for 4

^a B (eq) is the mean of the principal axes of the thermal ellipsoid.

R = 0.048 and $R_W = 0.044$, for 2582 reflections with $I > 2\sigma(I)$. A weighting scheme based on counting statistics was used with the weight modifier k in kF_o^2 being 0.0001. The residual electron density on the difference Fourier map is $-1.48/2.47 \ e/\text{Å}^3$.

Lattice parameters for complex 3 were determined from 25 randomly selected high angle reflections with 2θ angles in the range $17.6-22.8^{\circ}$. The minimum and maximum transmission factors were 0.39 and 1.00, respectively. Full matrix least-squares refinement with 46 atoms and 326 parameters gave R = 0.047 and $R_W = 0.045$ for 3187 reflections with $I > 2\sigma(I)$. A weighting scheme based on counting statistics was used with

	x	у	2	$B(eq)^a$
Os1	0.13834(7)	3/4	0.19675(7)	1.88(3)
Os2	0.25808(4)	0.62273(4)	0.06911(4)	1.630(22)
W	0.19363(7)	3/4	-0.12859(7)	1.71(3)
S	0.3705(4)	3/4	0.1085(4)	1.84(22)
C1	0.1923(24)	3/4	0.3544(18)	4.6(16)
C2	0.0523(11)	0.6491(11)	0.2234(12)	2.6(7)
C3	0.2729(11)	0.5773(10)	0.2185(12)	2.2(6)
C4	0.1597(12)	0.5339(10)	0.0404(11)	2.3(7)
C5	0.3469(13)	0.5359(10)	0.0020(12)	2.9(8)
C6	0.2862(12)	0.6596(11)	-0.1798(12)	2.6(7)
C7	0.1716(19)	3/4	0.0379(16)	3.0(12)
C8	0.4597(18)	3/4	0.0032(17)	2.8(11)
C9	0.0317(23)	3/4	-0.1381(22)	7.4(21)
C10	0.0637(18)	0.8306(13)	-0.1952(17)	7.0(13)
C11	0.1110(16)	0.8010(13)	-0.2852(15)	6.0(11)
01	0.2253(15)	3/4	0.4367(12)	6.3(13)
O2	0.0019(10)	0.5852(8)	0.2378(10)	4.5(6)
O3	0.2920(9)	0.5522(8)	0.3084(8)	3.7(6)
O4	0.1017(9)	0.4802(8)	0.0251(9)	3.7(6)
O5	0.3983(10)	0.4821(9)	-0.0320(10)	5.0(7)
O6	0.3430(9)	0.6092(8)	-0.2273(9)	4.2(6)

Table V. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients for 5

^a B (eq) is the mean of the principal axes of the thermal ellipsoid.

the weight modifier k in kF_o^2 being 0.00002. The residual electron density is $-3.13/3.28 \ e/\text{Å}^3$.

Lattice parameters of **4** were determined from 25 randomly selected high angle reflections with 2θ angles in the range $11.0-24.8^{\circ}$. The minimum and maximum transmission factors were 0.25 and 1.00, respectively. Refinement with 38 atoms and 272 parameters gave R = 0.036 and $R_W = 0.034$,

Table	VI	. Selected	Bond	Distance	(A)	and	Bond	Angle	es (°) f	or 2	2 (esc	lin	Parentl	neses)
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Os(1)-Os(2) Os(2)-Os(3) S-C(15) W-C(15)	2.847(2) 2.885(2) 1.77(3) 2.33(2)	Os(1)-Os(3) Os(1)-S S-C(16) Os-CO(mean)	2.894(1) 2.399(7) 1.76(2) 1.90(3)
w-CO(mean)	1.95(3)		
Os(1)-Os(2)-Os(3) Os(1)-Os(3)-Os(2)	60.65(4) 59.02(4)	Os(2)-Os(1)-Os(3) Os(1)-S-C15)	60.33(4) 109.7(8)
Os(1) - S - C(16)	107.6(9)	C(15)-S-C(16)	102.5(11)
W-C(15)-S Mean W-CO	120.2(11) 177(2)	Mean Os–CO	176(2)

