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Reaction of Heterotrinuclear Vinylacetylide Complexes $Cp^*WRe_2(CO)_9(C\equiv CR)$ with Alcohol and Dihydrogen. Formation of WRe_2 Allenylidene and Metallacyclopentadienyl Derivatives

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Heterometallic vinylacetylide clusters with the structural formula $Cp^*WRe_2(CO)_9(C\equiv CR)$ were obtained in high yields from condensation of mononuclear tungsten acetylide complexes $Cp^*W(CO)_3(C\equiv CR)$ and rhenium carbonyl complex $Re_2(CO)_8(NCMe)_2$. The acetylide ligand in these WRe_2 clusters is coordinated perpendicular to the unique Re—Re bond which also supports a bridging CO ligand. Treatment of the vinylacetylide complex $Cp^*WRe_2(CO)_9[C\equiv CC(Me){=}CH_2]$ (**1a**) with alcohols in refluxing toluene solution afforded complexes $Cp^*WRe_2(CO)_8(\mu\text{-}OR)(C{=}C{=}CMe_2)$ (**2a**, R = Me; **2b**, R = Et; **2c**, R = Ph), which contain an unusual μ_3-η^3-allylidene ligand and a bridging alkoxide ligand. The fluxional behavior of allenylidene complexes **2** in solution was confirmed by ^1H NMR measurements. When **1a** was heated in the presence of hydrogen, the metallacyclopentadienyl complex $Cp^*WRe_2(CO)_7(\mu\text{-}H)[CHCHC(Me)CH]$ was formed, as a mixture of two noninterconvertible isomers (**3a** and **3b**). Hydrogenation of **1b** under similar conditions initially produced a dihydride cluster $Cp^*WRe_2(CO)_8(\mu\text{-}H)_2[C\equiv C(C_6H_9)]$ (**4b**). Crystals of **4b** are orthorhombic of space group $Pna2_1$ with a = 20.170(6) Å, b = 16.854(3) Å, c = 9.320(3) Å, Z = 4, R = 0.035, and R_w = 0.031 for 2537 observed reflections with $I > 2\sigma(I)$. Upon extending the reaction time to 1 h, complex **1b** produced two metallacyclopentadienyl clusters **3c** and **5**, and their distinction lies in the location of the cyclohexenyl ring and the arrangement of the metal cluster skeleton. Elaborate structural analysis reveals the complex **3c** adopts a triangular arrangement with a metal—metal double bond which is essentially identical to that of **3a** and **3b**, whereas complex **5** is best considered as a M_3C_4 pentagonal-bipyramidal cluster with a W atom and one Re atom at the axial positions and the second Re atom in the equatorial plane. Crystal data for **3c**: space group $P\bar{1}$, a = 10.947(1) Å, b = 11.074(1) Å, c = 11.167(2) Å, α = 101.38(1)°, β = 104.10(1)°, γ = 94.65(1)°, Z = 2, R = 0.020, R_w = 0.020 for 3045 observed reflections with $I > 2\sigma(I)$. Crystal data for **5**: space group $P2_1/c$, a = 12.359(5) Å, b = 9.814(4) Å, c = 25.372(8) Å, β = 97.85(3)°, Z = 4, R = 0.036, R_w = 0.033 for 2654 observed reflections with $I > 2\sigma(I)$.

Our research group is interested in utilizing group 6 metal acetylide complexes $LM(CO)_3C\equiv CR$ (L = Cp and Cp*, M = Mo and W) and group 8 metal carbonyl complexes to prepare various tri- and tetranuclear mixed-metal clusters containing a cluster-bound, bridging acetylide fragment and to examine the physical properties and reactivities of these acetylide cluster compounds.[1] Herein we present the results of our ongoing project on the preparation of acetylide clusters containing metal elements in groups 6 and 7 and the exploration of the effect of an unsaturated substituent on the acetylide ligand by switching to vinylacetylides. According to our preliminary communication,[2] attack of the uncoordinated olefin portion of vinylacetylide in cluster complex $Cp^*WRe_2(CO)_9[C\equiv CC(Me){=}CH_2]$ by alcohols was the dominant reaction pathway, giving a multisite coordinated allenylidene functional group, μ_3-η^3-$C{=}C{=}CMe_2$. This reactivity pattern is somewhat related to that of the dehydration of propargyl alcohol derivatives employed by Selegue[3] and that of the protonation of vinylacetylide complexes reported by Dixneuf,[4] in the preparation of mononuclear ruthenium allenylidene and higher cumulene derivatives. Hydrogenation of $Cp^*WRe_2(CO)_9[C\equiv CC(Me){=}CH_2]$ also involved the olefin portion, but the product shows the existence of not allenylidene ligand but a metallacyclopentadienyl fragment.[2] We now give a full account of examples regarding the reactivity of WRe_2 clusters in which the ligated hydrocarbon is a vinylacetylide rather than the regular acetylide ligand. The consequence of changing

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the vinyl substituent on the acetylide ligand is disclosed. In addition, the structure of a WRe_2 metallacyclopentadienyl cluster with an M_3C_4 pentagonal-bipyramidal skeleton, but not the 46-electron triangular metal core, is reported for comparison.

Experimental Procedure

General Information and Materials. Infrared spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 or a Varian Unity-400 instrument; chemical shifts are quoted with respect to internal standard tetramethylsilane. Mass spectra were obtained on a JEOL-HX110 instrument operating in the fast atom bombardment (FAB) mode. The vinylacetylenes, 2-methyl-1-buten-3-yne and 1-ethynylcyclohexene, were used without purification; *cis*-1-methoxyl-1-buten-3-yne was purified according to the method of Corey.[5] The tungsten acetylides $Cp^*W(CO)_3C{\equiv}CR$[6] and the rhenium acetonitrile complex $Re_2(CO)_8(CH_3CN)_2$[7] were prepared according to literature procedures. All reactions were performed under a nitrogen atmosphere using deoxygenated solvents dried with an appropriate reagent. The progress of the reactions was monitored by analytical thin-layer chromatography (5735 Kieselgel 60 F_{254}, E. Merck) and the products were separated on commercially available preparative thin-layer chromatographic plates (Kieselgel 60 F_{254}, E. Merck). Elemental analyses were performed at the NSC Regional Instrumentation Center at National Cheng Kung University, Tainan, Taiwan.

Synthesis of $Cp^*WRe_2(CO)_9[C{\equiv}C(Me){=}CH_2]$. In a 100-mL round bottom reaction flask, $Re_2(CO)_{10}$ (500 mg, 0.77 mmol) treated with freshly sublimed Me_3NO (125 mg, 1.67 mmol) in refluxing acetonitrile solution (60 mL) for 30 min. After evaporation of acetonitrile solvent in vacuo, tungsten acetylide complex $Cp^*W(CO)_3[C{\equiv}CC(Me){=}CH_2]$ (360 mg, 0.78 mmol) was added, and the reaction mixture was then dissolved in a toluene solution (60 mL) and brought to reflux for 60 min. Finally, the solvent was evaporated, and the residue was separated by thin-layer chromatography (silica gel, dichloromethane:hexane = 1:2) and recrystallized from dichloromethane–methanol, giving 420 mg of **1a** as an orange material (0.416 mmol, 54%). The analogous compounds **1b** and **1c** were prepared from the reactions with $Cp^*W(CO)_3[C{\equiv}C(C_6H_9)]$ and $Cp^*W(CO)_3[C{\equiv}CCH{=}CH(OMe)]$, respectively.

Spectral data for **1a**: MS (FAB, ^{184}W, ^{187}Re) *m/z* 1010 (M^+); IR (CH_2Cl_2) ν(CO) 2064 (m), 2025 (vs), 1987 (s, sh), 1974 (vs), 1950 (w), 1935 (w), 1891 (br, vw) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 294 K) δ 5.35 (s, 1H, $C{=}CH_2$), 5.19 (s, 1H, $C{=}CH_2$), 2.31 (s, 3H, Me), 2.22 (s, 15H, C_5Me_5); ^{13}C NMR (100 MHz, $CDCl_3$, 294 K) (CO) δ 209.3 (J_{W-C} = 171 Hz), 195.4 (2C, br), 189.2 (2C, br), 187.2 (1C), 185.7 (2C, br); ^{13}C NMR (100 MHz, $CDCl_3$, 294 K) δ 160.8 (J_{W-C} = 134 Hz, $C{\equiv}CC{=}CH_2Me$), 140.6 ($C{\equiv}CC{=}CH_2Me$), 118.2 ($C{\equiv}CC{=}CH_2Me$), 103.0 (C_5Me_5), 94.7 (J_{W-C} = 24 Hz, $C{\equiv}CC{=}CH_2Me$), 27.3 (CH_3), 12.1 (C_5Me_5). Anal. Calcd for $C_{24}H_{20}O_9Re_2W$: C, 28.58; H, 2.00. Found: C, 28.56; H, 2.01.

Spectral data for **1b**: MS (FAB, ^{184}W, ^{187}Re) *m/z* 1050 (M^+); IR (C_6H_{12}) ν(CO) 2066 (w), 2026 (vs), 1978 (vs, br), 1951 (m, br), 1896 (w, br) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 294 K) δ 6.11 (m, 1H, $C{=}CH$), 2.49–2.46 (m, 2H, CH_2), 2.31–2.27 (m, 2H, CH_2), 2.20 (s, 15H, C_5Me_5), 1.80–1.75 (m, 2H, CH_2), 1.68–1.64 (m, 2H, CH_2). Anal. Calcd for $C_{27}H_{24}O_9Re_2W$: C, 30.92; H, 2.31. Found: C, 30.88; H, 2.38.

