Stepwise Formation of Heterometallic Cluster Compounds $(C_5Me_5)WRu_5(\mu_6\text{-}C)(\mu\text{-}CCH_2Ph)(\mu\text{-}H)_2(CO)_{13}$ and $(C_5Me_5)WRu_5(\mu_4\text{-}C)(\mu_3\text{-}CCH_2Ph)(\mu\text{-}H)_4(CO)_{12}$ from $Ru_5(\mu_5\text{-}C)(CO)_{15}$. Reactivity Studies of Carbido Clusters Bearing Acetylide Ligands

Wen-Ji Chao,[†] Yun Chi,*[,†] Ching-Juh Way,[†] Ipe J. Mavunkal,[†] Sue-Lein Wang,[†] Fen-Ling Liao,[†] and Louis J. Farrugia*[,‡]

Departments of Chemistry, National Tsing Hua University, Hsinchu 30043, Taiwan, ROC, and The University, Glasgow G12 8QQ, Scotland, U.K.

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Treatment of the carbido cluster $Ru_5(\mu_5\text{-}C)(CO)_{15}$ with Me_3NO followed by addition of the tungsten acetylide complexes $LW(CO)_3(CCPh)$ (L = Cp, C_5Me_5) affords the two heterometallic cluster complexes $LWRu_5(\mu_5\text{-}C)(CCPh)(CO)_{15}$ (**1a**, L = Cp; **1b**, L = C_5Me_5) and $LWRu_5(\mu_5\text{-}C)(CCPh)(CO)_{13}$ (**2a**, L = Cp; **2b**, L = C_5Me_5). Thermolysis of **1** results in the irreversible formation of **2**. The reactivity of **2** was studied. Thus, hydrogenation of **2b** furnishes the two cluster compounds $(C_5Me_5)WRu_5(\mu_6\text{-}C)(\mu\text{-}CCH_2Ph)(\mu\text{-}H)_2(CO)_{13}$ (**3**) and $(C_5Me_5)WRu_5(\mu_4\text{-}C)(\mu_3\text{-}CCH_2Ph)(\mu\text{-}H)_4(CO)_{12}$ (**4**), generated via 1,1-addition of H_2 to the ligated acetylide and concurrent formation of two or four bridging hydrides. Treatment of **3** with CO gives the octahedral cluster $(C_5Me_5)WRu_5(\mu_6\text{-}C)(\mu\text{-}CCH_2Ph)(CO)_{14}$ (**5**). The spectral and structural properties of all species are presented and discussed.

There is a great deal of research focusing on structural and reactivity studies of high-nuclearity metal carbido clusters.[1] This is due to the belief that the production of metal carbido intermediates is an important initiation step in the Fischer−Tropsch catalytic processes.[2] Recently, investigation of the chemistry of metal carbido clusters has become a rapidly expanding reseach domain, as the interstitial carbido carbon tends to confer high stability to the cluster, so that the skeleton can sustain the severe reaction conditions employed.[3] As a result, many methods of building the metal framework around the carbide atom have been established,[4] and the reactivity of these carbide clusters with both organic and organometallic substrates has also been studied in attempts to extend the scope of this area.[5]

Parallel to this research direction, Shriver and coworkers have reported seminal work using ketenylidene complexes to synthesize a variety of carbido clusters.[6] We surmised that the square-pyramidal cluster $Ru_5(\mu_5\text{-}C)(CO)_{15}$ might also be an ideal precursor for the purpose of building larger carbido clusters, because the pyramidal core can undergo rearrangement by edge cleavage to afford bridged-butterfly species on reactions with donor molecules.[7] The subsequent removal of a CO ligand results in the regeneration of the original square-pyramidal framework. Therefore, this reversible rearrangement is useful in designing new strategies for the incorporation of additional heterometal fragments.

In this paper we report studies on the reactions of $Ru_5(\mu_5\text{-}C)(CO)_{15}$ with the tungsten acetylide complexes $LW(CO)_3(CCPh)$ (L = Cp, C_5Me_5) to form the octahedral WRu_5 carbido cluster derivatives. It appears that the building of the cluster framework, which occurs via the initial coordination of the acetylide C−C multiple bond to the Ru_5 platform, proceeds via a rearrangement similar to the process described above.

† National Tsing Hua University.
‡ The University of Glasgow.
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(1) (a) Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219. (b) Chisholm, M. H.; Hammond, C. E.; Johnston, V. J.; Streib, W. E.; Huffman, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 7056. (c) Dyson, P. J.; Johnson, B. F. G.; Lewis, J.; Martinelli, M.; Braga, D.; Grepioni, F. *J. Am. Chem. Soc.* **1993**, *115*, 9062. (d) Bailey, P. J.; Johnson, B. F. G.; Lewis, J. *Inorg. Chim. Acta* **1994**, *227*, 197. (e) Ma, L.; Wilson, S. R.; Shapley, J. R. *J. Am. Chem. Soc.* **1994**, *116*, 787. (f) Adams, R. D.; Layland, R.; McBride, K. *Organometallics* **1996**, *15*, 5425. (g) Su, C.-J.; Su, P.-C.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *J. Am. Chem. Soc.* **1996**, *118*, 3289.

(2) (a) Wijeyesekara, S. D.; Hoffmann, R. *Organometallics* **1984**, *3*, 949. (b) Chisholm, M. H.; Clark, D. L.; Huffman, J. C.; Smith, C. A. *Organometallics* **1987**, *6*, 1280. (c) Halet, J.-F.; Evans, D. G.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1988**, *110*, 87. (d) Shriver, D. F. *J. Cluster Sci.* **1992**, *3*, 459.

(3) (a) Adams, R. D.; Wu, W. *Organometallics* **1993**, *12*, 1238. (b) Haggitt, J. L.; Johnson, B. F. G.; Blake, A. J.; Parsons, S. *J. Chem. Soc., Chem. Commun.* **1995**, 1263. (c) Izumi, Y.; Chihara, T.; Yamazaki, H.; Iwasawa, Y. *J. Am. Chem. Soc.* **1993**, *115*, 6462. (d) Adams, R. D.; Wu, W. *Organometallics* **1993**, *12*, 1243.

(4) (a) Henly, T. J.; Shapley, J. R.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1988**, *7*, 441. (b) Bailey, P. J.; Blake, A. J.; Dyson, P. J.; Johnson, B. F. G.; Lewis, J.; Parisini, E. *J. Organomet. Chem.* **1993**, *452*, 175. (c) Fumagalli, A.; Martinengo, S.; Albano, V. G.; Braga, D.; Grepioni, F. *J. Chem. Soc., Dalton Trans.* **1993**, 2047. (d) Adatia, T.; Curtis, H.; Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Morris, J. *J. Chem. Soc., Dalton Trans.* **1994**, 1109. (e) Johnson, B. F. G.; Lewis, J.; Curtis, H.; Adatia, T.; McPartlin, M.; Morris, J. *J. Chem. Soc., Dalton Trans.* **1994**, 243. (f) Ralph, S. F.; Simerly, S. W.; Shapley, J. R. *Inorg. Chim. Acta* **1995**, *240*, 615.

(5) (a) Braga, D.; Sabatino, P.; Dyson, P. J.; Blake, A. J.; Johnson, B. F. G. *J. Chem. Soc., Dalton Trans.* **1994**, 393. (b) Adams, R. D.; Falloon, S. B.; McBride, K. T. *Organometallics* **1994**, *13*, 4870. (c) Hsu, G.; Wilson, S. R.; Shapley, J. R. *Organometallics* **1994**, *13*, 4159. (d) Chihara, T.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1995**, 1369.

(6) (a) Kolis, J. W.; Holt, E. M.; Hriljac, J. A.; Shriver, D. F. *Organometallics* **1984**, *3*, 496. (b) Hriljac, J. A.; Swepston, P. N.; Shriver, D. F. *Organometallics* **1985**, *4*, 158. (c) Hirljac, J. A.; Holt, E. M.; Shriver, D. F. *Inorg. Chem.* **1987**, *26*, 2943. (d) Jensen, M. P.; Henderson, W.; Johnston, D. H.; Sabat, M.; Shriver, D. F. *J. Organomet. Chem.* **1990**, *394*, 121. (e) Karet, G. B.; Espe, R. L.; Stern, C. L.; Shriver, D. F. *Inorg. Chem.* **1992**, *31*, 2658.

(7) Johnson, B. F. G.; Lewis, J.; Nicholls, N. J.; Puga, J.; Raithby, P. R.; Rosales, M. J.; McPartlin, M.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **1983**, 277.