Os(1)-Os(2) Os(2)-Os(3) Os(1)-S Os(1)-C(14) S-C(13) W-CO(mean)	2.855(1) 2.840(1) 2.447(6) 2.09(2) 1.80(2) 1.99(3)	Os(1)-Os(3) Os(1)-W W-S W-C(14) Os-CO(mean)	2.875(1) 2.863(1) 2.452(5) 2.21(2) 1.91(3)	
$ \begin{array}{l} Os(1)-Os(2)-Os(3) \\ Os(1)-Os(3)-Os(2) \\ W-Os(1)-Os(3) \\ W-S-Os(1) \\ W-S-C(13) \\ Mean W-CO \end{array} $	60.65(3) 59.94(3) 47.35(4) 71.5(1) 110.1(7) 174(2)	Os(2)-Os(1)-Os(3) W-Os(1)-Os(2) W-C(14)-Os(1) Os(1)-S-C(13) Mean Os-CO	59.41(4) 132.97(4) 83.5(7) 113.4(8) 175(2)	

Table VII. Selected Bond Distances (Å) and Bond Angles (°) for 3 (esd in Parentheses)

Table VIII. Selected Bond Distances (Å) and Bond Angles (°) for 4 (esd in Parentheses)

Os(1)-Os(2) Os(2)-Os(3) Os(3)-W Os(2)-C(10) W-C(10) W-S Os(1)-C(2) Os(2)-C(4) Os(2)-C(6)	2.847(1) 2.870(1) 2.875(1) 1.95(2) 1.97(2) 2.394(4) 1.89(2) 1.87(2) 1.87(2)	$\begin{array}{c} Os(1) - Os(3) \\ Os(1) - W \\ Os(1) - C(10) \\ Os(3) - C(10) \\ Os(3) - S \\ Os(1) - C(1) \\ Os(1) - C(3) \\ Os(2) - C(5) \\ Os(3) - C(7) \end{array}$	2.873(1) 2.998(1) 2.17(1) 2.18(2) 1.395(5) 1.92(2) 1.90(2) 1.95(2) 1.87(2)
Os(2)-C(6) Os(8)-C(8) S-C(11)	1.87(2) 1.88(2) 1.79(2)	Os(3)-C(7) W-C(9)	1.87(2) 1.96(2)
Os(2)-C(10)-W Os(3)-S-W	175.4(9) 73.8(1)	Os(1)-C(10)-Os(3)	82.8(4)

Table IX. Selected Bond Distances (Å) and Bond Angles (°) for 5 (esd in Parentheses)

Os(1)-Os(2)	2.886(1)	Os(2)-Os(2)	3.490(2)
Os(2)–W	3.054(1)	Os(1) - C(7)	1.93(2)
Os(2) - C(7)	2.18(1)	W-C(7)	1.98(2)
Os(2)-S	2.435(4)	S-C(8)	1.79(2)
Os(1) - C(1)	2.01(3)	Os(1) - C(2)	1.89(2)
Os(2) - C(3)	1.88(2)	Os(2)-C(4)	1.91(2)
Os(2) - C(5)	1.93(2)	W-C(6)	1.93(2)
Os(1)-C(7)-W	175(2)	Os(2) - C(7) - Os(2)	106(1)
Os(2)-S-Os(2)	91.5(2)		

for 2780 reflections with $I > 2\sigma(I)$. A weighting scheme based on counting statistics was used with the weight modifier k in kF_o^2 being 0.00005. The residual electron density is $-1.90/1.56 \ e/Å^3$.