Spectra data for **1c**: MS (FAB, ^{184}W, ^{187}Re) *m/z* 1026 (M^+); IR (C_6H_{12}) ν(CO) 2059 (m), 2025 (vs), 1976 (vs), 1960 (w), 1949 (m), 1894 (vw) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 294 K) δ 6.12 (d, 1H, J_{H-H} = 5.6 Hz), 5.92 (d, 1H, J_{H-H} = 5.6 Hz), 3.76 (s, 3H, OMe), 2.09 (s, 15H, C_5Me_5); ^{13}C NMR (100 MHz, $CDCl_3$, 294 K) (CO) δ 210.2 (2C, J_{W-C} = 172 Hz), 194.6 (2C, br), 187.4 (2C, br), 185.6 (1C), 184.2 (2C, br); ^{13}C NMR (100 MHz, $CDCl_3$, 294 K) δ 156.7 (J_{W-C} = 134 Hz, $CCCH{=}CHOMe$), 151.3 ($CCCH{=}CHOMe$), 101.0 (C_5Me_5), 99.1 ($CCCH{=}CHOMe$), 77.6 ($CCCH{=}CHOMe$), 59.3 (OMe), 10.3 (C_5Me_5). Anal. Calcd for $C_{24}H_{20}O_{10}Re_2W$: C, 28.13; H, 1.97. Found: C, 28.09, H, 2.07.

Preparation of $Cp^*WRe_2(CO)_8(\mu\text{-}OR)(C{=}C{=}CMe_2)$. A mixture of toluene (25 mL), anhydrous methanol (10 mL), and **1a** (70 mg, 0.069 mmol) was refluxed under nitrogen for 35 min, during which period the color changed from orange to 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 = 1:3), giving 33 mg of dark-brown $Cp^*WRe_2(CO)_8(\mu\text{-}OMe)(C{=}C{=}CMe_2)$ (**2a**, 0.033 mmol, 47%). Crystals of **2a** suitable for X-ray analysis were obtained from a layered solution of dichloromethane–heptane at room temperature. The analogous allenylidene cluster compounds **2b** and **2c** were prepared from reactions with anhydrous ethanol and phenol in 57% and 27% yields, respectively.

Spectral data for **2a**: MS (FAB, ^{184}W, ^{187}Re) *m/z* 1014 (M^+); IR (C_6H_{12}) ν(CO) 2034 (m), 2010 (vs), 1974 (vs), 1937 (m), 1919 (s), 1901 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 294 K) δ 2.87 (s, 3H, OMe), 2.63 (s, br, 3H, Me), 2.42 (s, br, 3H, Me), 2.25 (s, 15H, C_5Me_5); ^{13}C NMR (100 MHz, $CDCl_3$, 294 K) (CO) δ 215.9 (2C, J_{W-C} = 173 Hz), 200.4 (2C, br), 197.5 (4C, br); ^{13}C NMR (100 MHz, $CDCl_3$, 294 K) δ 186.7 ($CCCMe_2$, J_{W-C} = 163 Hz), 140.3 ($CCCMe_2$, J_{W-C} = 32 Hz), 116.1 ($CCCMe_2$), 106.1 (C_5Me_5), 70.9 (OMe), 36.2 (Me, br), 29.5 (Me, br), 11.9 (C_5Me_5). Anal. Calcd for $C_{24}H_{24}O_9Re_2W$: C, 28.46; H, 2.23. Found: C, 28.50; H, 2.46.

Spectral data for **2b**: MS (FAB, ^{184}W, ^{187}Re) *m/z* 1028 (M^+); IR (CH_2Cl_2) ν(CO) 2031 (m), 2007 (vs), 1971 (s, br), 1929 (s, br), 1906 (s, br) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 294 K) δ 2.89 (q, 2H, J_{H-H} = 6.9 Hz), 2.62 (s, br, 3H, Me), 2.43 (s, br, 3H, Me), 2.25 (s, 15H, C_5Me_5), 0.46 (t, 3H, J_{H-H} = 6.9 Hz). Anal. Calcd for $C_{25}H_{26}O_9Re_2W$: C, 29.25; H, 2.55. Found: C, 29.11; H, 2.54.

Spectral data for **2c**: MS (FAB, ^{184}W, ^{187}Re) *m/z* 1076 (M^+); IR (CH_2Cl_2) ν(CO) 2040 (m), 2017 (vs), 1976 (vs), 1952 (w), 1943 (m), 1920 (s), 1904 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 294 K) δ 7.00 (t, 2H, J_{H-H} = 7.2 and 6.8 Hz), 6.60 (t, 1H, J_{H-H} = 6.8 Hz), 6.34 (d, 2H, J_{H-H} = 7.2 Hz), 2.68 (s, br, 3H, Me), 2.48 (s, br, 3H, Me), 2.27 (s, 15H, C_5Me_5). Anal. Calcd for $C_{29}H_{26}O_9Re_2W$: C, 32.41; H, 2.44. Found: C, 32.20; H, 2.44.

Hydrogenation of $Cp^*WRe_2(CO)_9[C{\equiv}CC(Me){=}CH_2]$. The toluene solution (30 mL) of **1a** (290 mg, 0.288 mmol) was refluxed under 1 atm of hydrogen for 1 h, during which the color changed from orange to red-brown. After cooling the solution to room temperature, the solvent was evaporated and the residue was separated by thin-layer chromatography (dichloromethane: hexane = 1:1), giving 185 mg of red-brown $Cp^*WRe_2(CO)_7(\mu\text{-}H)[CHCHC(Me)CH]$ (0.193 mmol, 67%) as a mixture of two isomers (**3a** and **3b**). Crystals of **3** suitable for X-ray analysis were recrystallized from a layered solution of chloroform–heptane at room temperature.

Spectral data for **3**: MS (FAB, ^{184}W, ^{187}Re) *m/z* 956 (M^+); IR (CH_2Cl_2) ν(CO) 2037 (vs), 2002 (s), 1959 (vs, br), 1906 (w, br) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 294 K) δ 6.53 (dd, J_{H-H} = 2.9 and 6.1 Hz, R_2, **a**), 6.43 (dd, J_{H-H} = 2.1 and 5.8 Hz, R_3, **b**), 6.10 (dd, J_{H-H} = 3.5 and 5.8 Hz, H_4, **b**), 5.97 (d, J_{H-H} = 6.1 Hz, H_1, **a**), 5.86 (t, J_{H-H} = 2.9 and 3.2 Hz, H_4, **a**), 5.71 (d, J_{H-H} = 2.1 Hz, H_1, **b**), 2.64 (s, Me, **a**), 2.62 (s, Me, **b**), 2.00 (s, C_5Me_5, **b**), 1.99 (s, C_5Me_5, **a**), –5.74 (d, J_{H-H} = 3.5 Hz, J_{W-H} = 99 Hz, **b**), –5.77 (d, J_{H-H} = 3.2 Hz, J_{W-H} = 99 Hz, **a**); ^{13}C NMR (100 MHz, THF-d_8, 294 K) (CO) δ 238.1 (J_{W-C} = 126 Hz, **a**), 237.9 (J_{W-C} = 126 Hz, **b**), 201.2 (3C, **a** and **b**), 196.3 (1C, br, **a** and **b**), 191.9 (2C, br, **a** and **b**); ^{13}C NMR (100 MHz, THF-d_8, 294 K) δ 146.6 (CH, J_{W-C} = 64 Hz, **a**), 145.8 (CH, J_{W-C} = 67 Hz, **b**), 135.9 (CH, J_{W-C} = 65 Hz, **b**), 134.6 (CH, J_{W-C} = 67 Hz, **a**), 126.2 (*C*Me, **a**), 120.6 (*C*Me, **b**), 108.5 (CH, **a**), 106.3 (C_5Me_5, **a** and **b**), 103.7 (CH, **b**),

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Table 1. Experimental Data for the X-ray Diffraction Studies of 4b, 3c, and 5

compd	4b	3c	5
formula	$C_{27}H_{28}Cl_2O_8Re_2W$	$C_{25}H_{26}O_7Re_2W$	$C_{25}H_{26}O_7Re_2W\cdot CHCl_3$
mol wt	1107.79	994.76	1114.28
cryst syst	orthorhombic	triclinic	monoclinic
space group	$Pna2_1$	$P\bar{1}$	$P2_1/c$
a (Å)	20.170(6)	10.947(1)	12.359(5)
b (Å)	16.854(3)	11.074(1)	9.814(4)
c (Å)	9.320(3)	11.167(2)	25.372(8)
α (deg)		101.38(1)	
β (deg)		104.10(1)	97.85(3)
γ (deg)		94.65(1)	
V (Å^3)	3168(2)	1275.1(3)	3049(2)
Z	4	2	4
D_c (g/cm^3)	2.322	2.591	2.427
$F(000)$	2048	912	2056
cryst size, mm.	0.30 × 0.40 × 0.50	0.10 × 0.15 × 0.45	0.30 × 0.35 × 0.50
h, k, l ranges	0–23, 0–20, 0–11	−11 to +11, 0–11, −12 to +11	−13 to +13, 0–10, 0–27
transm factors; max, min	1.00, 0.67	1.00, 0.59	1.00, 0.35
μ (mm^{-1})	11.47	14.24	12.18
no. of unique data [$2\theta_{max}$ (deg)]	2967 (50)	3316 (45)	3985 (45)
no. of data with $I > 2\sigma(I)$	2537	3045	2654
no. of params	361	321	353
max Δ/σ ratio	0.043	0.010	0.010
R; R_w	0.035; 0.031	0.020; 0.020	0.036; 0.033
GOF	2.14	2.35	1.50
residual electron density, e/Å^3	1.31/−1.52	0.90/−0.65	1.51/−1.19

22.0 (Me, **b**), 21.9 (Me, **a**), 13.1 (C_5Me_5, **b**), 13.0 (C_5Me_5, **a**). Anal. Calcd for $C_{22}H_{22}O_7Re_2W$: C, 27.68; H, 2.32. Found: C, 27.56; H, 2.40.

Hydrogenation of $Cp^*WRe_2(CO)_9[C{\equiv}C(C_6H_9)]$. A toluene solution (30 mL) of **1b** (63 mg, 0.053 mmol) was refluxed under 1 atm of hydrogen for 30 minutes, during which the color changed from orange to light yellow. After cooling the solution to room temperature, the solvent was evaporated and the residue was separated by thin-layer chromatography (dichloromethane: hexane = 1:1), giving 46 mg of pale yellow $Cp^*WRe_2(CO)_8(\mu\text{-}H)_2[C{\equiv}C(C_6H_9)]$ (**4b**, 0.04 mmol, 75%). Crystals suitable for X-ray analysis were recrystallized from a solution of dichloromethane–heptane at room temperature.

