

# Syntheses and Reactivity Studies of the Carbido-Alkylidyne Cluster Complexes $\text{LWRu}_4(\mu_5\text{-C})(\mu\text{-CPh})(\text{CO})_{12}$ and $\text{LWRu}_5(\mu_6\text{-C})(\mu\text{-CPh})(\text{CO})_{14}$ , $\text{L} = \text{Cp}$ and $\text{Cp}^*$ , Obtained from Reversible Scission of Acetylide Ligand

Shu-Fen Hwang,<sup>†</sup> Yun Chi,<sup>\*,†</sup> Shun-Jean Chiang,<sup>†</sup> Shie-Ming Peng,<sup>‡</sup> and Gene-Hsiang Lee<sup>‡</sup>

Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan, Republic of China, and Department of Chemistry and Instrumentation Center, National Taiwan University, Taipei 10764, Taiwan, Republic of China

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Treatment of a 1:1 mixture of  $\text{Ru}_3(\text{CO})_{12}$  and the acetylide cluster  $\text{LWRu}_2(\text{CO})_8(\text{C}_2\text{Ph})$  (**1**,  $\text{L} = \text{Cp}$  and  $\text{Cp}^*$ ) in hydrocarbon solvents afforded two carbido-alkylidyne cluster complexes,  $\text{LWRu}_4(\mu_5\text{-C})(\text{CO})_{12}(\mu\text{-CPh})$  (**2**) and  $\text{LWRu}_5(\mu_6\text{-C})(\text{CO})_{14}(\mu\text{-CPh})$  (**3**). Complexes **2** contain a square pyramidal cluster skeleton with a  $\mu_5$ -carbide and an accompanying bridging alkylidyne ligand, while  $\text{WRu}_5$  complexes **3** possess a distorted octahedral  $\text{WRu}_5(\mu_6\text{-C})$  framework. The transformation from **1** to **2** and **3** illustrates a reversible cleavage of an acetylide carbon–carbon bond induced by the cluster-building reaction. Moreover, the hydrogenation of complexes **2** and **3** was found to depend on the ancillary ligand on the W atom, showing selective formation of only two hydride complexes,  $\text{CpWRu}_4(\mu_5\text{-C})(\mu\text{-CPh})(\mu\text{-H})_2(\text{CO})_{11}$  (**4**) and  $\text{Cp}^*\text{WRu}_5(\mu_6\text{-C})(\mu\text{-CPh})(\mu\text{-H})_2(\text{CO})_{13}$  (**5**), respectively. Single-crystal X-ray analysis on complex **4** indicated that the hydrides resided near the apical Ru atom, while the hydrides in complex **5** were associated with the unique W metal atom. Finally, treatment of **2** with thiophenol has led to formation of the wingtip-bridged butterfly complexes  $\text{LWRu}_4(\mu_5\text{-C})(\mu\text{-CPh})(\mu\text{-H})(\mu\text{-SPh})(\text{CO})_{11}$  (**7a**,  $\text{L} = \text{Cp}$ ; **7b**,  $\text{L} = \text{Cp}^*$ ), in which the thiolate ligand is bonded to the Ru atoms separated by a nonbonding distance of 3.4186(8) Å.

The chemistry of carbido metal cluster compounds has developed in recent years to constitute a distinct research domain.<sup>1</sup> It has been established from the successful synthesis of many group 8 metal-containing carbido carbonyl clusters that the interstitial carbides can be derived either by activation of C–H or C–S bond,<sup>2</sup> by disproportionation of the carbon monoxide ligand,<sup>3</sup> or by scission of the coordinated isocyanide fragment.<sup>4</sup> The acetylide ligand, which possesses a

formal carbon–carbon triple bond, is obviously related to the above-mentioned carbon monoxide and isocyanide fragments; thus scission of the acetylide carbon–carbon bond is theoretically feasible within the coordination sphere of cluster complexes.

Indeed, some scattered examples have been documented in the literature. These are best illustrated by the oxidative decarbonylation of the acetylide in the complexes  $[\text{Cp}(\text{CO})_2\text{MC}_2\text{Ph}][\text{Co}_2(\text{CO})_6]$  ( $\text{M} = \text{Fe}, \text{Ru}$ )<sup>5</sup> and carbon–carbon bond cleavage of the phosphinoalkyne ligand in the cluster complex  $\text{Ru}_5(\mu_5\text{-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_{13}$ , demonstrating the potential of the acetylide ligand in exhibiting such reactivity pattern.<sup>6</sup> However, these reactions are not fully understood in terms of the completeness of the process. For example, in the oxidative decarbonylation reaction the acetylide ligand expels its  $\alpha$ -carbon atom to produce the alkylidyne clusters  $\text{CpMCo}_2(\mu_3\text{-CPh})(\text{CO})_7$  as the final product. Thus, study of the reverse reaction, i.e., carbide and alkylidyne coupling, can never be investigated due to the irreversible loss of carbide as carbon monoxide during the experiments. Moreover, mechanistic details

\* Corresponding author. Fax: (886) 3-572 0864. E-mail: ychi@mx.nthu.edu.tw.

<sup>†</sup> National Tsing Hua University.

<sup>‡</sup> National Taiwan University.

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of the C–C bond cleavage of the phosphinoalkyne ligand are also lacking due to the low yields and unwanted complex side reactions.

Now, we wish to report a full account of our studies on the reversible formation of carbide and alkylidyne ligands in building the cluster complexes  $\text{LWRu}_4(\mu_5\text{-C})(\text{CO})_{12}(\mu\text{-CPh})$  (**2**) and  $\text{LWRu}_5(\mu_6\text{-C})(\text{CO})_{14}(\mu\text{-CPh})$  (**3**), which are obtained from condensation of acetylide clusters  $\text{LWRu}_2(\text{CCPh})(\text{CO})_8$  (**1**),  $\text{L} = \text{Cp}$  and  $\text{Cp}^*$ , with binary metal carbonyl  $\text{Ru}_3(\text{CO})_{12}$ .<sup>7</sup> Upon treatment of CO, complexes **2** and **3** are found to revert back to the original acetylide complexes **1** in excellent yields, thus verifying the conformity between the ligated acetylide and the carbide-alkylidyne proposed by Carty and co-workers.<sup>8</sup> Detailed studies of our synthetic investigations, basic reaction chemistry of the products, and X-ray structural studies of this series of carbido-alkylidyne products will be presented in this paper.

## Experimental Section

**General Information and Materials.** Infrared spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer. <sup>1</sup>H and <sup>13</sup>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 fast atom bombardment modes (FAB). 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<sub>254</sub>, E. Merck), and products were separated on commercially available preparative thin-layer chromatographic plates (Kieselgel 60 F<sub>254</sub>, E. Merck). Elemental analyses were performed at the NSC Regional Instrumentation Center at National Cheng Kung University, Tainan, Taiwan.