For complex 5, the lattice parameters were determined from 25 randomly selected high angle reflections with 2θ angles in the range $18.5-30.0^{\circ}$. The minimum and maximum transmission factors were 0.15 and 1.00, respectively. Refinement with 26 atoms and 167 parameters gave R = 0.038and $R_W = 0.037$ for 1826 reflections with $I > 2\sigma(I)$. A weighting scheme based on counting statistics was used with the weight modifier k in kF_o^2 being 0.00001. The residual electron density is $-2.81/1.96 e/Å^3$.

RESULTS AND DISCUSSION

Condensation of $Os_3(CO)_{10}(NCMe)$, and $CpW(CO)_3(CH_2SMe)$. Treatment of the triosmium acetonitrile complex $Os_3(O)_{10}(NCMe)_2$ with 1.2 equivalent of the tungsten sulfido complex $CpW(CO)_3(CH_2 SMe)$ in refluxing THF solution produced the thiolate cluster $Os_3(CO)_{10}(\mu-H)$ $(\mu$ -SMe) (1) in 41% yield and two additional WOs₃ heterometallic clusters $Os_3(CO)_{11}[S(Me)CH_2W(CO)_3Cp]$ (2) and $CpWOs_3(CO)_{12}(\mu-CH_2)$ $(\mu$ -SMe) (3) in 19% and 8% yield, respectively (Scheme I). The reactivity of the sulfido reagent $CpW(CO)_3(CH_2SMe)$ is almost identical to that of the related decarbonylated species $CpW(CO)_2(\eta^2-CH_2SMe)$, which contains two CO ligands and a C and S-bound CH₂SMe group. Attempts to carry out the reaction in toluene at reflux failed to give any heterometallic complexes 2 and 3, but produced homometallic 1 as the only isolable product, suggesting that this condensation reaction is sensitive to both the solvent and the temperature employed. These three cluster compounds were separated by thin-layer chromatography on silica gel and were fully characterized by microanalysis, spectroscopic, and structural methods.



Scheme 1

Compound 1 is related to the derivatives of the type $Os_3(CO)_{10}$ $(\mu-H)(\mu-SR)$ and $Ru_3(CO)_{10}(\mu-H)(\mu-SR)$, R = Et and Ph, which have been well-characterized by Lewis and Johnson, and by Adams and co-workers independently [9]. The key spectral feature of 1 involves the observation of a methyl signal at $\delta 2.43$ and a hydride signal at $\delta - 17.16$ in the ¹H NMR spectrum. The ¹³C NMR spectrum measured at room temperature showed six CO signals at $\delta 180.8$, 180.2, 176.3, 173.7, 170.7, 169.2 in a ratio 1:1:2:2:2:2. This six-line pattern reveals the presence of C_s symmetry, which is typical for this type of cluster compounds with formula $Os_3(CO)_{10}(\mu-H)(\mu-X)$, X = halides, alkoxides and thiolate functional groups [10].

Characterization of $Os_3(CO)_{11}[S(Me)CH_2W(CO)_3Cp]$ (2). Complex 2 can be considered as a derivative of $Os_3(CO)_{11}(L)$ and the unique ligand is a sulfur-containing fragment. The molecular structure is depicted in Fig. 1 and the selected data of bond lengths and angles is presented in Table VI. The molecule has an isosceles triangular geometry, in which the sulfur atom of ligand CpW(CO)₃(CH₂SMe) is coordinated to the Os₃ metal triangle through trivalent sulfur atom at an equatorial site. The tungsten center is considered to adopt a characteristic four-leg piano stool structure. The Os(1)-Os(2) distance of 2.847(2) Å is slightly longer than the other two Os–Os distances within this molecule (Os(1)-Os(3) =2.894(1) Å and Os(2)-Os(3) = 2.885(1) Å), which are comparable to the average Os–Os distance 2.877 Å observed in the parent cluster Os₃(CO)₁₂ [11]. The shortening of the Os(1)–Os(2) distance is a result of π -bond competition because the sulfur atom of the sulfido ligand tends to form a much weaker metal-to-ligand back π -bonding with respect to the CO ligand. Therefore, the Os(1) atom would interact much stronger with the



Fig. 1. Molecular structure of 2 and the atomic numbering scheme.