Spectral data for **4b**: MS (FAB, ^{184}W, ^{187}Re) m/z 1024 (M^+); IR (CH_2Cl_2) ν(CO) 2043 (s), 2014 (vs), 1984 (m), 1952 (s, br), 1929 (w, sh), 1915 (w, br) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 294 K) δ 6.44 (m, br, 1H, C=CH), 2.49–2.46 (m, 2H, CH_2), 2.31–2.26 (m, 2H, CH_2), 2.20 (s, 15H, C_5Me_5), 1.85–1.77 (m, 2H, CH_2), 1.70–1.63 (m, 2H, CH_2), −15.73 (s, J_{W-H} = 42 Hz), −17.89 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 294 K) (CO) δ 214.9 (J_{W-C} = 135 Hz), 207.3 (J_{M-C} = 148 Hz), 197.5 (1C), 192.4 (1C), 191.8 (1C), 185.9 (1C), 185.5 (1C), 183.5 (1C); ^{13}C NMR (100 MHz, $CDCl_3$, 294 K) δ 135.3 (C=CH), 129.4 (*C*=CH), 125.3 (J_{W-C} = 111 Hz), 103.7 (C_5Me_5), 100.8 (CCC_6H_9), 34.6 (CH_2), 26.5 (CH_2), 23.7 (CH_2), 22.0 (CH_2), 11.3 (C_5Me_5). Anal. Calcd for $C_{26}H_{26}O_8Re_2W$: C, 30.53; H, 2.56. Found: C, 31.32, H, 2.66.

Hydrogenation of $Cp^*WRe_2(CO)_8(\mu\text{-}H)_2[C{\equiv}C(C_6H_9)]$. A toluene solution (30 mL) of **4b** (46 mg, 0.04 mmol) was further refluxed under 1 atm of hydrogen; the color of the solution changed from light-yelow to red-brown within 1 h. After removal of solvent under vacuum, the residue was separated by thin-layer chromatography (dichloromethane:hexane = 1:1), providing dark-brown $Cp^*WRe_2(CO)_7(\mu\text{-}H)[CHCH(C_6H_8)]$ (**3c**, 16 mg, 0.016 mmol, 10%) and another dark-brown complex $Cp^*WRe_2(CO)_7(\mu\text{-}H)[CHCH(C_6H_8)]$ (**5**, 5 mg, 0.005 mmol, 3%). Crystals of **3c** and **5** suitable for X-ray analysis were obtained from a layered solution of dichloromethane–heptane and chloroform–heptane, respectively.

Spectral data for **3c**: MS (FAB, ^{184}W, ^{187}Re) m/z 996 (M^+); IR (CH_2Cl_2) ν(CO) 2035 (vs), 2001 (s), 1956 (s), 1939 (w), 1917 (w), 1903 (w), 1853 (vw, br) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 294 K) δ 6.57 (d, 1H, J_{H-H} = 7.1 Hz, CH), 5.87 (d, 1H, J_{H-H} = 7.1 Hz, CH), 3.18–3.13 (m, 1H, CH_2), 3.04–3.00 (m, 1H, CH_2), 2.66–2.62 (m, 1H, CH_2), 2.36–2.29 (m, 1H, CH_2), 1.99 (s, 15H, C_5Me_5), 1.77–1.75 (m, 1H, CH_2), 1.52–1.42 (m, 2H, CH_2), 1.27–1.23 (m, 1H, CH_2), −5.14 (s, J_{W-H} = 98 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 294 K) (CO) δ 235.6 (J_{W-C} = 135 Hz), 199.0 (3C, br), 193.4 (1C), 191.3 (1C), 190.4 (1C); ^{13}C NMR (100 MHz, $CDCl_3$, 294 K) δ 163.4 (J_{W-C} = 68 Hz, CH), 132.4 (J_{W-C} = 67 Hz, CH), 119.8 (CH), 105.4(CH), 104.1 (C_5Me_5), 47.4 (CH_2), 28.9 (CH_2), 27.0 (CH_2), 23.2 (CH_2), 11.6 (C_5Me_5). Anal. Calcd for $C_{25}H_{26}O_7Re_2W$: C, 30.19; H, 2.63. Found: C, 29.92, H, 2.63.

Spectral data for **5**: MS (FAB, ^{184}W, ^{187}Re) m/z 996 (M^+). IR (CH_2Cl_2): ν(CO) 2034 (vs), 2002 (s), 1988 (m, sh), 1940 (s, br), 1900 (m, br), 1799 (vw, br) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 294 K) δ 6.15 (d, 1H, J_{H-H} = 6.8 Hz, CH), 3.78–3.73 (m, 1H, CH_2), 3.65 (d, 1H, J_{H-H} = 6.8 Hz, CH), 3.64–3.60 (m, 1H, CH_2), 2.97–2.90 (m, 1H, CH_2), 2.77–2.74 (m, 1H, CH_2), 2.03 (s, 15H, C_5Me_5), 1.89–1.71 (m, 1H, CH_2), 1.40–1.36 (m, 1H, CH_2), 1.25–1.23 (m, 1H, CH_2), 1.17–1.13 (m, 1H, CH_2), −3.94 (s, J_{W-H} = 100 Hz). Anal. Calcd for $C_{25}H_{26}O_7Re_2W$: C, 30.19; H, 2.63. Found: C, 29.96; H, 2.63.

Hydrogenation of $Cp^*WRe_2(CO)_9[C{\equiv}CCH{=}CH(OMe)]$. A toluene solution (30 mL) of **1c** (70 mg, 0.068 mmol) was refluxed under 1 atm of hydrogen for 2 h, during which period the color changed from orange to light-yellow and then gradually to red-brown. After cooling the solution to room temperature, the solvent was evaporated and the residue was separated by thin-layer chromatography (dichloromethane:hexane = 1:1), giving 8 mg of red-brown $Cp^*WRe_2(CO)_7(\mu\text{-}H)[CHCHCHCH]$ (**3d**, 0.008 mmol, 12%).

Spectral data for **3d**: MS (FAB, ^{184}W, ^{187}Re) m/z 942 (M^+); IR (CH_2Cl_2) ν(CO) 2037 (vs), 2003 (s), 1957 (s), 1907 (m), 1860 (w, br) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 294 K) δ 6.50 (dt, 1H, J_{H-H} = 2 and 6.1 Hz), 6.41 (dt, 1H, J_{H-H} = 2 and 5.9 Hz), 6.11 (m, 1H, J_{H-H} = 2, 3.4 and 5.9 Hz), 6.01 (dd, 1H, J_{H-H} = 2 and 6.1 Hz), 1.99 (s, 15H, C_5Me_5), −5.74 (d, 1H, J_{H-H} = 3.4 Hz, J_{W-H} = 98 Hz). Anal. Calcd for $C_{21}H_{20}O_7Re_2W$: C, 26.81; H, 2.14. Found: C, 27.06; H, 2.20.

X-ray Crystallography. Diffraction measurements of complexes **4b**, **3c**, and **5** were carried out on a Nonius CAD-4 diffractometer. All reflections were corrected for Lorentz, polarization, and absorption effects. Data deduction and refinement were performed using the NRCC-SDP-VAX packages. Lattice parameters of **4b** were determined from 25 randomly selected high angle reflections with 2θ angles in the range 20.0–26.4°. The space group $Pna2_1$ was identified on the basis of systematic absences and confirmed by solving the crystal structure. Absorption corrections were made by the Ψ scan method; the minimum and maximum transmission factors were 0.67 and 1.00, respectively. Anisotropic thermal parameters were introduced for all non-hydrogen atoms. Full matrix least-squares

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients for 4b

	x	y	z	$B_{eq}{}^a$ (Å^3)
Re(1)	0.75103(4)	0.44679(4)	0.29491	2.09(3)
Re(2)	0.76374(3)	0.50349(5)	−0.00003(11)	1.94(3)
W	0.85647(4)	0.56960(4)	0.23575(11)	1.96(3)
C(1)	0.8034(12)	0.3600(15)	0.3777(24)	6.1(14)
C(2)	0.7201(10)	0.4708(10)	0.4806(25)	3.6(11)
C(3)	0.6719(11)	0.3848(17)	0.277(3)	7.9(16)
C(4)	0.6778(10)	0.4664(12)	−0.0652(24)	4.1(11)
C(5)	0.7577(9)	0.5966(12)	−0.1258(18)	2.7(10)
C(6)	0.8098(11)	0.4417(12)	−0.1399(20)	3.4(11)
C(7)	0.9029(12)	0.4676(12)	0.260(3)	5.6(14)
C(8)	0.8467(11)	0.5532(11)	0.4522(21)	4.0(11)
C(9)	0.7561(7)	0.5726(9)	0.2120(16)	1.0(6)
C(10)	0.6994(9)	0.5530(11)	0.1863(19)	2.6(9)
C(11)	0.6209(12)	0.5749(13)	0.1750(24)	5.6(14)
C(12)	0.5752(12)	0.5338(14)	0.239(4)	7.2(17)
C(13)	0.5073(12)	0.5546(14)	0.218(5)	10.7(25)
C(14)	0.4946(14)	0.6203(23)	0.119(4)	11.9(27)
C(15)	0.5432(15)	0.6739(21)	0.097(4)	11.5(25)
C(16)	0.6166(10)	0.6512(13)	0.106(3)	4.8(13)
C(17)	0.8798(10)	0.6957(10)	0.3199(21)	2.6(10)
C(18)	0.9455(9)	0.6434(11)	0.3191(23)	3.3(10)
C(19)	0.9561(9)	0.6244(13)	0.1786(23)	3.7(12)
C(20)	0.9080(11)	0.6634(12)	0.0865(22)	3.7(11)
C(21)	0.8592(9)	0.7058(11)	0.1752(21)	2.9(10)
C(22)	0.8535(14)	0.7378(12)	0.446(3)	6.4(15)
C(23)	0.9899(11)	0.6273(15)	0.4334(24)	4.9(13)
C(24)	1.0216(10)	0.5806(13)	0.126(3)	4.8(13)
C(25)	0.9120(11)	0.6609(15)	−0.0790(23)	4.7(13)
C(26)	0.8032(11)	0.7536(13)	0.119(3)	4.6(12)
O(1)	0.8347(9)	0.3099(10)	0.4198(19)	6.9(11)
O(2)	0.6978(8)	0.4824(10)	0.6026(16)	5.3(9)
O(3)	0.6294(8)	0.3387(8)	0.2622(20)	6.0(9)
O(4)	0.6284(7)	0.4409(9)	−0.1028(17)	5.0(9)
O(5)	0.7499(8)	0.6460(7)	−0.1967(18)	4.8(8)
O(6)	0.8331(8)	0.4006(9)	−0.2218(17)	5.7(9)
O(7)	0.9405(7)	0.4145(8)	0.2564(18)	4.8(8)
O(8)	0.8457(7)	0.5504(8)	0.5806(15)	4.4(8)
C(27)	0.3793(18)	0.3322(17)	0.120(4)	13.4(30)
CL(1)	0.3500(5)	0.2689(7)	0.0049(16)	14.4(9)
CL(2)	0.4681(6)	0.3281(7)	0.1410(16)	16.5(10)
H(1)	0.763	0.408	0.063	1.9
H(2)	0.844	0.534	0.063	1.9

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid.

refinement with 68 atoms and 361 parameters gave $R = 0.035$ and $R_w = 0.031$, for 2534 reflections with $I > 2\sigma(I)$. The residual electron density on the difference Fourier map is about 1.31 e/Å^3.