**Reaction of 1a with Ru<sub>3</sub>(CO)<sub>12</sub>.** A heptane solution (60 mL) of  $\text{CpWRu}_2(\text{CCPh})(\text{CO})_8$  (**1a**, 120 mg, 0.155 mmol) and  $\text{Ru}_3(\text{CO})_{12}$  (98 mg, 0.153 mmol) was heated at reflux under nitrogen for 17 h, during which time the color turned from orange to deep black. After removal of the solvent, the residue was dissolved in  $\text{CH}_2\text{Cl}_2$  and separated by thin-layer chromatography ( $\text{CH}_2\text{Cl}_2/\text{hexane} = 1:1$ ) followed by recrystallization from a mixture of  $\text{CH}_2\text{Cl}_2$  and methanol, giving 115 mg of dark brown  $\text{CpWRu}_4(\mu_5\text{-C})(\mu\text{-CPh})(\text{CO})_{12}$  (**2a**, 0.105 mmol, 68%) and 36 mg of black  $\text{CpWRu}_5(\mu_6\text{-C})(\mu\text{-CPh})(\text{CO})_{14}$  (**3a**, 0.029 mmol, 19%).

Spectral data of **2a**: MS (FAB, <sup>102</sup>Ru, <sup>184</sup>W),  $m/z$  1092 ( $\text{M}^+$ ). IR ( $\text{C}_6\text{H}_{12}$ ):  $\nu(\text{CO})$ , 2076 (m), 2039 (vs), 2025 (s), 2008 (m), 1982 (w), 1975 (w), 1962 (vw), 1788 (s)  $\text{cm}^{-1}$ . <sup>1</sup>H NMR ( $\text{CD}_2\text{Cl}_2$ , RT):  $\delta$  7.29 (t, 2H,  $J_{\text{HH}} = 7.4$  Hz), 7.21 (t, 1H,  $J_{\text{HH}} = 7.4$  Hz), 6.79 (d, 2H,  $J_{\text{HH}} = 7.4$  Hz), 5.78 (s, 5H). <sup>13</sup>C NMR ( $\text{CD}_2\text{Cl}_2$ , RT):  $\delta$  424.0 ( $\mu_5\text{-C}$ ,  $J_{\text{WC}} = 88$  Hz), 302.3 ( $\mu\text{-CPh}$ ,  $J_{\text{WC}} = 156$  Hz), 159.1 (i- $\text{C}_6\text{H}_5$ ), 128.7 (2C, o- $\text{C}_6\text{H}_5$ ), 128.0 (p- $\text{C}_6\text{H}_5$ ), 121.8 (2C, m- $\text{C}_6\text{H}_5$ ), 97.2 ( $\text{C}_5\text{H}_5$ ). Anal. Calcd for  $\text{C}_{25}\text{H}_{10}\text{O}_{12}\text{Ru}_4\text{W}$ : C, 27.54; H, 0.92. Found: C, 27.42; H, 0.96.

Spectral data of **3a**: MS (FAB, <sup>102</sup>Ru, <sup>184</sup>W),  $m/z$  1249 ( $\text{M}^+$ ). IR ( $\text{C}_6\text{H}_{12}$ ):  $\nu(\text{CO})$ , 2075 (s), 2034 (vs), 1982 (m, br), 1894 (w, br), 1849 (vw, br), 1784 (m, br)  $\text{cm}^{-1}$ . <sup>1</sup>H NMR ( $\text{CDCl}_3$ , RT):  $\delta$  7.35 (t, 2H,  $J_{\text{HH}} = 7.4$  Hz), 7.26 (t, 1H,  $J_{\text{HH}} = 7.4$  Hz), 6.68 (d, 2H,  $J_{\text{HH}} = 7.4$  Hz), 5.53 (s, 5H). <sup>13</sup>C NMR ( $\text{CDCl}_3$ , RT):  $\delta$  425.1 ( $\mu_6\text{-C}$ ), 335.9 ( $\mu\text{-CPh}$ ), 163.7 (i- $\text{C}_6\text{H}_5$ ), 129.5 (2C, o- $\text{C}_6\text{H}_5$ ), 128.7 (p- $\text{C}_6\text{H}_5$ ), 120.4 (2C, m- $\text{C}_6\text{H}_5$ ), 93.7 ( $\text{C}_5\text{H}_5$ ). Anal. Calcd for  $\text{C}_{27}\text{H}_{10}\text{O}_{14}\text{Ru}_5\text{W}$ : C, 25.99; H, 0.81. Found: C, 25.98; H, 0.90.

**Reaction of 1b with Ru<sub>3</sub>(CO)<sub>12</sub>.** A toluene solution (60 mL) of  $(\text{C}_5\text{Me}_5)\text{WRu}_2(\text{CO})_8(\text{CCPh})$  (**1b**, 140 mg, 0.165 mmol) and  $\text{Ru}_3(\text{CO})_{12}$  (107 mg, 0.167 mmol) was heated at reflux for 5 h, during which time the color turned from orange to dark brown. After evaporation of the solvent, the residue was redissolved in  $\text{CH}_2\text{Cl}_2$  and separated by thin-layer chromatography ( $\text{CH}_2\text{Cl}_2/\text{hexane} = 1:2$ ), giving 36 mg of red-brown  $(\text{C}_5\text{Me}_5)\text{WRu}_4(\mu_5\text{-C})(\mu\text{-CPh})(\text{CO})_{12}$  (**2b**, 0.031 mmol, 19%) and 53 mg of dark brown  $(\text{C}_5\text{Me}_5)\text{WRu}_5(\mu_6\text{-C})(\mu\text{-CPh})(\text{CO})_{12}$  (**3b**, 0.041 mmol, 24%).