Os(2) atom, which is located at the *trans*-position, and this results in the short Os–Os bond. Similar variation in Os–Os and Ru–Ru distances has been noted for the phosphine derivatives $Os_3(CO)_{11}[P(OMe)_3]$ [2] and $Ru_3(CO)_{11}(PPh_3)$ [3].

In accordance with the result of X-ray diffraction study, the ¹³C NMR spectrum of a ¹³CO enriched sample at 230 K displays two W-CO resonances at δ 225.6 and 217.3 in the ratio 1:2, and a set of nine Os–CO signals at δ 194.7 (*d*, J_{C-C} = 36.5 Hz), 185.5 (*d*, J_{C-C} = 36.5 Hz), 185.5 (2C), 183.5 (2C), 177.0, 176.3, 171.8, 171.3, 170.8. For the first two Os-CO resonances, the observed ${}^{2}J_{GC}$ coupling falls in the range expected for the diaxial trans-CO ligands, thus they are assigned to the axial CO ligands of the Os(1) atom. The Os–CO signals at δ 185.5 and 183.5, which possess an intensity corresponding to two CO ligands, are assigned to the axial CO ligands of the atoms Os(2) and Os(3), as the molecules may contain a time averaged plane of mirror symmetry in solution which coincides with the osmium triangle. Upon raising the temperature to 294 K, all Os-CO signals broaden and merge into the baseline simultaneously. This behavior is in consistent with the coexistence of rapid intra and intermetallic CO exchange on the ligand sphere of osmium triangle. No attempt was made to further elucidate the mechanistic details of the CO exchange.

Characterization of $CpWOs_3(CO)_{12}(\mu-CH_2)(\mu-SMe)$ (3). The ¹H NMR spectrum of **3** exhibits Cp and methyl resonances at δ 5.47 and 2.19 in addition to two methylene hydrogen signals at δ 3.84 and 3.41 with ²J_{H-H} = 4.0 Hz. The ¹³C NMR spectrum clearly shows the presence of seven CO signals. Two downfield resonance signals of equal intensity at δ 222.0 and 215.2 are due to the W–CO ligands. Five other highfield CO signals at δ 187.2, 185.1, 183.8 (4C), 174.1 (2C) and 167.8 (2C, br) are assigned to the Os–CO ligands. Based on these spectral information, a formula CpWOs₃(CO)₁₂(μ -CH₂)(μ -SMe), which involves a CpWOs₃(CO)₁₂ core, one bridging methylene and methylthiolato group, is proposed for this complex.

Complex 2 was further characterized by single crystal X-ray diffraction. As indicated in Fig. 2, this molecule adopts a spiked-triangular core arrangement, in which the atoms Os(2) and Os(3) are each associated with four terminal CO ligand. The Os(1) atom, which is located at the pivotal position, carries two CO ligands, and the W atom bears a cyclopentadienyl and two terminal CO ligands. All metal-metal bonds fall in a narrow range 2.840–2.875 Å (Table VII), showing the metal-metal single bond interactions. The methylene and methylthiolato ligands are both coordinated to



Fig. 2. Molecular structure of 3 and the atomic numbering scheme.

the metal atoms, Os(1) and W. The methylthiolate ligands bridges symmetrically with typical distances Os(1)–S = 2.447(6) Å and W–S = 2.452(5) Å. The methylene ligand is asymmetrical with Os(1)–C(14) bond (2.09(2) Å) and is substantially shorter than that of W–C(14) bond (2.21(2) Å). The M–C bond distances are in the range observed for the M–C (alkylidene) distances of CpWOs₃(μ -O)(μ -H)(μ -CHTol)·(W–C = 2.08 Å and Os–C = 2.24 Å) [4] and the Os–C distances of Os₃(CO)₁₁(μ -CHSiMe₃) (2.16–2.19)(2) Å) [15], which possess unsymmetrical and symmetrical alkylidene group, respectively.