For complex **3c**, the lattice parameters were determined from 25 randomly selected high angle reflections with 2θ angles in the range 20.0–31.3°. The minimum and maximum transmission factors were 0.59 and 1.00, respectively. Anisotropic temperature factors were assigned to all other non-hydrogen atoms. The bridging hydride was located on the Fourier map and refined accordingly. Hydrogen atoms of the methyl and methylene groups were calculated at idealized positions with fixed temperature coefficients and were also included in the structure factor calculation. Refinement was made by full matrix least squares with 61 atoms and 321 parameters, giving $R = 0.020$ and $R_w = 0.020$ for 3045 reflections with $I > 2\sigma(I)$.

Lattice parameters of **5** were determined from 25 selected reflections with 2θ angles in the range 17.0–32.7°. The space group $P2_1/c$ was identified on the basis of systematic absences. Absorption corrections were performed and the minimum and maximum transmission factors were 0.35 and 1.00, respectively. The structures were solved by direct methods and refined by least-squares cycles. The presence of a $CHCl_3$ solvent molecule was unambiguously identified on the difference Fourier map. Full matrix least-squares refinement with 65 atoms and 353 parameters gave $R = 0.036$ and $R_w = 0.033$ for 2654 reflections with $I > 2\sigma(I)$. The combined data collection and refinement parameters are given in Table 1. ATomic positional parameters for **4b**, **3c**, and **5** are presented in Tables 2–4, whereas selected bond angles and lengths are given in Tables 5–7, respectively.

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

	x	y	z	B_{eq} (Å^2)
W	0.24204(3)	0.26722(3)	0.17756(3)	1.713(15)
Re(1)	0.46652(3)	0.17954(3)	0.23735(3)	2.394(15)
Re(2)	0.24447(3)	0.11006(3)	0.35809(3)	2.256(16)
C(1)	0.2658(8)	0.1068(7)	0.0725(7)	2.5(4)
C(2)	0.5171(9)	0.0179(8)	0.1925(9)	4.0(5)
C(3)	0.5745(8)	0.2390(8)	0.1485(8)	3.7(5)
C(4)	0.6091(8)	0.2164(8)	0.3828(8)	3.6(4)
C(5)	0.2697(8)	−0.0517(7)	0.2717(8)	3.3(4)
C(6)	0.4011(9)	0.1406(8)	0.4880(8)	3.5(5)
C(7)	0.1848(9)	0.0301(8)	0.4717(8)	4.1(5)
C(8)	0.0897(8)	0.1424(7)	0.1894(7)	2.5(4)
C(9)	0.0448(8)	0.1614(8)	0.2979(8)	3.4(5)
C(10)	0.1209(8)	0.2653(7)	0.3995(7)	2.5(4)
C(11)	0.2268(7)	0.3153(6)	0.3706(7)	2.1(3)
C(12)	0.3185(8)	0.4218(7)	0.4720(7)	3.0(4)
C(13)	0.2860(14)	0.4471(12)	0.5953(10)	9.0(8)
C(14)	0.1760(12)	0.4075(16)	0.6096(11)	11.5(10)
C(15)	0.0828(9)	0.3074(9)	0.5208(8)	4.0(5)
C(16)	0.0676(7)	0.3482(7)	0.0654(7)	2.5(4)
C(17)	0.1361(8)	0.2980(7)	−0.0199(7)	2.5(4)
C(18)	0.2581(7)	0.3655(6)	0.0172(6)	1.9(4)
C(19)	0.2658(8)	0.4627(7)	0.1252(7)	2.4(4)
C(20)	0.1478(7)	0.4514(7)	0.1554(7)	2.4(4)
C(21)	−0.0706(8)	0.3138(9)	0.0566(9)	4.2(5)
C(22)	0.0823(9)	0.1985(8)	−0.1393(8)	4.1(5)
C(23)	0.3562(9)	0.3598(8)	−0.0566(8)	3.7(5)
C(24)	0.3736(9)	0.5651(7)	0.1894(8)	3.6(5)
C(25)	0.1062(9)	0.5396(8)	0.2535(9)	4.0(5)
O(1)	0.2470(6)	0.0139(5)	−0.0046(5)	4.1(3)
O(2)	0.5445(8)	−0.0796(6)	0.1645(7)	7.2(5)
O(3)	0.6412(6)	0.2815(7)	0.0962(7)	6.7(5)
O(4)	0.6970(6)	0.2432(6)	0.4695(6)	6.1(4)
O(5)	0.2774(6)	−0.1481(5)	0.2200(6)	5.1(4)
O(6)	0.4898(6)	0.1603(6)	0.5753(6)	5.7(4)
O(7)	0.1449(7)	−0.0171(7)	0.5426(7)	7.5(5)
H	0.411(6)	0.330(5)	0.281(5)	1.4(14)

Results and Discussion

Treatment of $Cp^*W(CO)_3(C{\equiv}CR)$, R = $C(Me){=}CH_2$, C_6H_9 (cyclohexenyl) and $CH{=}CHOMe$, with the dirhenium complex $Re_2(CO)_8(NCMe)_2$ in refluxing toluene (110 °C, 30 min) afforded trinuclear, red-orange acetylide complexes, $Cp^*WRe_2(CO)_9(C{\equiv}CR)$ (**1**) in 41–54% yield. These cluster compounds were characterized initially by spectroscopic methods. The FAB mass spectra show the expected composition for molecular ions, whereas the ^{1}H NMR spectra present the characteristic signals of each R substituent. An X-ray diffraction measurement on **1a** reveals its structure (Figure 1) to be similar to that of the trinuclear, symmetric WRu_2 and WFe_2 acetylide complexes.[8] Other related, structurally characterized examples include the $CoFe_2$ and $NiFe_2$ clusters: $CoFe_2(CO)_9(C{\equiv}CSiMe_3)$ and $CpNiFe_2(CO)_6(C{\equiv}CPr^i)$.[9] Complex **1a** comprises a WRe_2 metal triangle with metal—metal distances W—Re(1) = 3.083(2) Å, W—Re(2) = 3.027(2) Å, and Re(1)—Re(2) = 2.829(1) Å, in which the acetylide ligand bridges the unique Re—Re bond. Because a Re atom possesses one electron less than a Ru atom in the trinuclear cluster $CpWRu_2(CO)_8(C{\equiv}CPh)$, the WRe_2 complex possesses an extra bridging CO group on the Re—Re edge to maintain an 18-electron shell for the rhenium atoms. The exceptionally short Re—Re distance

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Table 4. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients for 5

	x	*y*	*z*	B_{eq} (Å^2)
W	0.17205(4)	0.88207(6)	0.117061(21)	2.280(24)
Re(1)	0.33024(5)	1.10235(6)	0.139055(24)	2.73(3)
Re(2)	0.48667(4)	0.89615(7)	0.166767(23)	3.04(3)
C(1)	0.1236(11)	1.0730(15)	0.1147(6)	3.8(8)
C(2)	0.3035(13)	1.2263(16)	0.0792(6)	4.4(8)
C(3)	0.2660(12)	1.2170(14)	0.1887(6)	3.7(7)
C(4)	0.4629(13)	1.2015(15)	0.1584(6)	4.4(9)
C(5)	0.5671(11)	0.9655(16)	0.2287(7)	5.2(9)
C(6)	0.6055(11)	0.9452(18)	0.1311(7)	5.4(10)
C(7)	0.5585(9)	0.7257(18)	0.1837(6)	3.9(8)
C(8)	0.3121(10)	0.9251(13)	0.1872(5)	2.6(6)
C(9)	0.3211(10)	0.7900(13)	0.1644(6)	2.9(7)
C(10)	0.3445(11)	0.7959(14)	0.1102(5)	3.0(7)
C(11)	0.3551(9)	0.9252(14)	0.0907(5)	2.5(6)
C(12)	0.3795(11)	0.9381(16)	0.0333(6)	3.8(7)
C(13)	0.3780(15)	0.8084(21)	0.0014(6)	6.2(10)
C(14)	0.4303(14)	0.6913(19)	0.0352(7)	5.8(10)
C(15)	0.3644(11)	0.6640(17)	0.0816(6)	4.2(8)
C(16)	0.0416(11)	0.7306(13)	0.0764(5)	3.0(7)
C(17)	−0.0095(10)	0.8506(14)	0.0921(5)	3.0(7)
C(18)	0.0082(11)	0.8615(15)	0.1487(6)	3.6(7)
C(19)	0.0730(11)	0.7457(15)	0.1664(6)	3.7(7)
C(20)	0.0912(11)	0.6646(14)	0.1230(7)	4.1(8)
C(21)	0.0322(13)	0.6757(20)	0.0202(7)	6.1(10)
C(22)	−0.0896(10)	0.9345(18)	0.0556(6)	4.3(9)
C(23)	−0.0484(13)	0.9578(20)	0.1822(6)	5.5(9)
C(24)	0.1042(13)	0.7132(20)	0.2251(7)	6.2(10)
C(25)	0.1383(14)	0.5214(15)	0.1268(8)	5.8(10)
O(1)	0.0682(7)	1.1699(10)	0.1101(5)	5.9(6)
O(2)	0.2855(11)	1.2936(13)	0.0424(5)	7.1(7)
O(3)	0.2247(9)	1.2768(11)	0.2192(4)	5.3(6)
O(4)	0.5413(9)	1.2676(12)	0.1678(6)	7.6(8)
O(5)	0.6120(10)	1.0089(13)	0.2686(5)	7.8(8)
O(6)	0.6754(9)	0.9796(17)	0.1087(6)	9.2(9)
O(7)	0.5952(8)	0.6187(11)	0.1927(5)	5.9(6)
C(26)	0.7677(13)	0.4617(18)	0.1314(6)	5.0(8)
CL(1)	0.8420(4)	0.5561(7)	0.1801(3)	9.5(4)
CL(2)	0.7374(6)	0.5531(8)	0.0730(3)	11.8(5)
CL(3)	0.8390(6)	0.3182(7)	0.1188(3)	12.0(5)