Experimental Section

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 (400.13 MHz) or a Bruker AMX-300 (300.6 MHz) instrument. Mass spectra were obtained on a JEOL HX110 instrument operating in the fast atom bombardment mode (FAB). The $Ru_5(\mu_5\text{-}C)(CO)_{15}$ carbido cluster was prepared using published procedures.[8] All reactions were performed under a nitrogen atmosphere using solvents dried with an appropriate reagent. Reactions were monitored by analytical thin-layer chromatography (5735 Kieselgel 60 F_{254}, E. Merck), and 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.

Reaction of $Ru_5(\mu_5\text{-}C)(CO)_{15}$ with $CpW(CO)_3(CCPh)$. An acetonitrile solution (10 mL) of freshly sublimed Me_3NO (17.6 mg, 0.235 mmol) was added dropwise to a CH_2Cl_2 solution (30 mL) of $Ru_5(\mu_5\text{-}C)(CO)_{15}$ (100 mg, 0.106 mmol) over a period of 30 min. After the addition of Me_3NO was completed, the color of solution faded from dark red to light red. The solvents were removed under vacuum, the acetylide complex $CpW(CO)_3(CCPh)$ (40 mg, 0.092 mmol) was added, and the mixture was redissolved in 30 mL of CH_2Cl_2. The solution was stirred at room temperature for 30 min until the color changed back to dark red. The solution was concentrated and separated by thin-layer chromatography. Development with a 1:2 mixture of dichloromethane and hexane produced two bands, which were extracted from silica gel to yield 24 mg of brown $CpWRu_5(\mu_5\text{-}C)(CCPh)(CO)_{15}$ (**1a**; 0.018 mmol, 28%) and 2.7 mg of dark green $CpWRu_5(\mu_5\text{-}C)(CCPh)(CO)_{13}$ (**2a**; 0.002 mmol, 3%) in order of elution.

Spectral data for **1a**: MS spectrum (FAB, ^{102}Ru, ^{184}W) *m*/*z* 1292 (M$^+$); IR (C_6H_{12}) ν(CO) 2086 (m), 2052 (s), 2039 (s), 2033 (vs), 2018 (vw), 2011 (w), 1997 (w), 1984 (vw), 1976 (vw), 1970 (vw), 1948 (vw), 1931 (w), 1909 (vw) cm^{-1}; ^{1}H NMR (CD_2Cl_2, 294 K) δ 7.15 (t, 2H, J_{HH} = 7.0 Hz), 7.04 (t, 1H, J_{HH} = 7.0 Hz), 6.88 (d, 2H, J_{HH} = 7.0 Hz), 5.89 (s, 5H); ^{13}C NMR (CD_2Cl_2, 294 K) δ 412.7 (μ_5-C), 216.0 (J_{WC} = 155 Hz, CO), 213.6 (J_{WC} = 176 Hz, CO), 206.4 (J_{WC} = 124 Hz, *C*CPh), 203.5 (CO), 203.4 (CO), 202.3 (CO), 201.5 (CO), 201.0 (CO), 200.0 (CO), 199.1 (CO), 196.7 (3CO, br), 190.4 (C*C*Ph), 147.2 (*i* C_6H_5), 131.2 (*o*,*m* C_6H_5), 130.3 (*m*,*o* C_6H_5), 129.0 (*p* C_6H_5), 90.8 (C_5H_5). Anal. Calcd for $C_{29}H_{10}O_{15}Ru_5W$: C, 27.05; H, 0.78. Found: C, 26.99; H, 0.83.

Spectral data for **2a**: MS spectrum (FAB, ^{102}Ru, ^{184}W) *m*/*z* 1236 (M$^+$); IR (C_6H_{12}) ν(CO) 2075 (m), 2037 (vs), 2017 (s), 1999 (vw), 1988 (vw), 1984 (w), 1877 (vw, br), 1808 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 294 K) δ 7.27−7.23 (m, 5H), 5.87 (s, 5H); ^{13}C NMR ($CDCl_3$, 294 K) δ 411.4 (J_{WC} = 94 Hz, μ_5-C), 251.7 (J_{WC} = 82 Hz, μ-CO), 201.7 (CO), 200.7 (CO), 200.6 (CO), 197.8 (3CO), 196.1 (CO, br), 192.6 (CO, br), 192.2 (CO), 178.2 (J_{WC} = 140 Hz, *C*CPh), 134.8 (*i* C_6H_5), 133.7 (C*C*Ph), 130.6 (*o*,*m* C_6H_5), 129.7 (*p* C_6H_5), 129.0 (*m*,*o* C_6H_5), 95.4 (C_5H_5). Anal. Calcd for $C_{27}H_{10}O_{13}Ru_5W$: C, 26.33; H, 0.82. Found: C, 26.40; H, 1.05.

Thermolysis of $CpWRu_5(\mu_5\text{-}C)(CCPh)(CO)_{15}$. A toluene solution (20 mL) of $CpWRu_5(\mu_5\text{-}C)(CCPh)(CO)_{15}$ (22 mg, 0.017 mmol) was stirred at reflux temperature for 70 min, during which time the color changed from brown to dark green. After solvent was removed *in vacuo*, the residue was taken up in CH_2Cl_2 and separated by thin-layer chromatography (1:2 dichloromethane−hexane), affording 17 mg of $CpWRu_5(\mu_5\text{-}C)$-$(CCPh)(CO)_{13}$ (0.013 mmol, 78%) as the only isolable product.

Reaction of $Ru_5(\mu_5\text{-}C)(CO)_{15}$ with $(C_5Me_5)W(CO)_3(CCPh)$. An acetonitrile solution (10 mL) of freshly sublimed Me_3NO (17.6 mg, 0.235 mmol) was added dropwise into a CH_2Cl_2 solution (30 mL) of $Ru_5(\mu_5\text{-}C)(CO)_{15}$ (100 mg, 0.106 mmol) over 30 min. After the addition of Me_3NO was completed, the solution faded from dark red to light red. The solvents were removed under vacuum, the acetylide complex $(C_5Me_5)W(CO)_3$-$(CCPh)$ (40 mg, 0.079 mmol) was added, and the mixture was taken up in 30 mL of CH_2Cl_2. The solution was stirred at room temperature for 10 min, during which time the color changed to dark red. The solvent was removed, and the residue was redissolved in the minimum amount of CH_2Cl_2 and separated by thin-layer chromatography. Development with a 1:2 mixture of dichloromethane and hexane produced two bands, which were extracted from silica gel to yield 28 mg of brown $(C_5Me_5)WRu_5(\mu_5\text{-}C)(CCPh)(CO)_{15}$ (**1b**; 0.020 mmol, 35%) and 3.4 mg of dark green $(C_5Me_5)WRu_5(\mu_5\text{-}C)(CCPh)(CO)_{13}$ (**2b**; 0.0026 mmol, 5%) in the order of elution.

Spectral data for **1b**: MS spectrum (FAB, ^{102}Ru, ^{184}W) *m*/*z* 1362 (M$^+$). IR (C_6H_{12}) ν(CO) 2083 (m), 2051 (s), 2035 (vs), 2029 (vs), 2015 (w), 2008 (w), 1993 (w), 1975 (w), 1970 (w), 1960 (w), 1932 (br, w) cm^{-1}; ^{1}H NMR (CD_2Cl_2, 294 K) δ 7.23 (t, 2H, J_{HH} = 7.0 Hz), 7.12 (t, 1H, J_{HH} = 7.0 Hz), 6.99 (d, 2H, J_{HH} = 7.0 Hz), 2.38 (s, 15H); ^{13}C NMR (THF-d_8, 313 K) δ 412.8 (μ_5-C), 217.9 (J_{WC} = 155 Hz, CO), 217.7 (J_{WC} = 176 Hz, CO), 208.6 (J_{WC} = 125 Hz, *C*CPh), 203.9 (CO), 202.6 (CO), 202.4 (2CO), 200.7 (CO), 200.0 (CO), 195.6 (3CO, br), 190.5 (C*C*Ph), 145.1 (*i* C_6H_5), 129.9 (*o*,*m* C_6H_5), 129.0 (*m*,*o* C_6H_5), 127.6 (*p* C_6H_5), 104.5 (*C*$_5$Me$_5$), 11.8 (5Me). Anal. Calcd for $C_{34}H_{20}O_{15}Ru_5W$: C, 30.08; H, 1.48. Found: C, 29.23; H, 1.56.