Generation of Carbido Clusters 4 and 5. Thermolysis of 3 was conducted in refluxing toluene solution for 1.5 hours. After chromatographic separation, we isolated two carbido clusters $CpWOs_3(CO)_9(\mu_4-C)$ $(\mu-H)_2(\mu-SMe)$ (4) and CpWOs₃(CO)₁₁ $(\mu_4-C)(\mu-SMe)$ (5) in moderate yields. The chemistry demonstrated yet another example of methylene to carbide transformation, which is parallel to other observed reactivity of methylene and methylidyne cluster compounds, viz., that $Os_3(CO)_{10}$ $(\mu-H)_2(\mu-CH_2)$ was converted to methylidyne cluster $Os_3(CO)_9(\mu-H)_3$ $(\mu_3$ -CH) upon heating, that methylene complex Cp₂Ru₂(CO)₂ $(\mu$ -CH₂)(NCMe) reacted with Pt(C₂H₄)₂(PR₃), $R = Pr^{i}$, Cy, to produce tetranuclear carbido cluster $Cp_2Ru_2Pt_2(CO)_2(PR_3)_2(\mu_4-C)(\mu-H)_2$ as principle product [16]. Furthermore, the methylidyne cluster $Os_3(O)_{10}$ $(\mu$ -H) $(\mu_3$ -CH) also was found to condense with Pt(C₂H₄)₂(PR₃), affording carbido clusters $PtOs_3(CO)_{10}(PR_3)(\mu_4-C)(\mu-H)_2$ and $Pt_2Os_3(CO)_{10}(PR_3)_2(\mu_5-C)(\mu-H)_2$ [17]. These interesting results illustrate a route to carbide clusters by metal-promoted double C-H bond activation, showing a unique model of stepwise transformation from CH₂, to CH + H and ultimately to C + 2H [18].

Characterization of 4. The identification of these two carbido clusters was achieved by using NMR spectroscopies and X-ray diffraction studies. The ¹H NMR spectrum of 4 exhibited one Cp signal at δ 5.46, one methyl singlet at δ 2.76 and two hydride resonances at δ –17.04 and –24.14, indicating the retention of CpWOs₃ metal fragment and the conversion of methylene hydrogen atoms into bridging hydride ligands. Also, the ¹³C NMR data were consistent with the generation of carbido ligand. The ¹³C NMR spectrum measured in CD₂ Cl₂ revealed a signal attributable to the carbido ligand at δ 305.4. This observed chemical shift is similar to the carbido resonance (δ 339.3) for cluster Cp₂MoWOs₃(CO)₈(μ_4 -C) (μ_3 -Ph)(CCPh) [19].

The structural features of 4 were fully in agreement with its spectral properties. As indicated in Fig. 3, this molecule possesses a butterfly arrangement with the CpW(CO) fragment located at a wing-tip position and the symmetrical thiolate ligand, μ -SMe, spanned the W-Os(3) distances. Os(3)-S = 2.395(5) Å, W-S = 2.394(4) Åand bond with W-Os(3) = 2.875(1) Å (Table VIII). The dihedral angle between the W-Os(1)-Os(3) and Os(1)-Os(2)-Os(3) planes is $102.27(3)^{\circ}$. The carbide atom C(10) located between the wing-tip atoms W and Os(2) with distances W-C(10) = 1.97(2) Å and Os(2)-C(10) = 1.95(2) Å and angle \angle W-C(10)-Os(2) = 175.4(9)°, and centered over the hinge Os(1)-Os(3) bond with distances $O_{S}(1)-C(10) = 2.17(1)$ Å and $O_{S}(3)-C(10) = 2.18(2)$ Å and angle $\angle Os(1) - C(10) - Os(3) = 82.8(4)^{\circ}$. These parameters resemble that observed for the carbide atom in the related heterometallic WRu₃ and homonuclear Ru₄ and Fe₄ carbido clusters [20], which showed short M(wingtip)-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. Finally, the hydride ligands have not been located, but it is likely that the hydrides are associated with the adjacent Os(1)-Os(3) and Os(2)-Os(3)edges. The supporting evidences are provided by the elongation of these Os-Os bonds (2.870-2.871 Å) with respect to the third Os-Os bond (2.847(3) Å) and the absence of J_{W-C} coupling for both hydride signals in the ¹H NMR spectrum.