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for 4b (Esd in Parentheses)

Re(1)–Re(2)	2.921(1)	W–Re(1)	3.019(1)
W–Re(2)	3.093(1)	W–C(9)	2.04(1)
Re(1)–C(9)	2.26(1)	Re(2)–C(9)	2.30(2)
Re(1)–C(10)	2.31(2)	Re(2)–C(10)	2.32(2)
C(9)–C(10)	1.22(2)	C(10)–C(11)	1.63(3)
C(11)–C(12)	1.30(4)	C(11)–C(16)	1.44(3)

W–C(9)–C(10)	162(1)	C(9)–C(10)–C(11)	150(2)
Re(1)–C(9)–Re(2)	79.7(5)	Re(1)–C(10)–Re(2)	78.3(6)
Re(1)–H(1)–Re(2)	93.3(1)	W–H(2)–Re(2)	122.2(2)
mean W–CO(terminal)	169(2)	mean Re–CO(terminal)	175(2)

Table 6. Selected Bond Distances (Å) and Bond Angles (deg) for 3c (Esd in Parentheses)

Re(1)–Re(2)	3.1655(6)	W–Re(1)	2.6964(5)
W–Re(2)	2.9085(6)	W–C(8)	2.124(8)
Re(2)–C(8)	2.315(8)	Re(2)–C(9)	2.278(9)
Re(2)–C(10	2.317(8)	W–C(11)	2.166(7)
Re(2)–C(11)	2.276(7)	C(8)–C(9)	1.40(1)
C(9)–C(10)	1.47(1)	C(10)–C(11)	1.38(1)
W–C(1)	2.000(8)	Re(1)–C(1)	2.454(8)
W–H	1.92(6)	Re(1)–H	1.84(6)

W–C(1)–O(1)	162.3(7)	Re(1)–C(1)–O(1)	123.9(6)
W–H–Re(1)	91(2)	mean Re–CO(terminal)	176.7(8)

Table 7. Selected Bond Distances (Å) and Bond Angles (deg) for 5 (Esd in Parentheses)

W–Re(1)	2.917(1)	Re(1)–Re(2)	2.821(1)
W–C(8)	2.35(1)	Re(1)–C(8)	2.16(1)
Re(2)–C(8)	2.31(1)	W–C(9)	2.25(1)
Re(2)–C(9)	2.317(8)	W–C(10)	2.166(7)
Re(2)–C(10)	2.29(1)	W–C(11)	2.48(1)
Re(1)–C(11)	2.17(1)	Re(2)–C(11)	2.37(1)
C(8)–C(9)	1.46(2)	C(9)–C(10)	1.45(2)
C(10)–C(11)	1.38(2)	W–C(1)	1.97(2)
Re(1)–C(1)	2.56(1)	mean Re–CO(terminal)	1.90(2)

W–Re(1)–Re(2)	86.26(4)	W–C(1)–O(1)	162(1)
Re(1)–C(1)–O(1)	119(1)	mean Re–CO(terminal)	176(1)

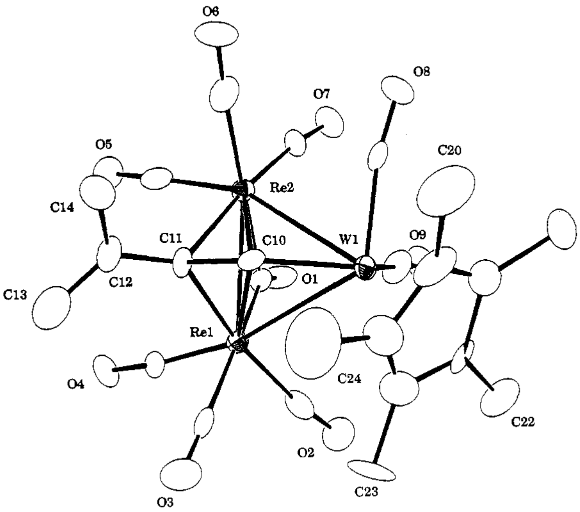

Figure 1. Molecular structure of **1a**. Selected bond lengths (Å) and angles (deg) of one molecule: W–Re(1) = 3.083(2), W–Re(2) = 3.027(2), Re(1)–Re(2) = 2.829(1), Re(1)–C(1) = 2.03(2), Re(2)–C(1) = 2.33(2), C(1)–O(1) = 1.20(3), W–C(10) = 2.06(3), Re(1)–C(10) = 2.28(2), Re(2)–C(10) = 2.16(2), Re(1)–C(11) = 2.31(2), Re(2)–C(11) = 2.31(2), C(10)–C(11) = 1.25(4), and C(11)–C(12) = 1.48(3); W–C(10)–C(11) = 165(2), C(10)–C(11)–C(12) = 138(2), Re(1)–C(10)–Re(2) = 79.2(7), Re(1)–C(11)–Re(2) = 75.6(7), Re(1)–C(1)–O(1) = 148(2), Re(2)–C(1)–O(1) = 131(2), and Re(1)–C(1)–Re(2) = 80.6(8).

in **1a**, relative to the Re—Re bond (3.041(1) Å) in Re$_2$(CO)$_{10}$,[10] is attributed both to the presence of the triply bridging acetylide ligand and to an asymmetric bridging CO ligand with Re(1)—C(1) = 2.03(2) Å and Re(2)—C(1) = 2.33(2) Å.

The solid-state structure of these acetylide clusters is preserved in solution. For example, the ^{13}C NMR spectrum of **1a** exhibits one W–CO and four Re–CO signals at δ 209.3 (J_{W-C} = 171 Hz), 195.4, 189.2, 187.2, and 185.7 in a ratio 2:2:2:1:2, suggesting the existence of a mirror plane which bisects the tungsten atom, the acetylide and bridging CO ligands, and the middle of the Re–Re bond. The signal at δ 187.2 is assigned to a bridging CO ligand, although its chemical shift is comparable with those of other terminal CO ligands within the molecule. The C$_\alpha$ and C$_\beta$ resonances of the acetylide ligand of **1a** appear at 160.8 (J_{W-C} = 134 Hz) and 94.7 (J_{W-C} = 24 Hz), which are consistent with a μ_3-η^2 bonding mode.[11] A similar ^{13}C NMR pattern for CO and acetylide resonances was observed for derivative **1c**.

Reaction with Alcohol. Heating of vinylacetylide compound **1a** in refluxing toluene with alcohol in a large excess gave the brown allenylidene clusters Cp*WRe$_2$(CO)$_8$(μ-OR)(C=C=CMe$_2$) (**2a**, R = Me; **2b**, R = Et; **2c**, R = Ph), after TLC separation. An X-ray diffraction study

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(11) Carty, A. J.; Cherkas, A. A.; Randall, L. H. *Polyhedron* **1988**, *7*, 1045.

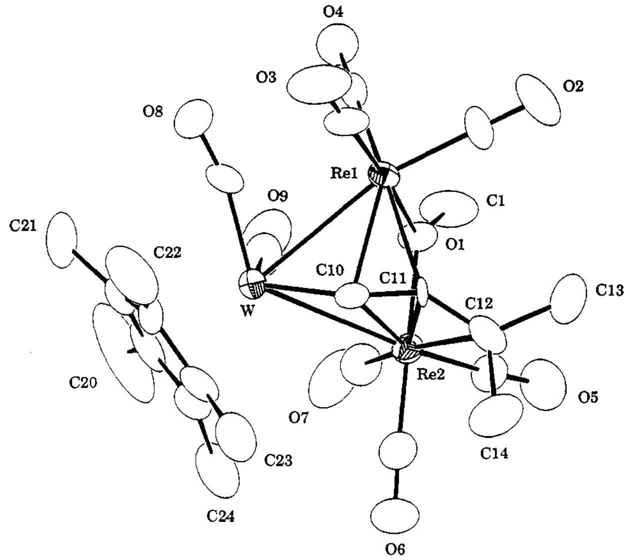

Figure 2. Molecular structure of **2a**. Selected bond lengths (Å): W–Re(1) = 3.0812(8), W–Re(2) = 3.1961(8), Re(1)–Re(2) = 3.3659(7), Re(1)–O(1) = 2.127(7), Re(2)–O(1) = 2.115(7), C(1)–O(1) = 1.38(2), W–C(10) = 1.99(1), Re(1)–C(10) = 2.24(1), Re(2)–C(10) = 2.23(1), Re(1)–C(11) = 2.28(1), Re(2)–C(11) = 2.31(1), Re(2)–C(12) = 2.54(1), C(10)–C(11) = 1.27(2), and C(11)–C(12) = 1.35(2). Bond angles (deg): W–C(10)–C(11) = 167.0(8), C(10)–C(11)–C(12) = 143(1), C(13)–C(12)–C(14) = 110(1), Re(1)–C(10)–Re(2) = 97.7(4), Re(1)–C(11)–Re(2) = 94.3(4), and Re(1)–O(1)–Re(2) = 105.0(3).