Spectral data for **2b**: MS spectrum (FAB, ^{102}Ru, ^{184}W), *m*/*z* 1306 (M$^+$); IR (C_6H_{12}) ν(CO) 2071 (m), 2033 (vs), 2028 (s), 2012 (s), 1985 (w), 1975 (w), 1967 (vw), 1880 (vw, br), 1794 (w) cm^{-1}; ^{1}H NMR (CD_2Cl_2, 294 K) δ 7.35−7.25 (m, 5H), 2.27 (s, 15H); ^{13}C NMR (THF-d_8, 294 K) δ 418.0 (μ_5-C), 256.8 (μ-CO), 204.7 (CO), 203.8 (CO), 203.3 (CO), 202.3 (3CO), 198.5 (CO), 195.1 (CO), 194.6 (CO), 183.1 (*C*CPh), 138.8 (C*C*Ph), 138.0 (*i* C_6H_5), 132.4 (*o*,*m* C_6H_5), 131.7 (*p* C_6H_5), 131.1 (*m*,*o* C_6H_5), 113.7 (C_5Me_5), 14.3 (5Me). Anal. Calcd for $C_{32}H_{20}O_{13}Ru_5W$: C, 29.53; H, 1.55. Found: C, 29.09; H, 1.60.

Thermolysis of $(C_5Me_5)WRu_5(\mu_5\text{-}C)(CCPh)(CO)_{15}$. A toluene solution (30 mL) of **1b** (50 mg, 0.037 mmol) was stirred at reflux for 5 h, during which time the color changed from brown to dark green. The solvent was removed *in vacuo*, and the residue was taken up in CH_2Cl_2 and separated by thin-layer chromatography (1:3 dichloromethane−hexane), affording 39 mg of **2b** (0.030 mmol, 81%).

Hydrogenation of $(C_5Me_5)WRu_5(\mu_5\text{-}C)(CCPh)(CO)_{13}$. A toluene solution (30 mL) of **2b** (50 mg, 0.038 mmol) was heated at 80 °C under an H_2 atmosphere for 3 h, during which time the color changed from dark green to brown. After removal of solvent, the residue was redissolved in CH_2Cl_2 and separated by thin-layer chromatography (1:2 dichloromethane−hexane), affording 23 mg of $(C_5Me_5)WRu_5(\mu_6\text{-}C)(\mu\text{-}CCH_2Ph)(\mu\text{-}H)_2(CO)_{13}$ (**3**; 0.022 mmol, 45%) and 14 mg of $(C_5Me_5)WRu_5(\mu_4\text{-}C)(\mu_3\text{-}CCH_2Ph)(\mu\text{-}H)_4(CO)_{12}$ (**4**; 0.011 mmol, 28%).

Spectral data for **3**: MS spectrum (FAB, ^{102}Ru, ^{184}W) *m*/*z* 1310 (M$^+$); IR (C_6H_{12}) ν(CO) 2073 (m), 2046 (m), 2032 (vs), 2026 (s), 2010 (m), 1984 (br, vw), 1964 (br, vw), 1892 (br, w), 1853 (br, w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 294 K) δ 7.24−7.21 (m, 3H), 6.65−6.61 (m, 2H), 4.10 (s, 2H, CH_2), 2.43 (s, 15H), −17.15 (s, 2H, J_{WH} = 76 Hz); ^{13}C NMR ($CDCl_3$, 294 K) δ 421.9 (μ_6-C), 338.3 (μ_3-*C*CH$_2$Ph), 235.8 (2CO), 219.5 (CO), 210.1 (3CO), 202.9 (CO), 198.1 (2CO), 196.4 (4CO), 137.9 (*i* C_6H_5), 129.3 (*o*,*m* C_6H_5), 127.8 (*p* C_6H_5), 127.5 (*m*,*o* C_6H_5), 105.7 (*C*$_5$Me$_5$), 63.4 (*C*H$_2$), 14.1 (Me). Anal. Calcd for $C_{32}H_{24}O_{13}Ru_5W$: C, 29.44; H, 1.85. Found: C, 29.23; H, 1.56.

Spectral data for **4**: MS spectrum (FAB, ^{102}Ru, ^{184}W) *m*/*z* 1284 (M$^+$); IR (C_6H_{12}) ν(CO) 2091 (m), 2066 (s), 2032 (vs), 2018 (s), 2013 (m), 2002 (m), 1992 (m), 1973 (w), 1957 (vw), 1929 (w), 1880 (br, vw), 1794 (vw) cm^{-1}; ^{1}H NMR ($CDCl_3$, 294 K) δ 7.43 (d, 2H, J_{HH} = 7.3 Hz), 7.36 (t, 2H, J_{HH} = 7.3 Hz), 7.27 (t, 1H, J_{HH} = 7.3 Hz), 5.08 (d, 1H, C*H*$_2$, J_{HH} = 16.2 Hz), 4.28 (d, 1H, C*H*$_2$, J_{HH} = 16.2 Hz), 2.19 (s, 15H), −13.58 (d, 1H, J_{HH} = 2.0 Hz), −13.90 (s, 1H, J_{WH} = 83 Hz), −14.73 (d, 1H, J_{HH} =

(8) Nicholls, J. N.; Vargas, M. D. *Inorg. Synth.* **1989**, *26*, 280.

Table 1. X-ray Structural Data of Complexes 1a, 2a, 3, and 4

	1a	**2a**	**3**	**4**
formula	$C_{30}H_{12}Cl_2O_{15}Ru_5W$	$C_{27}H_{10}O_{13}Ru_5W$	$C_{32}H_{22}O_{13}Ru_5W$	$C_{31}H_{22}O_{12}Ru_5W$
mol wt	1372.50	1231.55	1303.7	1275.7
cryst syst	orthorhombic	monoclinic	monoclinic	triclinic
space group	*Pbca*	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a (Å)	12.361(2)	11.0988(7)	21.8452(2)	10.6645(2)
b (Å)	18.833(1)	16.038(1)	18.4710(1)	19.1823(4)
c (Å)	31.887(4)	17.335(1)	18.4647(2)	20.0186(4)
α (deg)				102.794(1)
β (deg)	90.847(5)		99.039(1)	99.908(1)
γ (deg)				94.378(1)
V (Å^3)	7423(1)	3085.3(4)	7358(1)	3906(1)
Z	8	4	8	4
D_c (g/cm^3)	2.456	2.651	2.354	2.169
F(000)	5120	2280	4896	2392
instrument	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Siemens SMART CCD	Siemens SMART CCD
2θ(max) (deg)	47.3	50	51.4	51.2
hkl ranges	−13 to 0, 0−21, −35 to 0	−13 to +13, 0−19, 0−20	−22 to +25, −21 to +22, −19 to +21	−12 to +12, −23 to +23, −24 to +23
cryst size (mm)	0.53 × 0.27 × 0.10	0.40 × 0.33 × 0.20	0.41 × 0.10 × 0.05	0.09 × 0.11 × 0.31
μ(Mo Kα) (cm^{-1})	52.80	61.63	51.76	48.71
transmissn: max, min	1.00, 0.506	0.696, 0.488	0.957, 0.634	0.962, 0.556
no. of data in refinement	5579	5413	7976 with $I \geq 3\sigma(I)$	8906 with $I \geq 3\sigma(I)$
no. of params	457	395	920	883
max Δ/σ ratio	0.068	0.001	0.001	0.0001
R_F; R_w	0.034; 0.071	0.024; 0.058	0.050; 0.043	0.059; 0.069
GOF	1.02	1.047	1.37	1.57
D map, max/min (e/Å^3)	+1.15/−1.31	+0.79/−0.62	+1.13/−1.28	+4.34/−1.44

2.0 Hz), −23.40 (s, 1H); ^{13}C NMR ($CDCl_3$, 294 K) δ 380.7 (μ_4-C, J_{WC} = 114 Hz), 325.0 (μ_3-CCH_2Ph, J_{WC} = 126 Hz), 198.1 (CO), 197.2 (CO), 196.5 (CO), 194.0 (2CO), 193.3 (CO), 192.0 (CO), 190.6 (CO), 188.8 (3CO), 186.8 (CO), 146.1 (*i* C_6H_5), 130.7 (*o*,*m* C_6H_5), 128.3 (*m*,*o* C_6H_5), 126.7 (*p* C_6H_5), 106.5 (C_5Me_5), 65.5 (CH_2Ph), 12.1 (5Me). Anal. Calcd for $C_{31}H_{26}O_{12}Ru_5W$: C, 29.14; H, 2.05. Found: C, 29.05; H, 2.11.