Spectral data of **2b**: MS (FAB, <sup>102</sup>Ru, <sup>184</sup>W),  $m/z$  1160 ( $\text{M}^+$ ). IR ( $\text{C}_6\text{H}_{12}$ ):  $\nu(\text{CO})$ , 2071 (m), 2037 (vs), 2031 (s), 2021 (m), 2002 (w), 1973 (w), 1967 (m), 1960 (vw), 1777 (s)  $\text{cm}^{-1}$ . <sup>1</sup>H NMR ( $\text{CD}_2\text{Cl}_2$ , 294 K):  $\delta$  7.24 (t, 2H,  $J_{\text{HH}} = 7.4$  Hz), 7.14 (t, 1H,  $J_{\text{HH}} = 7.4$  Hz), 6.69 (d, 2H,  $J_{\text{HH}} = 7.4$  Hz), 2.02 (s, 15H). <sup>13</sup>C NMR ( $\text{CDCl}_3$ , 294 K): CO,  $\delta$  231.5 (2C,  $J_{\text{WC}} = 58$  Hz) 205.1 (3C, br), 200.9 (2C, br), 193.8 (3C), 193.1 (2C);  $\delta$  426.2 ( $\mu_5\text{-C}$ ,  $J_{\text{WC}} = 90$  Hz), 294.5 ( $\mu\text{-CPh}$ ,  $J_{\text{WC}} = 165$  Hz), 155.0 (i- $\text{C}_6\text{H}_5$ ,  $J_{\text{WC}} = 29$  Hz), 128.1 (2C, o- $\text{C}_6\text{H}_5$ ), 127.2 (p- $\text{C}_6\text{H}_5$ ), 121.2 (2C, m- $\text{C}_6\text{H}_5$ ), 108.6 ( $\text{C}_5\text{Me}_5$ ), 11.1 (Me). Anal. Calcd for  $\text{C}_{30}\text{H}_{20}\text{O}_{12}\text{Ru}_4\text{W}$ : C, 31.05; H, 1.74. Found: C, 31.03; H, 1.74.

Spectral data of **3b**: MS (FAB, <sup>102</sup>Ru, <sup>184</sup>W),  $m/z$  1318 ( $\text{M}^+$ ). IR ( $\text{C}_6\text{H}_{12}$ ):  $\nu(\text{CO})$ , 2072 (m), 2039 (s), 2029 (vs), 2009 (w), 1980 (w), 1971 (vw), 1962 (vw), 1887 (w), 1841 (w), 1781 (m)  $\text{cm}^{-1}$ . <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 294 K):  $\delta$  7.33 (t, 2H,  $J_{\text{HH}} = 7.2$  Hz), 7.25 (t, 1H,  $J_{\text{HH}} = 7.2$  Hz), 6.68 (d, 2H,  $J_{\text{HH}} = 7.2$  Hz), 2.14 (s, 15H). Anal. Calcd for  $\text{C}_{32}\text{H}_{20}\text{O}_{14}\text{Ru}_5\text{W}$ : C, 29.17; H, 1.53. Found: C, 28.98; H, 1.47.

**Reaction of 2a with Ru<sub>3</sub>(CO)<sub>12</sub>.** A toluene solution (40 mL) of **2a** (85 mg, 0.078 mmol) and  $\text{Ru}_3(\text{CO})_{12}$  (49.8 mg, 0.078 mmol) was heated at reflux under nitrogen for 14 h. After removal of the solvent in vacuo, the residue was redissolved in  $\text{CH}_2\text{Cl}_2$  and separated by thin-layer chromatography ( $\text{CH}_2\text{Cl}_2/\text{hexane} = 1:1$ ), giving complex **3a** (56.7 mg, 0.045 mmol, 58%) as a black crystalline solid.

**Treatment of 3a with CO.** In a 150 mL stainless steel autoclave, a toluene solution (40 mL) of **3a** (47 mg, 0.038 mmol) was heated at 80 °C under a pressurized CO atmosphere (14 atm) for 4 h. Then the autoclave was allowed to cool to room temperature, and the solution was transferred out of the reactor. The toluene was evaporated under vacuum, and the residue was purified by thin-layer chromatography ( $\text{CH}_2\text{Cl}_2/\text{hexane} = 1:2$ ), giving 28 mg of red-orange complex **1a** (0.036 mmol, 95%). For the reaction that was carried out under CO at 7 atm, we isolated 38% of **1a** and recovered 52% of starting material **3a**.

**Hydrogenation of 2a.** A toluene solution (40 mL) of **2a** (115 mg, 0.105 mmol) was heated at reflux under hydrogen (1 atm) for 5 min, during which time the color turned from dark brown to red-brown. After removal of the solvent, the residue was filtered and recrystallized from a mixture of  $\text{CH}_2\text{Cl}_2$  and pentane at –20 °C, giving 107 mg of  $\text{CpWRu}_4(\mu_5\text{-C})(\mu\text{-CPh})(\mu\text{-H})_2(\text{CO})_{11}$  (**4**, 0.01 mmol, 96%) as red-brown crystalline solids.

Spectral data of **4**: MS (FAB, <sup>102</sup>Ru, <sup>184</sup>W),  $m/z$  1068 ( $\text{M}^+$ ). IR ( $\text{C}_6\text{H}_{12}$ ):  $\nu(\text{CO})$ , 2084 (s), 2051 (vs, br), 2031 (vs), 2021 (m), 2000 (w), 1987 (w), 1971 (vw), 1787 (m)  $\text{cm}^{-1}$ . <sup>1</sup>H NMR ( $\text{CD}_2\text{Cl}_2$ , 294 K):  $\delta$  7.26 (t, 2H,  $J_{\text{HH}} = 7.6$  Hz), 7.11 (t, 1H,  $J_{\text{HH}} = 7.6$  Hz), 6.54 (d, 2H,  $J_{\text{HH}} = 7.6$  Hz), 5.70 (s, 5H), –21.15 (d, 1H,  $J_{\text{HH}} = 1.6$  Hz), –22.01 (d, 1H,  $J_{\text{HH}} = 1.6$  Hz). <sup>13</sup>C NMR ( $\text{CD}_2\text{Cl}_2$ , 253 K): CO,  $\delta$  268.7, 202.2 (2C), 199.1, 198, 196.7, 195.7, 193.8, 193.4, 190.0, 188.7;  $\delta$  405.2 ( $\mu_5\text{-C}$ ,  $J_{\text{WC}} = 88$  Hz), 324.8 ( $\mu\text{-CPh}$ ,  $J_{\text{WC}} = 154$  Hz), 161.7 (i- $\text{C}_6\text{H}_5$ ), 128.4 (2C, o- $\text{C}_6\text{H}_5$ ), 126.4 (p- $\text{C}_6\text{H}_5$ ), 119.9 (2C, m- $\text{C}_6\text{H}_5$ ), 96.6 ( $\text{C}_5\text{H}_5$ ). Anal. Calcd for  $\text{C}_{24}\text{H}_{12}\text{O}_{11}\text{Ru}_4\text{W}$ : C, 27.08; H, 1.14. Found: C, 26.88; H, 1.12.