Characterization of 5. The structure of 5 was also examined by single crystal X-ray analysis. This molecule crystallizes in an orthorhombic space group P nma with a crystallographic imposed plane of mirror symmetry. As indicated in Fig. 4, the cluster core composed of a cyclic arrangement of one W and three Os atoms, which are all bonded to the carbido atom with distances 2.18(1) Å-1.93(1) Å (Table IX). In addition, the W atom is coordinated to two CO and one Cp ligand, while each Os atoms are coordinated by three orthogonal CO ligands. The bridging thiolate ligand



Fig. 3. Molecular structure of 4 and the atomic numbering scheme.



Fig. 4. Molecular structure of 5 and the atomic numbering scheme.

is found to coordinate to two different Os(2) atoms, which are related to each other via reflection with distances Os(2)-S=2.435(4) Å and Os(2)-Os(2)=3.490(2) Å and angle $\angle Os(2)-S-Os(2)=91.5(2)^{\circ}$. The methyl substitutent C(8), which is tilted toward the unique W atom, is found to site at a position *trans* to the Cp ligand and is eclipsed to the CO ligands on the W atom. Finally, assuming that the carbido and thiolate fragments each provides four and three electrons to the cluster, this molecule contains 64 valence electrons, which agree with the electron counting of tetranuclear complexes having four metal-metal bonds.

Although the structural characterization of **5** showed a highly symmetrical structure in the solid state, the variable temperature ¹H NMR studies indicated the existence of three isomers in solution. The ¹H NMR spectrum measured at 218 K exhibited three Cp signals at δ 5.81, 5.47, and 5.40 in the ratio 1:2:3, and the respective μ -SMe signals at δ 1.83, 1.89, and 1.91. Upon raising the temperature to 297 K, we observed that the two downfield Cp resonances merged and coalesced into a broad signal at δ 5.60, while the corresponding highfield μ -SMe resonances merged to form a sharp signal at δ 1.89 (Fig. 5).



Fig. 5. Variable temperature ¹H NMR spectra of 5 in CD_2Cl_2 solution.

This behavior indicated that the first two isomers undergo fast equilibrium in solution at room temperature, while the exchange with the third isomer is much slower under the conditions examined. The structural relationship of these three isomers is unclear at present; however, according to the X-ray structure mentioned previously, we propose that the isomerization is caused by moving the bridging thiolate ligand between three different positions with respect to the carbido carbon and two nonbridged metal atoms. As indicated in Scheme 2, the first isomer (A) contains a thiolate ligand which is sitting on the plane defined by the carbido carbon and two bridged Os atoms, whereas the other two isomers (B) and (C) possess a related structure in which the thiolate ligand is either parallel to the WOs₂ plane or the second Os₃ plane. Finally, the identities of these carbido clusters was verified by the ¹³C NMR spectrum measured at 230 K, which clearly exhibited three characteristic μ_4 -C resonances at δ 329.9, 329.7, and 316.1 and three W-CO signals at δ 224.0 ($J_{W-C} = 161$ Hz), 219.4 $(J_{W-C} = 161 \text{ Hz})$, and 208.0 $(J_{W-C} = 162 \text{ Hz})$.