Reaction of (C_5Me_5)WRu$_5$(μ_6-C)(μ-CCH_2Ph)(μ-H)$_2$(CO)$_{13}$ with CO. A toluene solution (20 mL) of **3** (52 mg, 0.039 mmol) was heated at reflux under a CO atmosphere for 45 min. After removal of solvent, the residue was redissolved in CH_2Cl_2 and separated by thin-layer chromatography (1:3 dichloromethane−hexane), affording 21 mg of (C_5Me_5)WRu$_5$(μ_6-C)(μ-CCH_2Ph)-(CO)$_{14}$ (**5**; 0.016 mmol, 40%).

Spectral data for **5**: MS spectrum (FAB, ^{102}Ru, ^{184}W) *m/z* 1336 (M$^+$); IR (C_6H_{12}) ν(CO) 2073 (m), 2041 (s), 2028 (vs), 2009 (m), 1980 (w), 1971 (w), 1962 (vw), 1887 (br, w), 1842 (br, w), 1781 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 294 K) δ 7.32−7.23 (m, 3H), 6.96−6.90 (m, 2H), 3.95 (s, 2H, CH_2), 2.37 (s, 15H); ^{13}C NMR ($CDCl_3$, 294 K) δ 137.8 (*i* C_6H_5), 129.4 (*o*,*m* C_6H_5), 128.8 (*m*,*o* C_6H_5), 127.8 (*p* C_6H_5), 107.9 (C_5Me_5), 64.6 (CH_2Ph), 13.2 (5Me). Anal. Calcd for $C_{33}H_{22}O_{14}Ru_5W$: C, 29.76; H, 1.67. Found: C, 29.82; H, 1.74.

X-ray Crystallography. Diffraction measurements on complexes **1a** and **2a** were carried out on an Enraf-Nonius Turbo CAD-4 diffractometer, running under CAD4-Express software. Unit cell dimensions were determined by refinement of the setting angles of 25 optimal high-angle reflections, which were flagged during data collection. Standard reflections were measured every 2 h during data collection. Decay in intensities was noted for both complexes, and an interpolated correction was applied. All reflections were corrected for Lorentz, polarization, and absorption effects. The structures were solved by direct methods (SIR92)[9] for all non-hydrogen atoms. The non-hydrogen atoms were allowed anisotropic thermal motion. Hydrogen atoms were placed in calculated positions with C−H = 0.96 Å. An extinction correction was then applied. Refinement was by full-matrix least squares using the program SHELXL93.[10] The neutral atom scattering factors embedded in the SHELXL93 program were used, with corrections applied for anomalous dispersion.

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

W(1)−Ru(1)	2.9113(8)	W(1)−Ru(5)	2.9000(8)
Ru(1)−Ru(2)	2.851(1)	Ru(1)−Ru(3)	2.806(1)
Ru(1)−Ru(5)	2.7431(9)	Ru(2)−Ru(3)	2.845(1)
Ru(2)−Ru(4)	2.871(1)	Ru(3)−Ru(4)	2.814(1)
Ru(4)−Ru(5)	2.945(1)	W(1)−C(1)	2.019(8)
Ru(1)−C(1)	2.145(8)	Ru(5)−C(1)	2.165(8)
Ru(3)−C(2)	2.208(8)	Ru(5)−C(2)	2.371(8)
C(1)−C(2)	1.34(1)	Ru(1)−C(5)	1.955(8)
Ru(2)−C(5)	2.037(8)	Ru(3)−C(5)	2.125(8)
Ru(4)−C(5)	1.986(8)	Ru(5)−C(5)	2.061(8)
Ru(2)−C(31)	2.55(1)	Ru(3)−C(31)	1.95(1)
∠W(1)−C(1)−C(2)	152.5(6)	∠C(1)−C(2)−C(111)	125.1(7)

Crystal data for complexes **3** and **4** were collected on a Siemens Smart-CCD diffractometer equipped with a normal-focus, 3 kW sealed-tube X-ray source. Unit cell dimensions were determined by collecting reflections within angles 5° < 2θ < 50°, followed by spot integration and least-squares refinement. Data were collected in frames with increasing ω (0.30° per frame) and with the scan speed at 10.0 s per frame. Frame data were integrated using the SAINT program. Absorption correction was performed using the XPREP program.[11] The structures of **3** and **4** were solved by using the SHELXTL-PC package and refined by block-matrix and full-matrix least squares, respectively. All non-hydrogen atoms were given anisotropic thermal parameters, while hydrogen atoms were placed in idealized positions with fixed isotropic temperature factors.

The crystallographic refinement parameters of complexes **1a**, **2a**, **3**, and **4** are given in Table 1, while their selected bond distances and angles are presented in Tables 2−5, respectively.

Results

Synthesis and Characterization of 1 and 2. The carbido cluster Ru$_5$(μ_5-C)(CO)$_{15}$ reacts with 2 equiv of the oxidative decarbonylation reagent Me_3NO in acetonitrile solution at room temperature to afford an un-

(9) Altomare, A.; Cascarno, G.; Giacovazzo, C.; Gualiardi, A. *J. Appl. Crystallogr.* **1994**, *27*, 435.
(10) A program for crystal structure refinement: Sheldrick, G. M., University of Göttingen, Göttingen, Germany, 1993.
(11) Sheldrick, G. M. SHELXTL PC, version 5; Siemens Analytical X-ray Instruments, Madison, WI, 1994.

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

W(1)−Ru(2)	2.7841(4)	W(1)−Ru(4)	2.9735(5)
W(1)−Ru(5)	2.9780(5)	W(1)−Ru(6)	2.8685(5)
Ru(2)−Ru(3)	2.8534(6)	Ru(2)−Ru(4)	2.7953(6)
Ru(2)−Ru(5)	2.6958(6)	Ru(2)−Ru(6)	2.8535(6)
Ru(3)−Ru(4)	2.8185(6)	Ru(3)−Ru(6)	2.8319(6)
Ru(4)−Ru(5)	2.6623(6)	W(1)−C(1)	1.950(5)
Ru(2)−C(1)	2.203(5)	Ru(5)−C(1)	2.181(5)
Ru(2)−C(2)	2.270(5)	Ru(5)−C(2)	2.100(5)
C(1)−C(2)	1.347(7)	W(1)−C	2.026(5)
Ru(2)−C	2.178(5)	Ru(3)−C	2.020(5)
Ru(4)−C	2.057(5)	Ru(6)−C	2.073(5)
∠W(1)−C(1)−C(2)	154.2(4)	∠C(1)−C(2)−C(111)	138.2(4)

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

W(1)−Ru(1)	3.216(1)	W(1)−Ru(2)	3.039(1)
W(1)−Ru(3)	2.872(1)	W(1)−Ru(5)	3.015(1)
Ru(1)−Ru(2)	2.929(2)	Ru(1)−Ru(4)	2.816(2)
Ru(1)−Ru(5)	2.898(2)	Ru(2)−Ru(3)	2.895(2)
Ru(2)−Ru(4)	2.861(2)	Ru(3)−Ru(4)	2.785(2)
Ru(3)−Ru(5)	2.894(2)	Ru(4)−Ru(5)	2.858(1)
W(1)−C(14)	2.11(1)	Ru(1)−C(14)	2.01(1)
Ru(2)−C(14)	2.08(1)	Ru(3)−C(14)	2.08(1)
Ru(4)−C(14)	2.09(1)	Ru(5)−C(14)	2.06(1)
W(1)−C(15)	1.90(2)	Ru(3)−C(15)	2.19(1)
∠W−C(15)−Ru(3)	88.8(5)	∠W(1)−C(15)−C(16)	150.5(11)
∠Ru(3)−C(15)−C(16)	120.4(11)	∠C(15)−C(16)−C(17)	114.0(13)

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) of 4 (Esd's in Parentheses)