**Hydrogenation of 3b.** A toluene solution (40 mL) of **3b** (115 mg, 0.105 mmol) was heated at reflux under  $\text{H}_2$  (1 atm) for 5 h. After removal of the solvent on a rotary evaporator, the residue was dissolved in  $\text{CH}_2\text{Cl}_2$  and separated by thin-layer chromatography ( $\text{CH}_2\text{Cl}_2/\text{hexane} = 1:3$ ). Recrystallization

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from a mixture of  $\text{CH}_2\text{Cl}_2$  and methanol gave 115 mg of  $\text{Cp}^*\text{WRu}_5(\mu_6\text{-C})(\mu\text{-CPh})(\mu\text{-H})_2(\text{CO})_{13}$  (**5**, 0.064 mmol, 68%) as a dark brown solid.

Spectral data of **5**: MS (FAB,  $^{102}\text{Ru}$ ,  $^{184}\text{W}$ ),  $m/z$  1296 ( $\text{M}^+$ ). IR ( $\text{C}_6\text{H}_{12}$ ):  $\nu(\text{CO})$ , 2073 (m), 2046 (w), 2032 (vs), 2010 (m), 1986 (vw), 1964 (vw), 1892 (w, br), 1853 (vw), 1839 (vw)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 294 K):  $\delta$  7.28 (t, 2H,  $J_{\text{HH}} = 7.4$  Hz), 7.18 (t, 1H,  $J_{\text{HH}} = 7.4$  Hz), 6.27 (d, 2H,  $J_{\text{HH}} = 7.4$  Hz), 2.11 (s, 15H),  $-16.72$  (s, 2H,  $J_{\text{WC}} = 77$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 294 K): CO,  $\delta$  236.1 (3C), 212.3 (1C), 211.0 (2C), 203.0 (1C), 198.4 (2C), 197.0 (2C), 196.4 (2C);  $\delta$  420.8 ( $\mu_6\text{-C}$ ), 316.7 ( $\mu\text{-CPh}$ ), 157.7 (i- $\text{C}_6\text{H}_5$ ), 128.3 (2C, o- $\text{C}_6\text{H}_5$ ), 127.4 (p- $\text{C}_6\text{H}_5$ ), 122.3 (2C, m- $\text{C}_6\text{H}_5$ ), 107.1 ( $\text{C}_5\text{Me}_5$ ), 14.3 (Me). Anal. Calcd for  $\text{C}_{31}\text{H}_{22}\text{O}_{13}\text{Ru}_5\text{W}$ : C, 28.83; H, 1.72. Found: C, 28.67; H, 1.69.

**Reaction of 4 with CO.** A toluene solution (40 mL) of **4** (76.4 mg, 0.0717 mmol) was heated at reflux under a CO atmosphere (1 atm) for 3 min, during which time the color turned from red-brown to dark brown. After removal of the solvent, the residue was filtered and recrystallized from a mixture of  $\text{CH}_2\text{Cl}_2$  and methanol, giving **2a** (72 mg, 0.066 mmol, 92%) as crystalline solids.

**Reaction of 5 with CO.** A toluene solution (30 mL) of **5** (20.4 mg, 0.016 mmol) was heated at reflux under 1 atm of CO atmosphere for 2.5 h. Then the product was purified by thin-layer chromatography, giving 19.5 mg of **3b** (0.015 mmol, 94%) as crystalline solids.

**Reaction of 2a with Thiophenol.** A hexane solution (40 mL) of **2a** (63 mg, 0.06 mmol) and HSPH (18  $\mu\text{L}$ , 0.18 mmol) was heated at reflux for 60 min. After evaporation of the solvent, the residue was redissolved in  $\text{CH}_2\text{Cl}_2$  and separated by thin-layer chromatography ( $\text{CH}_2\text{Cl}_2/\text{hexane} = 1:2$ ), giving  $\text{CpWRu}_4(\mu_5\text{-C})(\mu\text{-CPh})(\mu\text{-H})(\mu\text{-SPh})(\text{CO})_{11}$  (**7a**, 41 mg, 0.03 mmol, 59%) as a red crystalline solid. Single crystals of **7a** suitable for X-ray diffraction study were obtained from a mixture of  $\text{CH}_2\text{Cl}_2$  and heptane at room temperature.

Spectral data for **7a**: MS (FAB,  $^{102}\text{Ru}$ ,  $^{184}\text{W}$ ),  $m/z$  1176 ( $\text{M}^+$ ). IR ( $\text{C}_6\text{H}_{12}$ ):  $\nu(\text{CO})$ , 2080 (m), 2048 (vs), 2027 (s), 2018 (m), 2001 (vw), 1988 (w, br), 1973 (w), 1789 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 273 K):  $\delta$  7.20–7.08 (m, 6H), 7.23–7.02 (m, 4H), 6.61–6.57 (m, 1H), 5.49 (s, 5H, 80%), 5.46 (s, 5H, 20%),  $-16.58$  (s, 1H, 20%),  $-17.09$  (s, 1H, 80%). Anal. Calcd for  $\text{C}_{30}\text{H}_{16}\text{O}_{11}\text{SRu}_4\text{W}$ : C, 30.73; H, 1.38. Found: C, 30.64; H, 1.44.

**Reaction of 2b with Thiophenol.** A hexane solution (40 mL) of **2b** (62 mg, 0.05 mmol) and HSPH (15  $\mu\text{L}$ , 0.15 mmol) was heated at reflux for 60 min, during which time the color of the solution changed from red-brown to dark brown. After evaporation of the solvent, the residue was dissolved in  $\text{CH}_2\text{Cl}_2$  and separated by thin-layer chromatography ( $\text{CH}_2\text{Cl}_2/\text{hexane} = 1:2$ ), giving 26.1 mg of red  $(\text{C}_5\text{Me}_5)\text{WRu}_4(\mu_5\text{-C})(\mu\text{-CPh})(\mu\text{-H})(\mu\text{-SPh})(\text{CO})_{11}$  (**7b**, 0.02 mmol, 40%).

Spectral data for **7b**: MS (FAB,  $^{102}\text{Ru}$ ,  $^{184}\text{W}$ ),  $m/z$  1246 ( $\text{M}^+$ ). IR ( $\text{C}_6\text{H}_{12}$ ):  $\nu(\text{CO})$ , 2076 (m), 2044 (vs), 2022 (s), 2013 (m), 1995 (w), 1989 (vw), 1982 (vw), 1963 (m), 1780 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 243 K):  $\delta$  7.19–6.99 (m, 8H), 6.54–6.36 (m, 2H), 1.91 (s, 15H, 80%,  $\text{C}_5\text{Me}_5$ ), 1.90 (s, 15H, 20%,  $\text{C}_5\text{Me}_5$ ),  $-16.34$  (s, 1H, 20%),  $-16.94$  (s, 1H, 80%). Anal. Calcd for  $\text{C}_{35}\text{H}_{26}\text{O}_{11}\text{SRu}_4\text{W}$ : C, 33.83; H, 2.11. Found: C, 33.63; H, 2.05.