of **2a** shows that addition of the methoxyl group of methanol has taken place at the Re—Re linkage, with the proton added to the CH_2 carbon of the vinylacetylide grouping. As depicted in Figure 2, the molecule adopts an open-edge triangular geometry, in which the methoxide ligand bridges both Re atoms with a distance 3.3659(7) Å; the Re—O distances are Re(1)—O(1) = 2.127(7) Å and Re(2)—O(1) = 2.115(7) Å, respectively. There is no direct interaction between these Re atoms, as the Re—Re contact is much larger than the Re—Re distance of **1a**. A similar elongation of the bond was observed in several triosmium clusters with a bridging alkoxide ligand[12] and dirhenium alkoxide compounds as well.[13] For the allenylidene ligand, the C_3 chain forms an angle 143(1)° with both α and β carbons connected to all three metal atoms; the γ carbon is linked to only one Re atom. The C(10)—C(11) distance (1.27(2) Å) is slightly shorter than the C(11)—C(12) distance (1.35(2) Å) but is comparable with the acetylide C_α—C_β distance in **1a** (1.25–1.28 Å). Apparently, the C(10)—C(11) fragment retains some contribution of acetylide triple-bond character. This feature is reminiscent of that found in several mono- and dinuclear allenylidene complexes.[14] Furthermore, the η^3-allenylidene ligand in **2a** represents a unique 6-electron hydrocarbon fragment. The allenylidene ligand in a η^2-mode, which is coordinated to the metal triangle through its α and β carbons and serves as a 4-electron donor, has been observed in allenylidene clusters $Fe_3(CO)_9(CCCPh_2)_2$ and $Fe_3(CO)_{10}(CCCPh_2)$.[15]

The solution dynamics of the allenylidene complexes **2a–2c** are of particular interest. The ^1H NMR spectrum at 300 MHz shows the presence of two broad methyl signals at 297 K for all three derivatives, in addition to the anticipated proton signals of alkoxide and Cp* ligands. These Me signals coalesce to a broad signal on increasing the temperature and turn to two sharp singlets when the temperature is lowered. The fluxional behavior involves parallel movement of the allenylidene ligand from one Re atom to the second (Scheme 1), which exchanges the environment of nonequivalent methyl substituents. Furthermore, the migrational motion of allenylidene is not coupled with rotational motion of the $Cp^*W(CO)_2$ unit because the ^{13}C NMR spectrum of **2a** shows only one broad W–CO signal instead of two CO signals at 223 K. This observation indicated that the pairwise exchange of W-bound CO ligands is more rapid than the motion of the allenylidene ligand. Upon warming to 294 K, the ^{13}C NMR spectrum shows one sharp W–CO signal at δ 215.9 (J_{W-C} = 173 Hz) and two broad Re–CO signals at δ 200.4 and 197.5 in the ratio 2:2:4, showing the rapid interchange of W-bound CO ligands and a separate fluxional motion of six terminal Re–CO ligands. The α, β, and γ carbons of the allenylidene ligand appear at δ 186.7 (J_{W-C} = 163 Hz), 140.3 (J_{W-C} = 32 Hz), and 116.1, respectively.

For the ethoxide derivative **2b**, we observed that the methylene quartet became a broad, featureless hump on lowering the temperature to 240 K together with broadening and coalescence of the methyl signals of the allenylidene ligand. The former is attributed to the fact that the slow movement of the allenylidene ligand prevents interchange of the nonequivalent magnetic environments of the methylene protons. The variation of the alkoxide ligand has little effect on the migration of the allenylidene ligand, as all three compounds possess similar energy barriers of activation. For compound **2b**, we obtained a kinetic barrier ($\Delta G^\ddagger$ = 59 kJ/mol) by using the ^1H NMR data, $\Delta\nu$ = 86.8 Hz, and T_c = 300 K, at 400 MHz. Indeed, this dynamic motion is in contrast to that observed for the vinylidene ligand ($C{=}CH_2$) and tilted ketenylidene fragment ($C{=}C{=}O$) of trinuclear cluster compounds.[16] In the case of vinylidene clusters, the migration of the $C{=}CH_2$ fragment on the triangular surface clearly occurred with counter-rotation along the C—C axis of the vinylidene ligand.

Hydrogenation of 1a. In view of the reactions with alcohols and phenol described, it was of interest to determine how complexes **1a–1c** would react with dihydrogen. Treatment of **1a** with molecular hydrogen generated not the expected hydrido–allenylidene complex $Cp^*WRe_2(CO)_8(\mu\text{-}H)(C{=}C{=}CMe_2)$ but instead an unsaturated, metallacyclopentadienyl cluster $Cp^*WRe_2(CO)_7(\mu\text{-}H)[CHCHC(Me)CH]$ and a trace amount of an unstable yellow complex, which is tentatively identified as $Cp^*WRe_2(CO)_8(\mu\text{-}H)_2[C{\equiv}CC(Me){=}CH_2]$ (**4a**) according to its IR ν(CO) data. The ^1H NMR spectrum of $Cp^*WRe_2(CO)_7(\mu\text{-}H)[CHCHC(Me)CH]$ exhibits a complicated pattern of proton signals in the region between

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[12] (a) Braga, D.; Sabatino, P.; Johnson, B. F. G.; Lewis, J.; Massey, A. *J. Organomet. Chem.* **1992**, *436*, 73. (b) Allen, V. E.; Mason, R.; Hitchcock, P. B. *J. Organomet. Chem.* **1977**, *140*, 297.

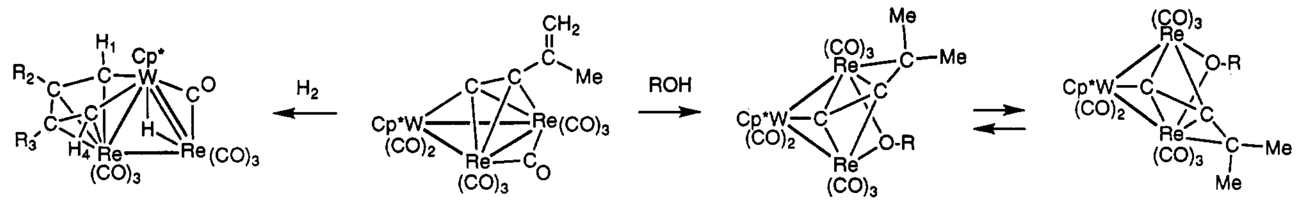
[13] Yan, Y. K.; Chan, H. S. O.; Andy Hor, T. S.; Tan, K.-L.; Liu, L.-K.; Wen, Y.-S. *J. Chem. Soc., Dalton Trans.* **1992**, 423.

[14] (a) Froom, S. F. T.; Green, M.; Mercer, R. J.; Nagle, K. R.; Orpen, A. G.; Schwiegk, S. *J. Chem. Soc., Chem. Commun.* **1986**, 1666. (b) Froom, S. F. T.; Green, M.; Mercer, R. J.; Nagle, K. R.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1305. (c) Froom, S. F. T.; Green, M.; Mercer, R. J.; Nagle, K. R.; Orpen, A. G.; Rodrigues, R. A. *J. Chem. Soc., Dalton Trans.* **1991**, 3171.

[15] Iyoda, M.; Kuwatani, Y.; Oda, M. *J. Chem. Soc., Chem. Commun.* **1992**, 399.

[16] (a) Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 4687. (b) Edidan, R. D.; Norton, J. R.; Mislow, K. *Organometallics* **1982**, *1*, 561. (c) Kolis, J. W.; Holt, E. M.; Shriver, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 7307.

Scheme 1



(3a), R_2 = H, R_3 = Me

(3b), R_2 = Me, R_3 = H

(1a)

(2a), R = Me

(2b), R = Et

(2c), R = Ph

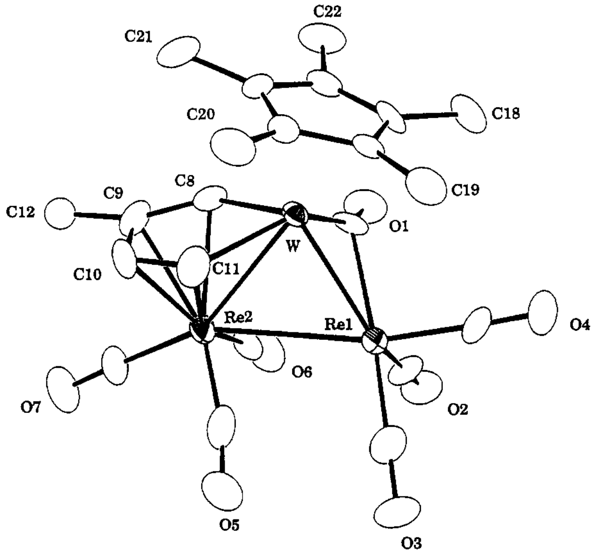


Figure 3. Molecular structure of **3** with the methyl group of isomer **3a** deleted for clarity. Selected bond lengths (Å): Re(1)-Re(2) = 3.151(2), Re(1)-W = 2.672(1), Re(2)-W = 2.898(1), W-C(1) = 2.00(2), Re(1)-C(1) = 2.34(2), W-C(8) = 2.12(2), W-C(11) = 2.11(2), Re(2)-(8) = 2.33(2), Re(2)-C(9) = 2.28(2), Re(2)-C(10) = 2.26(2), Re(2)-C(11) = 2.28(2), C(8)-C(9) = 1.43(3), C(9)-C(10) = 1.45(4), C(10)-C(11) = 1.36(3), C(9)-C(12) = 1.46(5), and C(10)-C(12′) = 1.39(4).