W(1)−Ru(2)	2.880(1)	W(1)−Ru(3)	3.078(1)
W(1)−Ru(4)	2.873(1)	W(1)−Ru(5)	2.849(1)
Ru(1)−Ru(2)	2.908(2)	Ru(1)−Ru(5)	2.880(2)
Ru(2)−Ru(3)	2.798(2)	Ru(2)−Ru(4)	2.986(2)
Ru(2)−Ru(5)	2.924(1)	Ru(3)−Ru(4)	2.673(2)
Ru(4)−Ru(5)	2.773(1)	W(1)−C(13)	1.91(1)
Ru(1)−C(13)	2.04(1)	Ru(2)−C(13)	2.12(1)
Ru(5)−C(13)	2.18(2)	W(1)−C(14)	2.01(2)
Ru(4)−C(14)	2.13(1)	Ru(5)−C(14)	2.17(2)
C(14)−C(15)	1.50(2)		
∠W(1)−C(13)−Ru(1)	174.0(9)	∠Ru(2)−C(13)−Ru(5)	85.6(5)

stable light red complex which is tentatively assigned to have the empirical formula $Ru_5(\mu_5\text{-}C)(CO)_{13}(NCMe)_2$.[12] It is also possible that this uncharacterized intermediate adopts an alternative edge-bridged butterfly geometry with the formula $Ru_5(\mu_5\text{-}C)(CO)_{13}(NCMe)_3$. This is due to the fact that dissolution of the parent carbido cluster $Ru_5(\mu_5\text{-}C)(CO)_{15}$ in acetonitrile results in the instantaneous formation of the cluster $Ru_5(\mu_5\text{-}C)(CO)_{15}(NCMe)$.[13] Thus, the further addition of 2 equiv of Me_3NO would replace two more CO ligands, affording the proposed $Ru_5(\mu_5\text{-}C)(CO)_{13}(NCMe)_3$. No attempt was made to isolate and characterize this unstable material.

However, upon the addition of excess tungsten acetylide complex $CpW(CO)_3(CCPh)$ to this solution, the two heterometallic clusters $CpWRu_5(\mu_5\text{-}C)(CCPh)(CO)_{15}$ (**1a**) and $CpWRu_5(\mu_5\text{-}C)(CCPh)(CO)_{13}$ (**2a**) were generated in moderate yields. The reaction of $Ru_5(\mu_5\text{-}C)(CO)_{15}$ with Me_3NO and $(C_5Me_5)W(CO)_3(CCPh)$ afforded the corresponding complexes $(C_5Me_5)WRu_5(\mu_5\text{-}C)(CCPh)(CO)_{15}$ (**1b**) and $(C_5Me_5)WRu_5(\mu_5\text{-}C)(CCPh)(CO)_{13}$ (**2b**) under similar conditions. Complexes **1** appear to be the precursors, because thermolysis of **1** afforded the respective complexes **2a** and **2b** in high yields. These two pairs of carbido cluster complexes were fully characterized by spectroscopic methods and, for the Cp derivatives **1a** and **1b**, by single-crystal X-ray diffraction studies.

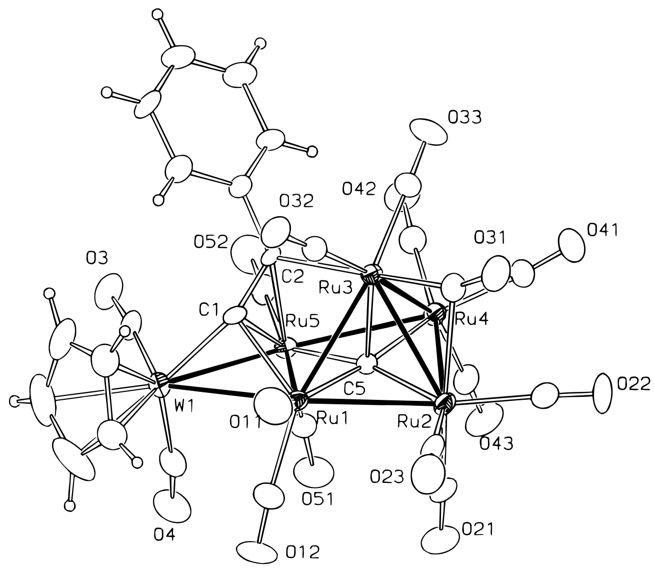
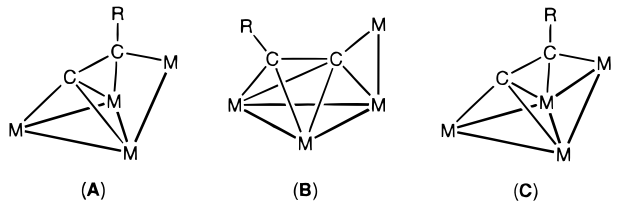


Figure 1. Molecular structure and atomic labeling scheme of the complex $CpWRu_5(\mu_5\text{-}C)(CCPh)(CO)_{15}$ (**1a**), with thermal ellipsoids shown at the 30% probability level.

The molecular geometry established for complex **1a** is shown in Figure 1 together with the atomic numbering scheme. Select bond angles and distances are presented in Table 2. The Ru_5 metal fragment forms a wingtip-bridged butterfly or a distorted square-base-pyramidal geometry, where the Ru(3)−Ru(5) bond is too long to be considered bonding (3.367(1) Å), which is similar to what is observed in several $Ru_5(\mu_5\text{-}C)$ and $Os_5(\mu_5\text{-}C)$ derivatives.[13,14] The Ru(1)−Ru(5) edge is symmetrically bridged by the W atom. The carbide carbon C(5) is almost coplanar, with the best plane defined by atoms Ru(1), Ru(2), Ru(3), and Ru(5), and is displaced by 0.056(8) Å toward the apical atom Ru(3). All carbonyl ligands apart from the unique CO(31) ligand are terminally bonded, the latter being very asymmetrically linked to the Ru(2)−Ru(3) hinge. The metal−metal distances are in the range 2.7431(9)−2.945(1) Å, with the W−Ru bonds being slightly longer than the Ru−Ru bond. The shortest Ru−Ru bond length of 2.7431(9) Å is that assigned to the Ru−Ru vector bridged by the unique $CpW(CO)_2$ vertex. The acetylide ligand, which adopts a μ_4-η^2 bonding mode, resides above the W(1)−Ru(1)−Ru(5) triangle (W(1)−C(1) = 2.019(8) Å, Ru(1)−C(1) = 2.145(8) Å, and Ru(5)−C(1) = 2.165(8) Å), and the β-carbon is coordinated to the Ru(3) and Ru(5) atoms (Ru(3)−C(2) = 2.208(8) Å and Ru(5)−C(2) = 2.371(8) Å). The acetylide ligand in this molecule represents an example in which the α-carbon is linked to a triangular face on the *pseudo*-spiked triangular metal arrangement (**A**), while the β-carbon is coordinated to the metal pendant which is perpendicular to the M_3 face (Chart 1). In contrast, tetranuclear metal complexes with the acetylide ligand coordinated to M_3 face via the μ_3-η^2(⊥) interaction and

(12) Way, C.-J.; Chi, Y.; Mavunkal, I. J.; Wang, S.-L.; Liao, F.-L.; Peng, S.-M.; Lee, G.-H. *J. Cluster Sci.* **1997,** *8,* 61.
(13) Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; Nicholls, J. N.; Vargas, M. D. *J. Organomet. Chem.* **1983**, *249,* 255.
(14) (a) Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Rosales, M. J.; Welch, D. A. *J. Chem. Soc., Dalton Trans.* **1986**, 453. (b) Johnson, B. F. G.; Lewis, J.; Raithby, W. P. R.; Saharan, V. P.; Wong, W. T. *J. Organomet. Chem.* **1992**, *434,* C10.