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**X-ray Crystallography.** The X-ray diffraction measurements were carried out on a Nonius CAD-4 diffractometer. For all experiments, the lattice parameters were determined from 25 randomly selected high-angle reflections. Three standard reflections were monitored every 3600 s. No significant change in intensities ( $\leq 2\%$ ) was observed during the course of data collection. Intensities of the diffraction signals were corrected for Lorentz, polarization, and absorption effects ( $\psi$  scans). The structure was solved using the NRCC-SDP-VAX package. All the non-hydrogen atoms had anisotropic temperature factors, while the hydrogen atoms of the organic substituents were placed at the calculated positions with  $U_{\text{H}} = U_{\text{C}} + 0.1$ .

The crystallographic refinement parameters of complexes **2a**, **3a**, **4**, and **7a** are given in Table 1, while their selected bond distances and angles are presented in Tables 2–5, respectively.

## Results

**Carbido-Alkylidyne Complexes 2 and 3.** As indicated in Scheme 1, the acetylide cluster  $\text{CpWRu}_2(\text{CO})_8\text{-}(\text{CCPh})$  (**1a**) reacted with  $\text{Ru}_3(\text{CO})_{12}$  in refluxing heptane solution to afford two carbido-alkylidyne cluster complexes which are assigned to have the empirical formulas  $\text{CpWRu}_4(\mu_5\text{-C})(\mu\text{-CPh})(\text{CO})_{12}$  (**2a**, 68%) and  $\text{CpWRu}_5(\mu_6\text{-C})(\mu\text{-CPh})(\text{CO})_{14}$  (**3a**, 19%). Reaction of the  $\text{Cp}^*$  derivative complex  $\text{Cp}^*\text{WRu}_2(\text{CO})_8(\text{CCPh})$  (**1b**,  $\text{Cp}^* = \text{C}_5\text{Me}_5$ ) with  $\text{Ru}_3(\text{CO})_{12}$  in refluxing toluene solution gave rise to the isolation of two closely related complexes,  $\text{Cp}^*\text{WRu}_4(\mu_5\text{-C})(\mu\text{-CPh})(\text{CO})_{12}$  (**2b**, 19%), and  $\text{Cp}^*\text{WRu}_5(\mu_6\text{-C})(\mu\text{-CPh})(\text{CO})_{14}$  (**3b**, 24%). These carbido-alkylidyne compounds were unambiguously characterized by spectroscopic as well as by single-crystal X-ray diffraction studies on **2a** and **3a**.

Compound **2a** contains two crystallographically distinct molecules in the asymmetric crystal unit. Both cluster molecules are structurally similar, and an ORTEP diagram of one of these molecules is shown in Figure 1. Generally speaking, the metal framework of **2a** is best described as a  $\text{WRu}_4$  square pyramidal arrangement with the unique W atom occupying the basal site. The metal–metal distances are in the range 2.794(1)–2.914(1) Å, with the W–Ru bonds being slightly longer than the Ru–Ru bonds. The W(1)–Ru(1) edge is bridged by an asymmetrical CO ligand, the W(1)–Ru(4) edge is associated with the alkylidyne ligand, and the third W(1)–Ru(3) edge which possesses no bridging ligand is the longest metal–metal edge of the whole molecule. The carbide atom is located at a position slightly below the  $\text{WRu}_3$  plane (0.177(6) Å) and forms a strong bonding interaction with all five metal atoms. The resulting core arrangement resembles that of many reported  $\text{Ru}_5$  square pyramidal carbido cluster compounds.<sup>9</sup>

In addition, the W(1)–C(14) distance (1.871(6) Å) of the alkylidyne ligand is substantially shorter than the Ru(4)–C(14) distance (2.291(6) Å), while the W(1)–C(14)–C(15) angle (150.4(4)°) is larger than the respective Ru(4)–C(14)–C(15) angle (123.2(4)°). These metric parameters indicate that the alkylidyne ligand is asymmetrically coordinated to the W(1)–Ru(4) edge and that a substantial  $\text{W}\equiv\text{C}$  bonding character is retained. The unusually short W–C separation compares well with that in the mononuclear alkylidyne complex  $\text{CpW}(\equiv\text{CTol})(\text{CO})_2$  (1.82(2) Å)<sup>10</sup> and the ionic carborane complex  $[(\text{C}_2\text{B}_9\text{H}_9\text{Me}_2)\text{W}(\text{CO})_2(\equiv\text{CPh})][\text{PPh}_4]$  (1.82(3)–1.84(3) Å).<sup>11</sup>

**Table 1. X-Ray Structural Data of Complexes 2a, 3a, 4, and 7a<sup>a</sup>**

	<b>2a</b>	<b>3a</b>	<b>4</b>	<b>7a</b>
formula	C <sub>25</sub> H <sub>10</sub> O <sub>12</sub> Ru <sub>4</sub> W	C <sub>27</sub> H <sub>10</sub> O <sub>14</sub> Ru <sub>5</sub> W	C <sub>24</sub> H <sub>12</sub> O <sub>11</sub> Ru <sub>4</sub> W	C <sub>30</sub> H <sub>16</sub> O <sub>11</sub> SRu <sub>4</sub> W·CH <sub>2</sub> Cl <sub>2</sub>
mol wt	1090.47	1247.57	1064.49	1257.57
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 1	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	12.855(3)	17.381(3)	10.574(2)	12.506(2)
<i>b</i> (Å)	13.603(4)	10.030(5)	16.771(9)	18.018(3)
<i>c</i> (Å)	16.746(3)	17.907(1)	15.589(3)	16.316(4)
$\alpha$ (deg)	79.00(2)			
$\beta$ (deg)	85.91(2)	97.744(9)	92.73(2)	95.71(2)
$\gamma$ (deg)	89.48(3)			
volume (Å <sup>3</sup> )	2867(1)	3093(2)	2761(2)	3658(1)
<i>Z</i>	4	4	4	4
<i>D</i> <sub>c</sub> (g/cm <sup>3</sup> )	2.526	2.679	2.558	2.283
<i>F</i> (000)	1998	2312	1976	2368
2 $\theta$ (max) (deg)	50.0	50.0°	45.0°	50.0
<i>h k l</i> ranges	−15 15, 0 16, −19 19	−20 20, 0 11, 0 21	−11 11, 0 18, 0 16	−14 14, 0 21, 0 19
cryst size (mm)	0.25 × 0.45 × 0.70	0.20 × 0.22 × 0.50	0.35 × 0.40 × 0.40	0.50 × 0.50 × 0.50
$\mu$ (Mo K $\alpha$ ) (cm <sup>−1</sup> )	61.65	61.88	63.96	50.42
transmission: max., min.	1.000, 0.670	1.000, 0.612	1.000, 0.542	1.000, 0.670
no. of data in refinement	8470 with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	4922 with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	2614 with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	5681 with <i>I</i> > 2 $\sigma$ ( <i>I</i> )
no. of atoms and params	104, 758	57, 424	51, 364	67, 465
weight modifier, <i>g</i>	0.00002		0.0001	
max. $\Delta$ / $\sigma$ ratio	0.005	0.018	0.028	0.020
<i>R</i> <sub>F</sub> ; <i>R</i> <sub>w</sub>	0.025; 0.026	0.023; 0.022	0.043; 0.043	0.025; 0.023
GOF	2.10	2.40	1.75	2.79
D-map, max./min., e/Å <sup>3</sup>	0.95/−0.81	1.29/−0.80	1.37/−1.34	1.00/−1.06