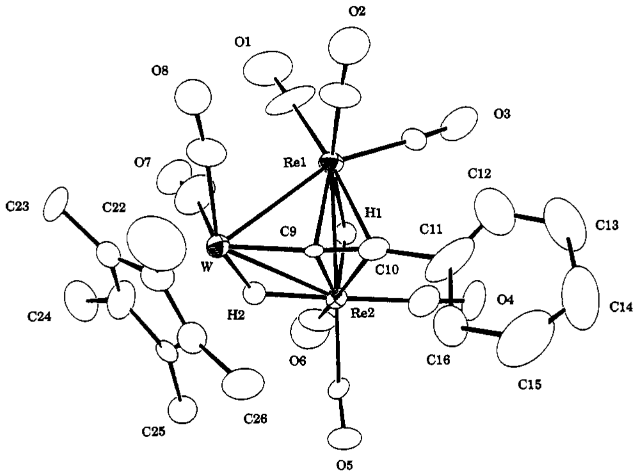


Figure 4. Molecular structure of **4b** and the atomic numbering scheme.

δ 6.52 and 5.72, two methyl signals at δ 2.64 and 2.62, two overlapping Cp* signals at δ 2.00 and 1.99, and most importantly, two hydride doublet signals at δ −5.74 and −5.77 with a ratio of 48:52. This spectrum is consistent with the presence of two isomers (**3a** and **3b**) that have similar molecular structures. We were unable to separate these two isomers or even to alter their relative proportions by varying the reaction times or by repeated recrystallization.

Identification of 3a and 3b. Despite the fact that complexes **3a** and **3b** are an inseparable mixture of two isomers, single crystals suitable for X-ray diffraction analysis were grown from a chloroform–heptane solution. Thus, an X-ray diffraction study has been carried out to delineate the structures. An ORTEP diagram is presented in Figure 3; the structure corresponds to the valence-bond description shown in Scheme 1, and the cluster has 46 cluster valence electrons. To our knowledge, this molecule provides a unique example of a cluster containing both Re—W single and double bonds. The double bond (2.672(1) Å) is substantially shorter than the respective single bond (2.898(1) Å) and is comparable to the Re═Re length (2.723 Å) of dinuclear complex $Cp^*{}_2Re_2(CO)_4$[17] and the W═W length (2.747–2.592 Å) observed in several heterometallic clusters prepared by Stone and co-workers[18] and by Chi and co-workers.[19] The bridging hydride was not located on the difference Fourier map, but we propose that it is associated with the short W═Re double bond in a position opposite the unique bridging CO ligand, because of the tilted arrangement of CO ligands on Re(1) and the observation of large $^1J_{W-H}$ coupling and small $^3J_{H-H}$ coupling to the adjacent proton (H_4) in its ^1H NMR spectrum (Scheme 1). The unambiguous assignment of the olefin hydrogen atoms and bridging hydrides was achieved by means of selective ^1H NMR decoupling and NOE experiments. Other notable features are associated with the cyclic C_4H_3Me fragment, on which the C(10)—C(11) distance (1.36(3) Å) is smaller than the C(8)—C(9) (1.43(3) Å) and the C(9)—C(10) distances (1.45(4) Å) and the methyl substituent is disordered between the C(9) and C(10) atoms. The crystallographic disorder confirms that the two noninterconvertible isomers **3a** and **3b** are due to repositioning of the methyl group.

Hydrogenation of 1b. Complex **1b** reacted with hydrogen in refluxing toluene solution to afford a light-yellow dihydride complex $Cp^*WRe_2(CO)_8(\mu\text{-}H)_2[C{\equiv}C(C_6H_9)]$ (**4b**) in 75% yield. The treatment involved simple tlc separation, after which the product was further purified by recrystallization. This complex is related to the previously mentioned unstable cluster **4a**, as indicated by its IR ν(CO) spectrum in solution. The mass spectrum

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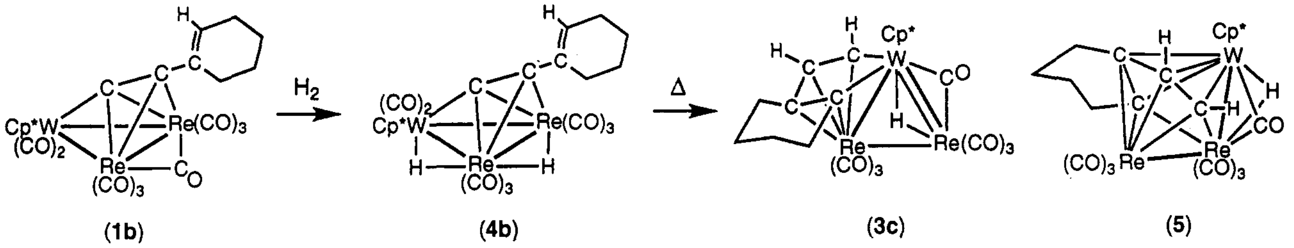
[17] Casey, C. P.; Sakaba, H.; Hazin, P. N.; Powell, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 8165.

[18] (a) Busetto, L.; Jeffery, J. C.; Mills, R. M.; Stone, F. G. A.; Went, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 101. (b) Carriedo, G. A.; Jeffery, J. C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 1597.

[19] Chi, Y.; Liu, L.-K.; Huttner, G.; Zsolnai, L. *J. Organomet. Chem.* **1990**, *390*, C50.

Scheme 2



and spectral properties are consistent with the replacement of one CO ligand with dihydrogen to afford two bridging hydride ligands. The ^{1}H NMR spectrum of **4b** exhibits two hydride resonances at δ −15.73 (J_{W-H} = 42 Hz) and −17.89, indicating one hydride to bridge a W—Re edge and the second, the unique Re—Re edge. Furthermore, the ^{13}C NMR spectrum shows the presence of two W—CO ligands at δ 214.9 (J_{W-C} = 135 Hz) and 207.3 (J_{W-C} = 148 Hz) and six Re—CO ligands in the region δ 197.5–183.5, confirming that complex **4b** contains one CO ligand less than that of **1b**. Additionally, the C_α and C_β resonances of the acetylide ligand appear at δ 125.3 (J_{W-C} = 111 Hz) and 100.8. This observation supports the formulation of a μ_3-η^2 bonding mode for the acetylide ligand.[11]

The crystal structure analysis was carried out to confirm the proposed structure. As indicated in Figure 4, this molecule has an expected triangular WRe_2 core structure with distances Re(1)—Re(2) = 2.921(1) Å, W—Re(1) = 3.019(1) Å, and W—Re(2) = 3.093(1) Å, in which the tungsten atom is associated with two CO ligands, whereas each rhenium atom is linked to three, mutually orthogonal, terminal CO ligands. The acetylide moiety, similar to that of cluster **1a**, is coordinated to the WRe_2 triangular face with its α carbon bound to all three metal atoms with bond distances W—C(9) = 2.04(1) Å, Re(1)—C(9) = 2.26(1) Å, and Re(2)—C(9) = 2.30(2) Å, and with its β carbon linked to two Re atoms with distances Re(1)—C(10) = 2.31(2) Å and Re(2)—C(10) = 2.32(2) Å. One bridging hydride ligand, which was located directly from the Fourier analysis, spans one W—Re linkage with W—H(2) = 1.742(1) Å and Re(2)—H(2) = 1.791(1) Å, whereas the hydride-bridged W—Re(2) bond is slightly longer than the unbridged W—Re(1) bond. The second hydride, which is not accurately defined, resides on the Re—Re bond with a large variation of the metal—hydride distances, Re(1)—H(1) = 2.274(1) Å and Re(2)—H(1) = 1.707(1) Å. Thus, the metal—acetylide interactions between **1a** and **4b** are identical within experimental error and the principal difference is substitution of a bridging CO by two hydride ligands. This observation contrasts sharply with that observed in acetylide clusters $LMRu_2(CO)_8(C{\equiv}CR)$ (L = Cp, Cp*; M = Mo, W; R = Ph, Pr^n, Bu^t) in which replacing the auxiliary ligand on the W and Mo atoms or changing the organic substituent on the acetylide fragment caused reorientation of the acetylide interaction on the metal triangle.[20]

Formation of Metallacyclopentadienyl Clusters 3c and 5. The generation of **3a** and **3b** from hydrogenation of **1a** prompted us to investigate the isomerization of **4b** under a hydrogen atmosphere, which hence becomes an intimate precursor of the expected metallocyclopentadienyl clusters. Thus complex **4b** was further heated in refluxing toluene under dihydrogen at 1 atm. After 45 min, two dark-orange complexes **3c** and **5** with a formula $Cp^*WRe_2(CO)_7(\mu\text{-}H)[CHCH(C_6H_8)]$ were isolated in low yields. The transformation from **1b** to **4b**, and finally to **3c** and **5**, is depicted in Scheme 2. Their identifications are based on the IR ν(CO) data, which show patterns that are not only similar to each other but are also identical to the IR ν(CO) spectrum of **3**. The ^{1}H NMR spectrum of **3c** displays two olefin CH=CH doublets at δ 6.57 and 5.87 with a *cis*-olefin coupling constant J_{H-H} = 7.1 Hz and a low-field hydride resonance at δ −5.14 (J_{W-H} = 98 Hz), whereas the spectrum of **5** exhibits two doublets at δ 6.15 and 3.65 (J_{H-H} = 6.8 Hz) and a singlet at δ −3.94 (J_{W-H} = 100 Hz). These spectroscopic properties are compatible with key features of metallacyclopentadienyl complexes **3a** and **3b** previously isolated. However, we are unable to determine the exact position of the cyclohexenyl substituent on the metallacyclopentadienyl framework based only on the spectral data alone. Thus the X-ray diffraction studies on **3c** and **5** were undertaken to establish the difference between them.

Crystal Structures of 3c and 5. Complex **3c** is basically isostructural with the previously established isomers **3a** and **3b**. An ORTEP drawing of **3c** is shown in Figure 5, while selected bond distances and angles are presented in Table 6. It was obvious that complex **3c** adopts a distorted triangular metal framework and the metallacyclopentadienyl bridges one elongated W-Re bond (2.9085(6) Å) in the previously established fashion. The terminal carbon atoms C(8) and C(11) are linked to the W atom via a metal–carbon σ-bond, while all four carbon atoms are coordinated to Re(2) via a η^4-interaction. The cyclohexenyl ring possesses two disordered methylene groups C(13) and C(14), indicated by the presence of large thermal ellipsoids, sharing the carbon atoms C(10) and C(11) with the metallacyclopentadienyl framework. The hydride ligand, located and refined crystallographically, is associated with the W-Re double bond in a position *trans* to the bridging CO ligand, with distances W-H = 1.92(6) Å and Re(1)-H = 1.84(6) Å and with angle W-H-Re(1) = 91(2)°. Assuming the metallacyclopentadienyl ligand to be a 6-electron donor, we calculate that this molecule possesses 46 cluster valence electrons, which fits the prediction for triangular clusters with one metal–metal double bond.