Chart 1



with the α-carbon spanning the extended metal spike (see **B**) or with the acetylide coordinated to the butterfly framework, which is represented by the structure **C**, have been reported in the literature.[15]

The overall molecular structure of **2a** is shown in Figure 2, and the selected distances are presented in Table 3. The cluster core is based on a WRu_4 square-pyramidal geometry, with an additional Ru atom occupying one of the WRu_2 metal triangles. All metal−metal distances are indicative of single bonds, of which the distances (Ru(4)−Ru(5) = 2.6623(6) Å and Ru(2)−Ru(5) = 2.6958(6) Å) are significantly shorter than the remaining metal−metal separations (2.7841(4) Å−2.9780(5) Å). This molecule possesses 13 CO ligands. Three carbonyl ligands act as semibridging or bridging ligands, while the remaining CO ligands are considered terminal. The ligand CO(32) is very asymmetrically bonded to the two Ru atom (Ru(3)−C(32) = 1.919(7) Å and Ru(6)−C(32) = 2.608(7) Å), while the other two bridging carbonyl ligands CO(42) and CO(61) are much more symmetrical. The carbide atom resides in the cavity of the central WRu_4 square pyramid. The metal−carbide distances are approximately equal, with W(1)−C = 2.026(5) Å and Ru−C distances within the range 2.020(5)−2.178(6) Å, which places the carbide atom 0.292(5) Å below the square base away from the apical site. The acetylide ligand is bonded to a WRu_2 face in the typical μ_3-η^2(⊥) fashion, similar to those detected in trinuclear metal complexes.[16]

The ^{13}C NMR spectra of both complexes **1** and **2** are in good agreement with the X-ray structure established. All these complexes exhibited a characteristic signal in the downfield region δ 412.8−418.0, which is assigned to the carbide carbon. The assignments for CO ligands are deceptive, as we only observed 12 CO signals for **1** and 10 CO signals for **2**, out of the expected 15 and 13 CO signals, respectively. We believe that it is due to the rapid exchange of CO in solution. On the other hand, the ^{13}C NMR spectra show signals at δ 206.4 (**1a**) and 208.6 (**1b**) for the α-carbons of the acetylide ligand and at δ 190.4 (**1a**) and 190.5 (**1b**) for the β-carbons, while the corresponding signals of **2** appeared at the high-field region of δ 178.2 (**2a**) and 183.1 (**2b**) and δ 133.7 (**2a**) and 133.8 (**2b**). The high-field shift of these ^{13}C NMR signals on changing from the μ_4-mode to the μ_3-mode is consistent with the trend observed in the iron-group polynuclear acetylide complexes.[17]

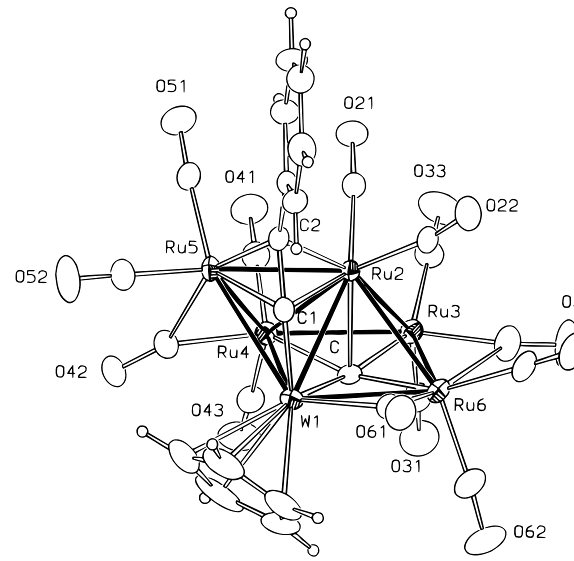


Figure 2. Molecular structure and atomic labeling scheme of the complex $CpWRu_5(\mu_5\text{-}C)(CCPh)(CO)_{13}$ (**2a**), with thermal ellipsoids shown at the 30% probability level.

Conversion to Carbido−Alkylidyne Clusters. Treatment of **2** with H_2 was carried out in an attempt to study its reactivity. Reaction of **2a** with H_2 has failed to provide any stable product, but the gentle heating of **2b** in toluene (80 °C, 3 h) under 1 atm of H_2 afforded two hexanuclear complexes $(C_5Me_5)WRu_5(\mu_6\text{-}C)(\mu\text{-}CCH_2Ph)(\mu\text{-}H)_2(CO)_{13}$ (**3**, 45%) and $(C_5Me_5)WRu_5(\mu_4\text{-}C)(\mu_3\text{-}CCH_2Ph)(\mu\text{-}H)_4(CO)_{12}$ (**4**, 28%). The identification was made using both spectroscopic and X-ray diffraction methods. These complexes are produced by two competing independent pathways, as no interconversion between **3** and **4** was noted by heating the solution of either **3** or **4** under nitrogen or dihydrogen or even under a carbon monoxide atmosphere.

For complex **3**, the ^1H NMR spectrum exhibits two sharp signals at δ 4.10 and −17.15 (J_{WH} = 76 Hz) in the ratio 2:2, in addition to the signals assigned to C_5Me_5 and the phenyl groups, showing the presence of two chemically equivalent hydride signals and the conversion of the acetylide ligand CCPh into the alkylidyne fragment CCH_2Ph. Further evidence in favor of this assignment is derived from the subsequent ^{13}C NMR study: one signal at δ 338.3 falls in the range expected for the doubly bridging alkylidyne ligand,[18] while the signals at δ 63.4 and 421.9 are assigned to the methylene and carbide fragments, respectively.

Complex **3** was found to crystallize within an asymmetric unit possessing two crystallographically distinct but structurally similar molecules. A perspective view of one of these molecules is depicted in Figure 3 (see also Table 4 for selected bond distances). The molecule contains a significantly distorted octahedral WRu_5 cluster core, with an idealized mirror plane passing through the metal atoms W(1), Ru(1), Ru(3), and Ru(4) of the cluster core. The Ru(4) atom is unique, as it is coordinated by four bridging CO ligands and one terminal CO ligand. Each of the remaining four Ru

(15) (a) Roland, E.; Vahrenkamp, H. *Organometallics* **1983**, *2*, 1048. (b) Weatherell, C.; Taylor, N. J.; Carty, A. J.; Sappa, E.; Tiripicchio, A. *J. Organomet. Chem.* **1985**, *291*, C9. (c) Seyferth, D.; Hoke, J. B.; Rheingold, A. L.; Cowie, M.; Hunter, A. D. *Organometallics* **1988**, *7*, 2163. (d) Bernhardt, W.; Vahrenkamp, H. *J. Organomet. Chem.* **1988**, *355*, 427. (e) Ewing, P.; Farrugia, L. J. *Organometallics* **1989**, *8*, 1246. (f) Farrugia, L. J. *Organometallics* **1990**, *9*, 105. (g) Akita, M.; Terada, M.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1992**, *11*, 3468. (h) Su, P.-C.; Chiang, S.-J.; Chang, L.-L.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1995**, *14*, 4844.

(16) (a) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203. (b) Hwang, D.-K.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1990**, *9*, 2709. (c) Sappa, E. *J. Cluster Sci.* **1994**, *5*, 211.

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

(18) Chi, Y.; Shapley, J. R. *Organometallics* **1985**, *4*, 1900.

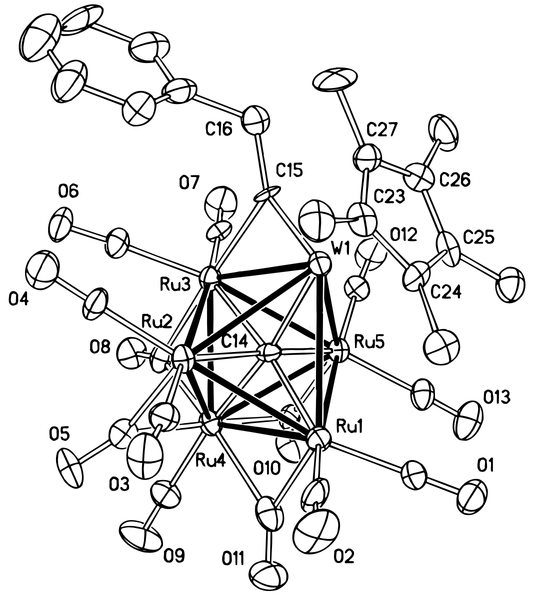


Figure 3. Molecular structure of $Cp^*WRu_5(\mu_6\text{-}C)(\mu\text{-}CCH_2Ph)(\mu\text{-}H)_2(CO)_{13}$ (**3**), showing the atomic labeling scheme and thermal ellipsoids at the 30% probability level.

atoms is linked to one bridging and two terminal CO ligands. The Ru–Ru distances span the narrow range 2.785(2)–2.929(2) Å. The W–Ru separations range from 2.872(1) to 3.216(1) Å, with the shortest W–Ru bond linking to a bridging alkylidyne ligand and the longest one located opposite to the alkylidyne ligand. The longest W–Ru distances of ~3.2 Å for both independent molecules indicate a rather weak metal–metal interaction, but since the overall electron count of 86 is normal for an octahedral cluster, this may arise from steric factors such as the bulk of the C_5Me_5 ligand or from the *trans* effect exerted by the bridging alkylidyne fragment (*vide infra*).