<sup>a</sup> Features common to all determinations:  $\lambda$ (Mo K $\alpha$ ) = 0.7107 Å; minimization function =  $\sum(w|F_o - F_c|^2)$ , weighting scheme =  $w^{-1} = \sigma^2(F_o) + |g|F_o^2$ ; GOF =  $[\sum w|F_o - F_c|^2 / (N_o - N_v)]^{1/2}$  (*N*<sub>o</sub> = number of observations; *N*<sub>v</sub> = number of variables).

**Table 2. Selected Bond Distances (Å) and Angles (deg) of 2a (esd's in parentheses)**

W(1)–Ru(1)	2.881(1)	W(1)–Ru(3)	2.914(1)
W(1)–Ru(4)	2.863(1)	Ru(1)–Ru(2)	2.820(1)
Ru(1)–Ru(4)	2.856(1)	Ru(2)–Ru(3)	2.801(1)
Ru(2)–Ru(4)	2.880(1)	Ru(3)–Ru(4)	2.794(1)
W(1)–C(1)	2.215(6)	Ru(1)–C(1)	2.006(6)
W(1)–C(13)	2.053(6)	Ru(1)–C(13)	2.029(6)
Ru(2)–C(13)	1.992(6)	Ru(3)–C(13)	2.031(6)
Ru(4)–C(13)	2.190(6)	W(1)–C(14)	1.871(6)
Ru(4)–C(14)	2.291(6)		
Ru(4)–C(14)–C(15)	123.2(4)	W(1)–C(14)–C(15)	150.4(4)

**Table 3. Selected Bond Distances (Å) and Angles (deg) of 3a (esd's in parentheses)**

W–Ru(1)	3.229(1)	W–Ru(2)	2.943(1)
W–Ru(3)	2.856(1)	W–Ru(4)	2.921(1)
Ru(1)–Ru(2)	2.925(1)	Ru(1)–Ru(4)	2.988(1)
Ru(1)–Ru(5)	2.817(1)	Ru(2)–Ru(3)	2.819(1)
Ru(2)–Ru(5)	2.877(1)	Ru(3)–Ru(4)	2.896(1)
Ru(3)–Ru(5)	2.839(1)	Ru(4)–Ru(5)	2.936(1)
W–C(15)	2.080(5)	Ru(1)–C(15)	2.037(5)
Ru(2)–C(15)	2.066(5)	Ru(3)–C(15)	2.106(5)
Ru(4)–C(15)	2.025(5)	Ru(5)–C(15)	2.103(5)
W–C(16)	1.893(5)	Ru(3)–C(16)	2.176(5)
Ru(3)–C(16)–C(17)	126.4(4)	W–C(16)–C(17)	144.7(4)

Mixed metal complexes with unsymmetrical alkylidyne ligands associated with various metal–metal edges have been reported by Stone and co-workers<sup>12</sup> and by us.<sup>13</sup> Moreover, complex **2a** contains 74 valence electrons and is isostructural to the RhFe<sub>4</sub> and CoFe<sub>4</sub> carbido cluster complexes, in which the heteroatom is also located at the basal position.<sup>14</sup>

In agreement with the solid-state structure, the carbide and the alkylidyne carbon signals of **2a** occurred

**Table 4. Selected Bond Distances (Å) and Angles (deg) of 4 (esd's in parentheses)**

W–Ru(1)	2.848(2)	W–Ru(3)	2.961(2)
W–Ru(4)	2.813(2)	Ru(1)–Ru(2)	2.889(2)
Ru(1)–Ru(4)	2.882(2)	Ru(2)–Ru(3)	2.843(2)
Ru(2)–Ru(4)	2.886(2)	Ru(3)–Ru(4)	2.854(2)
W–C(12)	2.00(1)	Ru(1)–C(12)	2.04(1)
Ru(2)–C(12)	2.06(1)	Ru(3)–C(12)	2.08(1)
Ru(4)–C(12)	2.14(2)	W–C(1)	2.20(2)
Ru(1)–C(1)	2.03(2)	W–C(13)	1.88(2)
Ru(4)–C(13)	2.12(2)		
Ru(4)–C(13)–C(14)	127.9(11)	W–C(13)–C(14)	142.6(11)
Ru(1)–Ru(4)–C(11)	70.0(5)	Ru(3)–Ru(4)–C(10)	113.5(5)
Ru(4)–Ru(3)–C(8)	115.0(5)	Ru(4)–Ru(3)–C(9)	101.1(5)