DISCUSSION

Condensation of $Os_3(CO)_{10}(NCMe)_2$ and $CpW(CO)_3(CH_2SMe)$ produced three cluster compounds 1, 2, and 3. The first cluster is a homonuclear cluster, while the other two WOs₃ compounds are produced from the 1:1 combination of the starting materials. The diversified structures of these three compounds indicated a poor selectivity of this synthetic approach. The formation of 1 probably involves the coordination of sulfur atom to the $Os_3(CO)_{10}$ framework followed by removal of $CpW(CO)_3(CH_2)$ fragment. The source of the hydride is possibly derived from the methylene group of $CpW(CO)_3(CH_2SMe)$, but no study was made to verify this speculation. The second possibility involves the formation of trace amount of MeSH from decomposition of $CpW(CO)_3(CH_2SMe)$, which then react with $Os_3(CO)_{10}(NCMe)_2$ to afford the isolated 1.

For complex 2, we speculate that it is formed via a combined process of sulfur coordination to $Os_3(CO)_{10}(NCMe)_2$ and capture of one additional CO ligand to afford the observed $Os_3(CO)_{11}$ core. Attempts to improve the synthesis of 2 by employing the monoacetonitrile complex $Os_3(CO)_{11}(NCMe)$ has not been successful. Attempts to use 2 as a precursor to other thiolate transition-metal clusters, which involved thermolysis in various common organic solvents and treatment with Me₃NO reagent to induce the prior CO elimination, have also been frustratingly unsuccessful.

On the other hand, the most interesting and thoroughly studied compound is the methylene-thiolate derivative 3, which is the only cluster compound containing a direct W-Os bond, and a bridging methylene and a bridging thiolate ligand attached to this W-Os bond. To test that the S atom is required to coordinate to the W atom before it would induce the cleavage of C-S bond, we carried out the reaction of $Os_3(CO)_{10}(NCMe)_2$ and the decarbonylated $CpW(CO)_2(\eta^2-CH_2SMe)$, as the latter possesses a cyclic W-CH₂-S interaction. After the coordination of $CpW(CO)_2(\eta^2-CH_2SMe)$ to Os_3 metal triangle, it would result in the formation of an intermediate with the S atom simultaneously bonded to both W and Os atoms, thus enhanced the yield for 3. However, the products distribution of this reference reaction showed no significant difference from that reported earlier for $CpW(CO)_3$ (CH₂SMe) reaction. At this point, one could argue that the pre-coordination to W atom is of no importance in promoting the formation of 3.

The spiked-triangular methylene cluster 3 can be converted to carbido clusters 4 and 5 through activation of the methylene group, as the extra W-Os bonding interaction observed in 3 provided good stability against the cluster degradation. The carbido cluster 4 is a tetranuclear butterfly cluster containing 10 CO and two bridging hydride ligands, while complex 5 contains 64 electrons and possesses 12CO ligands. Limited chemistry of these carbido clusters has been developed. Heating of 4 under 1 atm of CO in toluene failed to produce 5, but gave severe decomposition upon prolonged refluxing. In contrast, hydrogen reacted with 5 in toluene solution (1 atm, 110°C, 5 hr) to afford 4 in 12% yield and starting material (70%). In view of these results, it is appropriate to say that the initial formation of carbido clusters 4 and 5 from methylene complex 3 proceeded through two different reaction channels: generation of 4 involves loss of three CO ligands, while the complex 5 is formed via competitive H₂ elimination, without any accompanying CO elimination.

Finally, in summary, the condensation reaction reported in this article provides examples for the preparation of heterometallic thiolate clusters, and example for the conversion of methylene to carbido ligand. Despite that the chemistry observed for these compounds is very interesting, the poor thermal stability of $CpW(CO)_3(CH_2SMe)$ and the low yields for the isolated cluster products seriously restrict the utilization of this thiolate reagent as the building blocks for cluster condensation.

SUPPLEMENTARY MATERIAL AVAILABLE

A complete listing of thermal parameters, tables of nonessential bond distances, hydrogen atom coordinates, and listings of the observed and calculated structural factors for complexes 2, 3, 4, and 5 are available from one of the authors (Y.C.).

ACKNOWLEDGMENTS

We thank the National Science Council of Republic of China under Grant NSC 84-2113-M007-020 for financial support.

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