The W(1)–C(15) distance (1.90(2) Å) of the alkylidyne ligand is substantially shorter than the Ru(3)–C(15) distance (2.19(1) Å), while the W(1)–C(15)–C(16) angle (150.5(11)°) is larger than the respective Ru(3)–C(15)–C(16) angle (120.4(11)°). These data indicate that the alkylidyne ligand is unsymmetrically coordinated to the W–Ru(3) edge and that a substantial W≡C bonding character is retained. The unusually short W–C separation compares well with that in the mononuclear alkylidyne complex $CpW(CO)_2(\equiv CTol)$ (1.82(2) Å)[19] and the ionic carborane complex $[(C_2B_9H_9Me_2)W(CO)_2(\equiv CPh)][PPh_4]$ (1.82(3)–1.84(3) Å).[20] Mixed-metal complexes with an alkylidyne ligand forming an unsymmetrical bridge on the W–Pt, W–Rh, and W–Re edges have been reported by Stone and co-workers[21] and by us.[22] In addition, the elongation of the opposite W(1)–Ru(1) distance seems to complement the short W–C multiple bond and is presumably due to the poor competition for bonding vs the bridging alkylidyne ligand. The lengthening of the W(1)–carbide distance (W(1)–C(14) = 2.11(1) Å) with respect to other Ru–carbide distances (2.01(1)–2.09(1) Å) is also subject to the same kind of competing effect.

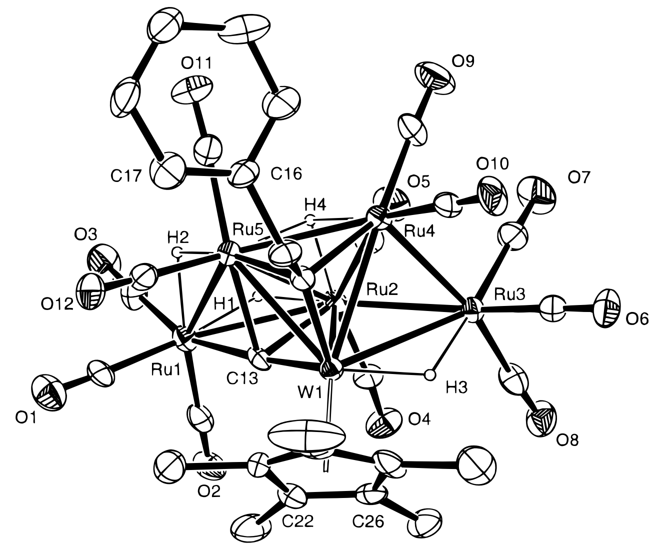


Figure 4. Molecular structure of $Cp^*WRu_5(\mu_4\text{-}C)(\mu\text{-}CCH_2Ph)(\mu\text{-}H)_4(CO)_{12}$ (**4**), showing the atomic labeling scheme and thermal ellipsoids at the 30% probability level.

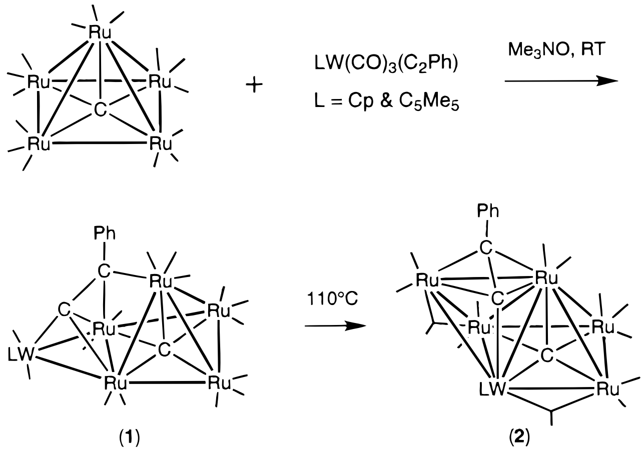
The bridging hydrides of **3** are found to associate with the W(1)–Ru(2) and W(1)–Ru(5) edges. Although these hydride ligands were not directly observed, their positions were independently confirmed using HYDEX potential energy calculations.[23] In addition, this proposal is entirely consistent with the expansion of the W(1)–Ru-CO angles associated with these edges and with the ^1H NMR data, which show a large J_{WH} coupling constant for the hydride resonance at δ −17.15.

The spectroscopic and structural properties of complex **4** differ greatly from those of **3**. The ^1H NMR spectrum of **4** is more complicated, showing two doublets at δ 5.08 and 4.28 ($^2J_{HH}$ = 16.2 Hz), an indication of the formation of a methylene fragment, and four high-field signals at δ −13.58 (J_{HH} = 2.0 Hz), −13.90 (J_{WH} = 83 Hz), −14.73 (J_{HH} = 2.0 Hz), and −23.40 in the ratio 1:1:1:1, suggesting the formation of four hydride ligands. From these NMR data we can assume that one H_2 molecule is now added to the acetylide ligand to give the bridging CCH_2Ph ligand, while the other two H_2 molecules are coordinated to the cluster core, forming four inequivalent hydrides. These features were confirmed by a single-crystal X-ray diffraction study.

The metal core arrangement of **4** is based on a WRu_4 trigonal-bipyramidal configuration, with the W(1) atom occupying an equatorial position (Figure 4). The Ru(2)–Ru(5) edge is further bridged by the Ru(1) metal atom, giving the observed edge-bridged trigonal-bipyramidal geometry with 12 terminal CO ligands. The alkylidyne ligand caps a WRu_2 face of the central trigonal bipyramid, having a short W–C distance (2.01(2) Å) and two longer Ru-C distances (2.13(1) and 2.17(2) Å). The carbide is located in the butterfly cavity constituted by the four metal atoms W(1), Ru(1), Ru(2), and Ru(5). The M(hinge)–C(carbide) distances (Ru(2)–C(13) = 2.12(1) Å and Ru(5)–C(13) = 2.18(2) Å) are slightly longer, compared to the other M(wingtip)–C(carbide) distances

(19) Fischer, E. O.; Lindner, T. L.; Huttner, G.; Friedrich, P.; Kreissl, F. R.; Besenhard, J. O. *Chem. Ber.* **1977**, *110*, 3397.
(20) Baumann, F. E.; Howard, J. A. K.; Musgrove, R. J.; Sherwood, P.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1988**, 1879.
(21) (a) Byers, P. K.; Carr, N.; Stone, F. G. A. *J. Organomet. Chem.* **1990**, *384*, 315. (b) Devore, D. D.; Howard, J. A. K.; Jeffery, J. C.; Pilotti, M. U.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1989**, 303. (c) Green, M.; Howard, J. A. K.; Jelfs, A. N. d. m.; Nunn, C. M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 2219.
(22) Peng, J.-J.; Peng, S.-M.; Lee, G.-H.; Chi, Y. *Organometallics* **1995**, *14*, 626.
(23) Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.

Scheme 1



(W(1)−C(13) = 1.91(1) Å and Ru(1)−C(13) = 2.04(1) Å). This pattern of M−C distances has been observed in other butterfly carbide cluster complexes[24] and was described in a theoretical study.[25]

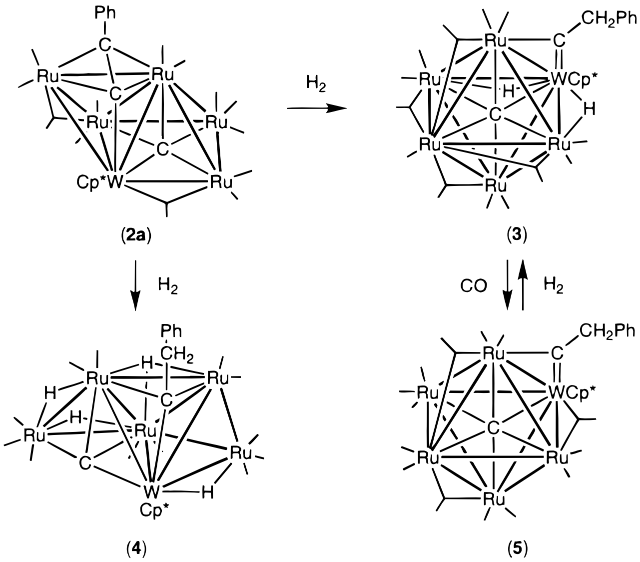
Another very interesting structural feature for **4** is the position of the hydride ligands. These four hydride ligands were not directly located, but on the basis of potential energy calculations using the HYDEX program,[23] we propose that they are associated with the edges W(1)−Ru(3), Ru(1)−Ru(2), and Ru(1)−Ru(5) and the face Ru(2)−Ru(4)−Ru(5). This proposal is consistent with the ^{1}H NMR data, which show three signals in the range δ −13.58 to −14.73, which may be assigned to edge-bridging hydrides, and a lower frequency signal at δ −23.40 ascribable to the face-bridging hydride.[26]