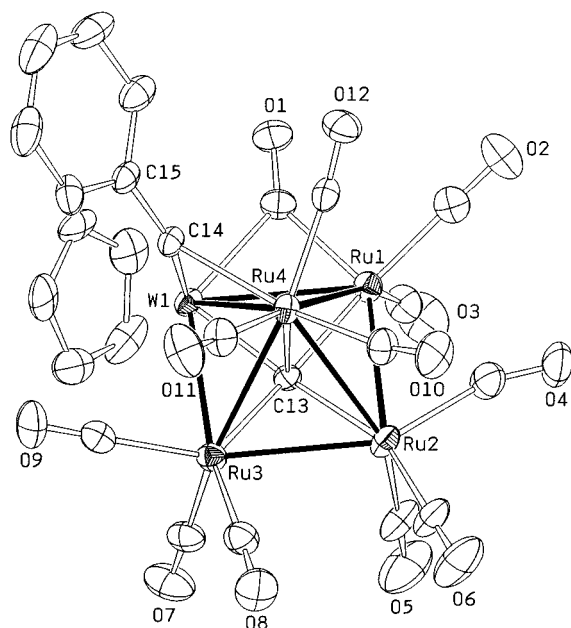
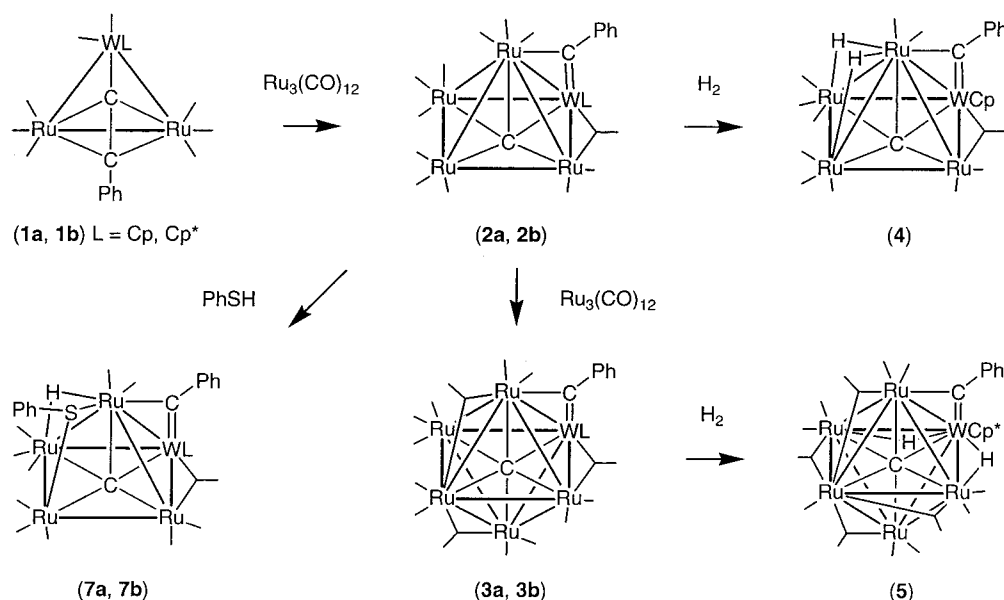
**Table 5. Selected Bond Distances (Å) and Angles (deg) of 7a (esd's in parentheses)**

W–Ru(1)	2.9170(6)	W–Ru(3)	2.8378(8)
W–Ru(4)	2.8030(7)	Ru(1)–Ru(2)	2.8979(9)
Ru(1)–Ru(4)	2.9097(7)	Ru(2)–Ru(3)	2.9321(7)
Ru(2)–Ru(4)	3.4186(8)	Ru(3)–Ru(4)	2.9230(9)
W–C(12)	2.062(5)	Ru(1)–C(12)	2.050(5)
Ru(2)–C(12)	2.096(5)	Ru(3)–C(12)	1.972(5)
Ru(4)–C(12)	2.206(5)	W–C(9)	2.222(5)
Ru(3)–C(9)	1.997(5)	W–C(13)	1.872(5)
Ru(4)–C(13)	2.200(5)	Ru(2)–S	2.477(2)
Ru(4)–S	2.441(1)	Ru(1)–H	1.68(5)
Ru(4)–H	1.80(5)		
Ru(4)–C(13)–C(14)	126.7(4)	W–C(13)–C(14)	146.3(4)
Ru(1)–Ru(4)–C(11)	109.8(2)	Ru(4)–Ru(1)–C(1)	97.1(2)
Ru(4)–Ru(1)–C(2)	114.5(2)	Ru(2)–S–Ru(4)	88.09(5)

at  $\delta$  424.0 (*J*<sub>C–W</sub> = 88 Hz) and 302.3 (*J*<sub>C–W</sub> = 156 Hz) in the <sup>13</sup>C NMR spectrum. Furthermore, seven CO signals were observed at  $\delta$  231.1 (br), 209.2, 200.7, 195.9 (br), 192.7 (br), 191.4, and 190.1 (br) with relative intensities 2:2:2:1:2:2:1 in the spectrum recorded at −50 °C. The chemical shift of the first CO signal at  $\delta$  231.1 seems to be an arithmetic average of one bridging CO and one terminal CO ligand, indicating the occurrence of rapid exchange between the bridging carbonyl C(1)O(1) and the terminal carbonyl C(9)O(9) on the atom Ru-

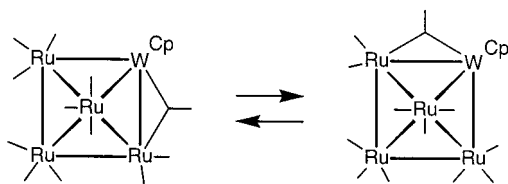
(14) (a) Tachikawa, M.; Sievert, A. C.; Muetterties, E. L.; Thompson, M. R.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1980**, *102*, 1725. (b) Lopatin, V. E.; Gubin, S. P.; Mikova, N. M.; Tsybenov, M. T.; Slovokhotov, Y. L.; Struchkov, Y. T. *J. Organomet. Chem.* **1985**, *292*, 275.

Scheme 1



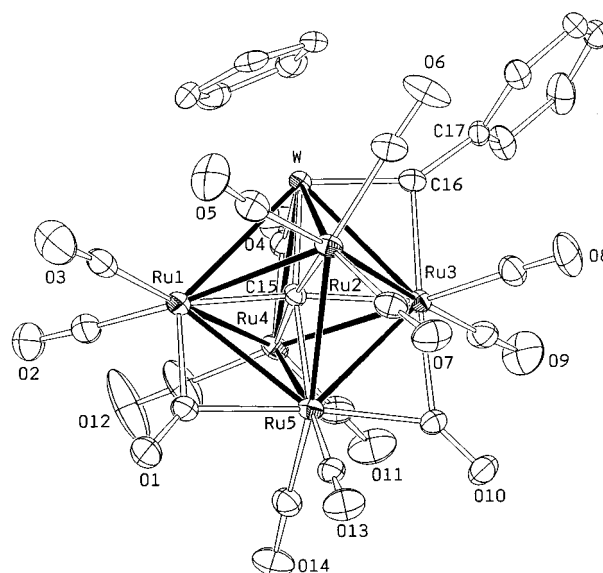
**Figure 1.** Molecular structure and atomic labeling scheme of the complex  $\text{CpWRu}_4(\mu_5\text{-C})(\text{CO})_{12}(\mu\text{-CPh})$  (**2a**) with thermal ellipsoids shown at the 30% probability level.

Scheme 2



(3) and the production of a time-averaged  $C_s$  symmetry in solution (Scheme 2).