Although the structure of **5** was initially determined to confirm the stereochemistry of the cyclohexenyl group, the final results of X-ray analysis reveal, in addition to the expected change in the position of the cyclohexenyl group, an extensive variation in the cluster core arrangement. As can be seen in Figure 6, the metal core consists of an open triangular geometry with bond distances W—Re(1) = 2.917(1) Å and Re(1)—Re(2) = 2.821(1) Å, which are characteristic of a metal—metal single bond. The W—Re-

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[20] Hwang, D.-K.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1990**, *9*, 2709.

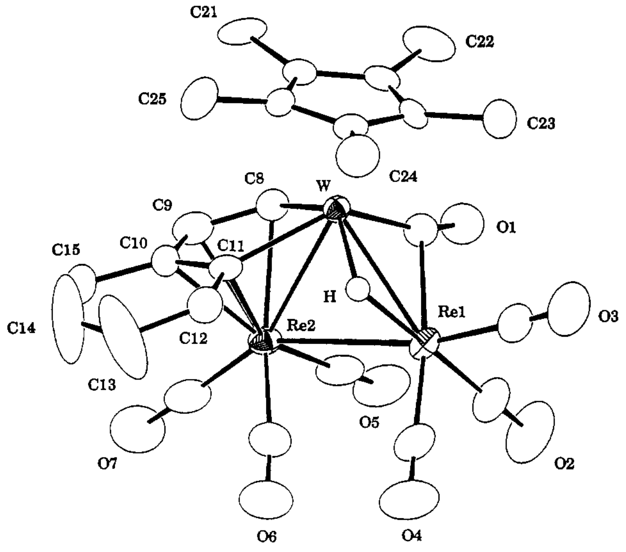


Figure 5. Molecular structure of **3c** and the atomic numbering scheme.

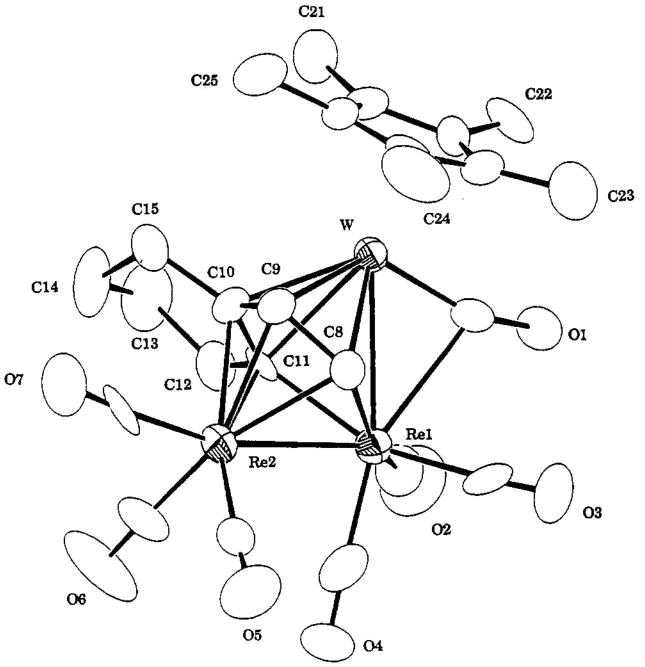
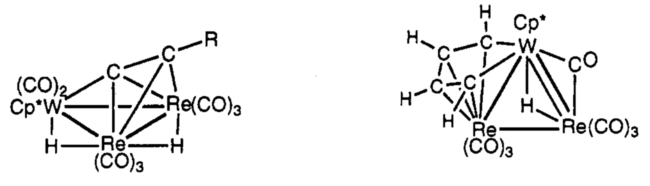


Figure 6. Molecular structure of **5** and the atomic numbering scheme.

(2) distance of 3.923(2) Å is outside the range of direct metal—metal bonding. The bridging CO ligand is associated with the W—Re(1) edge. The hydride, although it was not located, is associated with the W—Re(1) edge, due to the observation of large coupling J_{W-H} = 100 Hz in its ^{1}H NMR spectrum. The carbon atoms C(8) and C(11) of the metallacyclopentadienyl system are σ-bonded to the Re(1) atom; all four carbon atoms are simultaneously coordinated to both atoms W and Re(2) via two η^4-interactions. The resulting metallacyclopentadienyl ring is coplanar and perpendicular to the plane defined by metal atoms W, Re(1), and Re(2) (the dihedral angle is 89.1(4)°). Consequently, this molecule can be alternatively considered to adopt the M$_3$C$_4$ pentagonal-bipyramidal skeletal arrangement, in which W and one Re atom attach at the apical positions and the second Re atom and all carbon atoms occupy the equatorial positions, when considering the carbon atoms to be part of the cluster core. The structurally characterized pentagonal-bipyramidal metal clusters with a metallacyclopentadienyl fragment include Fe$_3$(CO)$_8$(C$_2$Ph$_2$)$_2$,[21] Fe$_3$(CO)$_8$[C(Me)C(OEt)CRCR] (R = Ph),[22] Ru$_3$(CO)$_8$(C$_2$Ph$_2$)$_2$,[23] and Re$_2$Fe(CO)$_9$(μ_3-η^4-CH=CHC$_6$H$_4$).[24] The allyl complex CpNiRu$_3$(CO)$_8$(C$_5$H$_7$)[25] and alkyne cluster Cp$_2$Ni$_2$Ru$_3$(CO)$_x$(C$_2$Ph$_2$)[26] also exhibit the isolobal pentagonal-bipyramidal metal core with four and five metal atoms, respectively. The structural relationship of these derivatives with differing numbers of metal and carbon atoms becomes evident in counting and comparing the sum of cluster valence electrons. In fact, the core geometry of **5** is also consistent with Wade's prediction for a seven-vertex *closo* cluster with eight pairs of cluster skeletal electrons, while each CH or C(CH$_2$) unit is counted as a 3-electron vertex and the Cp*WRe$_2$(CO)$_7$(μ-H) fragment is considered to donate 40 − 12 × 3 = 4 electrons to cluster bonding.[27]

Chart 1



(**4c**, R = CH=CHOMe) (**3d**)

Hydrogenation of 1c. Hydrogenation of complex **1c** in refluxing toluene solution within 10 min afforded a light-yellow complex in approximately 20% yield, which is tentatively identified as dihydride complex Cp*WRe$_2$(CO)$_8$(μ-H)$_2$[C≡C(CH=CHOMe)] (**4c**). Unambiguous characterization of **4c** is not possible because it is contaminated with several unknown impurities which cannot be removed despite all attempts. The spectroscopic data for **4c** leading to its identification are its solution IR ν(CO) spectrum and the two hydride signals at δ −15.64 (J_{W-H} = 42 Hz) and −17.60 in the ^{1}H NMR spectrum. We believe that the complication is due to the presence of an electron-releasing methoxy group, which is rather reactive and can enhance the reactivity of vinylacetylide toward dihydrogen. This hypothesis is consistent with the experimental result that extension of the reaction time to 2 h caused the removal of the methoxyl group, producing dark-brown Cp*WRe$_2$(CO)$_7$(μ-H)(CHCHCHCH) (**3d**) as the sole cluster product in 12% yield. The molecular drawings of **4c** and **3d** are shown in Chart 1.

Summary. Two reactions beginning with vinylacetylide derivatives **1a**–**1c** were elaborated to yield allenylidene and metallacyclopentadiene complexes in good yield. For the reactions that afforded dimethylallenylidene complexes **2a**, **2b**, and **2c**, the second methyl substituent was produced by addition of a hydrogen to an olefin CH$_2$ terminus, whereas the other part of the alcohol molecule

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gives rise to an alkoxide fragment bridging the unique Re—Re edge. The rhenium atoms play an important role in activating the O—H bond of alcohols via formation of strong rhenium—alkoxide interactions, as heating the related tungsten—ruthenium complex $Cp^*WRu_2(CO)_8[C{\equiv}CC(Me){=}CH_2]$ exhibited no such reactivity under similar conditions.

In accompanying work, the vinylacetylide cluster **1a** was found to react with hydrogen to afford the metallacyclopentadiene complexes **3a** and **3b**, which differ in the location of the methyl substituent on the cyclic C_4 chain. Hydrogenation of cyclohexenyl derivative **1b** under similar conditions yielded **4b** as the initial product; when the reaction time was extended to 1 h, further addition of dihydrogen occurred and we isolated two metallacyclopentadiene complexes **3c** and **5** (Scheme 2). Their structural properties were established and compared. Complex **3c** adopts a triangular framework with one W–Re double bond, but complex **5** is best considered as having a delocalized C_4M_3 pentagonal-bipyramidal skeleton. Thus, the former achieves an 18-electron configuration by forming a metal–metal double bond, but the latter prefers the delocalized framework of the electron-deficient cluster compounds. The change in skeletal arrangement between **3c** and **5** is surely induced by the repositioning of the $(CH_2)_4$ fragment at the cyclic C_4 fragment. This rather uncommon variation of cluster bonding characteristics, which is caused by minimal purturbations of the coordination environment from the viewpoint of both steric demand and electronic requirement, illustrates a subtle balance of the metal–metal and the metal–carbon interactions within the cluster core.[28] Finally, the parent metallacyclopentadiene cluster **3d**, which has no alkyl substituent on the cyclic C_4 ligand, was obtained by hydrogenation of derivative **1c**.

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Supplementary Material Available: Listings of parameters of data collection and refinement, tables of nonessential bond distances and angles, atomic positions, and anisotropic thermal parameters for complex **1a**, and tables of nonessential bond distances and angles, atomic positions, and anisotropic thermal parameters for **4b**, **3c**, and **5** (32 pages). Ordering information is given on any current masthead page.

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