Discussion

As shown in Scheme 1, the combination of Ru$_5$(μ_5-C)(CO)$_{15}$ with LW(CO)$_3$(CCPh) (L = Cp, C$_5$Me$_5$) in the presence of Me$_3$NO at room temperature initially gave the WRu$_5$ complexes **1** with 15 CO ligands. It is possible that the reaction proceeds through the coordination of the acetylide C−C triple bond to the Ru$_5$ framework, which links the LW(CO)$_3$ pendant in the vicinity of the Ru$_5$ framework, and then promotes the formation of two W−Ru bonds via CO elimination. The isolation of the alkyne complex Ru$_5$(μ_5-C)[C$_2$(CO$_2$Me)$_2$](CO)$_{15}$ from addition of dimethyl acetylenedicarboxylate to the parent carbido cluster Ru$_5$(μ_5-C)(CO)$_{15}$ serves as evidence in favor of this postulate.[12]

Although complexes **1** are the initial products of these cluster-building reactions, they undergo thermally induced transformation to afford cluster products **2** in refluxing toluene solution. The whole transformation involves the elimination of two CO ligands, the formation of two new metal-metal bonds compared with the precursors **1**, and conversion of the acetylide ligand from

Scheme 2



a μ_4 to a μ_3 bonding mode. Most importantly, the W atom also exchanges position with one adjacent Ru atom and occupies an equatorial site of the central square pyramid. We suggest that the formation of such a closely packed geometry in **2** results in a considerably higher chemical stability. This is confirmed by the fact that no regeneration of **1** was observed by treatment of both **2a** and **2b** with a CO atmosphere.

Hydrogenation of complexes **2** was also investigated (Scheme 2), but the results were dependent on the ancillary ligand on the W atom. Thus, only decomposition was observed for the Cp derivative **2a**. When the C$_5$Me$_5$ derivative **2b** was utilized as the starting material, two cluster products, one with a μ_6-carbide ligand and the second with a μ_4-carbide and four hydride ligands, were obtained in 45% and 28% yields, respectively.

The efficient formation of the bridging CCH$_2$Ph alkylidyne ligands in **3** and **4** can be compared with the hydrogenation of butterfly acetylide complexes LWOs$_3$(CCR)(CO)$_{11}$ (L = Cp, C$_5$Me$_5$; R = Bu^n, CH$_2$OMe) and (C$_5$Me$_5$)WRu$_3$(μ-NPh)(CCPh)(CO)$_9$, also reported by us.[27] For the WOs$_3$ clusters, the hydrogenation reaction afforded alkylidyne complexes LWOs$_3$(μ_3-CCH$_2$R)(CO)$_{11}$ with transfer of hydrogen atoms only to the β-carbon of the acetylide ligand. It was speculated that these reactions proceeded via the stepwise formation of a dihydride−acetylide intermediate (2H + CCR), followed by formation of a hydride−vinylidene ligand (H + CCHR), and finally the alkylidyne ligand (μ_3-CCH$_2$R).[28] No incorporation of another H$_2$ molecule as hydrides was detected in these cases. In contrast, hydrogenation of the second WRu$_3$ cluster gave the cluster compound (C$_5$Me$_5$)WRu$_3$(μ-NPh)(CHCHPh)(μ-H)$_2$(CO)$_8$ with the formation of a pair of hydrides as well as one *trans*-vinyl fragment, formed by 1,2-addition of H$_2$ to the acetylide ligand. In the present system, the formation of **3** and **4** involves both the 1,1-addition of hydrogen to acetylide and the generation of two or four more hydride

(24) (a) Chi, Y.; Chuang, S.-H.; Chen, B.-F.; Peng, S.-M.; Lee, G.-H. *J. Chem. Soc., Dalton Trans.* **1990**, 3033. (b) Gong, J.-H.; Tsay, C.-W.; Tu, W.-C.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *J. Cluster Sci.* **1995**, *6*, 289. (c) Whitmire, K. H.; Shriver, D. F. *J. Am. Chem. Soc.* **1981**, *103*, 6754. (d) Kolis, J. W.; Holt, E. M.; Drezdzon, M.; Whitmire, K. H.; Shriver, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 6134.

(25) Harris, S.; Bradley, J. S. *Organometallics* **1984**, *3*, 1086.

(26) (a) Freeman, M. J.; Green, M.; Orpen, A. G.; Salter, I. D.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1983**, 1332. (b) Lin, R.-C.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *Inorg. Chem.* **1992**, *31*, 3818. (c) Adams, R. D.; Barnard, T. S.; Li, Z.; Wu, W.; Yamamoto, J. *Organometallics* **1994**, *13*, 2357. (d) Su, C.-J.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1995**, *14*, 4286.

(27) (a) Chi, Y.; Hwang, D.-K.; Chen, S.-F.; Liu, L.-K. *J. Chem. Soc., Chem. Commun.* **1989**, 1540. (b) Chi, Y.; Lee, G.-H.; Peng, S.-M.; Wu, C.-H. *Organometallics* **1989**, *8*, 1574.

(28) (a) Chi, Y.; Wu, C.-H.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1991**, *10*, 1676. (b) Farrugia, L. J.; MacDonald, N.; Peacock, R. D. *J. Chem. Soc., Chem. Commun.* **1991**, 163.

ligands, respectively. Furthermore, although both complexes **3** and **4** contain hydride ligands, only the hydrides in **3** can be removed without inducing the unwanted cluster fragmentation. Thus, treatment of **3** with a CO atmosphere at elevated temperature produced the new octahedral cluster compound $(C_5Me_5)WRu_5(\mu_6\text{-}C)(\mu\text{-}CCH_2Ph)(CO)_{14}$ (**5**) in 40% yield, which can react with H_2 to re-form the parent WRu_5 cluster compound **3** in approximately 60% yield. The characterization of **5** was achieved by comparing the spectroscopic data with those of the derivatives $LWRu_5(\mu_6\text{-}C)(\mu\text{-}CPh)(CO)_{14}$ (L = Cp, C_5Me_5), which have been identified by X-ray structural analysis.[29]

Summary

The mononuclear acetylide complexes $CpW(CO)_3$-(CCPh) and $(C_5Me_5)W(CO)_3(CCPh)$ were used to prepare the WRu_5 carbido-alkylidyne cluster complexes. We have shown that the acetylide ligand can link to the Ru_5 framework through its unsaturated C−C π-bonding, followed by formation of the W−Ru linkages. The subsequent skeletal rearrangement led to the generation of the face-bridged square-pyramidal core in **2**, with the W atom located at a basal position. This cluster core configuration is relatively more stable compared with the precursors **1**. Conversion of an acetylide to an alkylidyne ligand can be easily achieved through hydrogenation. Complexes **3** and **4** were isolated in moderate yields: one with a μ_6-carbide and two bridging hydrides and the second possessing a μ_4-carbide and four hydride ligands. Treatment of **3** with CO removed the hydrides and gave **5** reversibly. Thus, this sequence of reactions has provided an alternative method to the preparation of octahedral WRu_5 carbido−alkylidyne derivatives related to complex **5**. An independent synthesis of the phenyl derivatives has been achieved by combining $(C_5Me_5)WRu_2(CCPh)(CO)_8$ and $Ru_3(CO)_{12}$ through the direct cleavage of an acetylide ligand.

Finally, the carbide atom of these cluster compounds has failed to react with an acetylide ligand or hydrogen molecules but serves as an anchor to hold together the metal atoms. Such a pattern of reactivity is in sharp contrast to those observed in the WOs_3 system, where the carbide has shown a higher tendency in forming C−C bonding with ligated alkylidyne or alkyne fragments.[30]

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Supporting Information Available: Tables of atomic coordinates and the corresponding anisotropic thermal parameters for complexes **1a**, **2a**, **3**, and **4** (15 pages). Ordering information is given on any current masthead page.

OM970211L

(29) Chiang, S.-J.; Chi, Y.; Su, P.-C.; Peng, S.-M.; Lee, G.-H. *J. Am. Chem. Soc.* **1994**, *116*, 11181.

(30) (a) Chi, Y.; Su, P.-C.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1995**, *14*, 5483. (b) Chi, Y.; Chung, C.; Chou, Y.-C.; Su, P.-C.; Chiang, S.-J.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1997**, *16*, 1702.