On the other hand, the  $^{13}\text{C}$  NMR spectrum of the Cp\* derivative complex **2b** at room temperature showed two downfield signals at  $\delta$  426.2 ( $J_{\text{WC}} = 90$  Hz) and 294.5 ( $J_{\text{WC}} = 165$  Hz) for the carbide and the alkylidyne carbons, while the CO signals appeared at  $\delta$  231.5 ( $J_{\text{WC}} = 58$  Hz), 205.1, 200.9, 193.8, and 193.1 with the ratio



**Figure 2.** Molecular structure and atomic labeling scheme of the complex  $\text{CpWRu}_5(\mu_6\text{-C})(\text{CO})_{14}(\mu\text{-CPh})$  (**3a**) with thermal ellipsoids shown at the 30% probability level.

2:3:2:3:2. Again, the first CO signal with a distinct  $J_{\text{WC}}$  coupling is attributed to the rapid exchange of the W–Ru bridging CO ligand and the equatorial CO ligand pointing to the W atom, as only the W-bound CO ligands would give the observed  $J_{\text{WC}}$  coupling. The CO signals at  $\delta$  205.1 and 193.8, each possessing an intensity ratio corresponding to three CO ligands, can be assigned to the axial  $\text{Ru}(\text{CO})_3$  unit and the  $\text{Ru}(\text{CO})_3$  unit trans to the Cp\*W fragment, due to the existence of fast tripodal CO rotation on these Ru metal atoms.

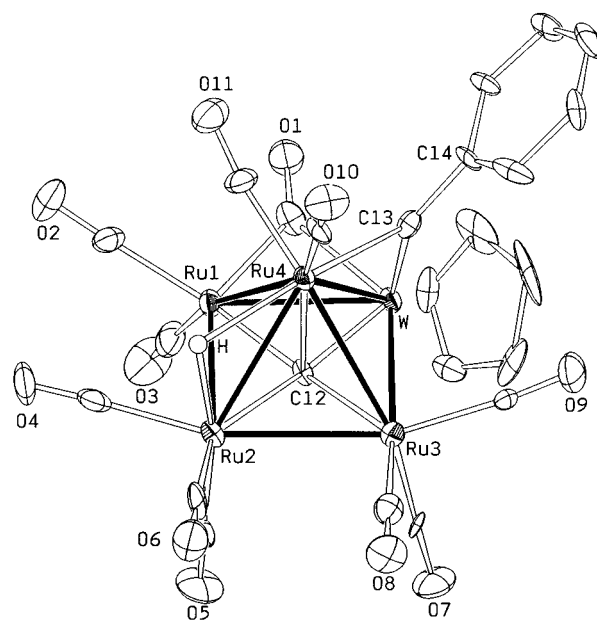
The structure of the hexametallic carbido clusters was also established by X-ray diffraction study. As indicated in Figure 2, the molecular core of **3b** contains a significantly distorted octahedral  $\text{WRu}_5$  metal core, which fully encapsulated the central carbide atom. The W and Ru(2) atoms are unique, as they are coordinated by a Cp ligand and by three terminal CO ligands, while each of the remaining four Ru atoms is linked by two



terminal CO ligands plus one or two bridging CO ligands. The metal–carbide distances are within the range 2.025(5)–2.106(5) Å. The Ru–Ru separations range from 2.819(1) to 2.936(1) Å. The Ru–Ru edges supporting the bridging CO ligand are found to be significantly shorter than the unbridged Ru–Ru edges. In contrast, the W–Ru distances span a much larger range, 2.856(1)–3.229(1) Å, of which the shortest W–Ru bond is the one coordinated by the bridging alkylidyne ligand, while the longest one, W–Ru(1) = 3.229(1) Å, is located opposite the alkylidyne ligand, even longer than those observed in the parent acetylide complex **1a** (2.965–2.998 Å), indicating the formation of a rather weakened metal–metal interaction.<sup>15</sup> However, the overall electron count of 86e is normal for *closo*-cluster complexes;<sup>16</sup> the lengthening of this W–Ru distance is probably not due to the electronic effect, but arises from the less pronounced, *trans*-effect exerted by the bridging alkylidyne fragment.

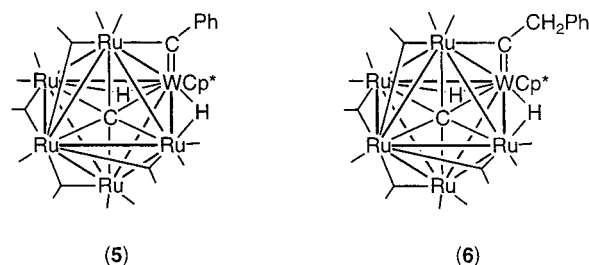
**Hydrogenation of 2.** In contrast with the reaction of **2b**, which gave no isolable product, heating of the Cp-substituted complex **2a** in toluene (80 °C, 3 h) under 1 atm of H<sub>2</sub> afforded a new complex, CpWRu<sub>4</sub>(μ<sub>5</sub>-C)(μ-CPh)(μ-H)<sub>2</sub>(CO)<sub>11</sub> (**4**), in near quantitative yield. The identification of **4** was first achieved using spectroscopic methods. In the <sup>1</sup>H NMR spectrum, two prominent high-field signals were observed at δ –21.15 and –22.01 with coupling *J*<sub>HH</sub> = 1.6 Hz, suggesting the formation of two hydride ligands via addition of H<sub>2</sub>. In addition, the <sup>13</sup>C NMR spectrum showed two sharp signals at δ 405.2 (*J*<sub>WC</sub> = 88 Hz) and 324.8 (*J*<sub>WC</sub> = 154 Hz). These are clearly attributed to the carbide and alkylidyne carbon signals, suggesting that the CpWRu<sub>4</sub>(μ<sub>5</sub>-C)(μ-CPh) cluster framework is retained during the hydrogenation reaction.

These spectroscopic features are further confirmed by the single-crystal X-ray diffraction study. As depicted in Figure 3, the expected square pyramidal geometry is clearly observed with the tungsten atom located at the basal plane. The axial Ru atom showed one less terminal CO ligand than that of the axial Ru atom in complex **2a**, suggesting that this Ru atom is the reaction site for hydrogenation reaction. In addition, only one hydride ligand was located on the Fourier map, spanning the Ru(2)–Ru(4) edge which is *trans* to the bridging alkylidyne ligand. The second hydride was not detected by difference Fourier synthesis, but it is proposed to associate with the nearby Ru(3)–Ru(4) edge, as it appears to possess more void space along the corresponding Ru–Ru vector. In agreement with this assignment, the location of hydride is further suggested by the elongated Ru(3)–Ru(4) distance of 2.854(2) Å and by the slightly expanded Ru(3)–Ru(4)–C(10) angle of 113.5(5)° in comparison with the more acute Ru(1)–Ru(4)–C(11) angle (70.0(5)°), which ruled out the association of the hydride with the Ru(1)–Ru(4) edge (2.882(2)



**Figure 3.** Molecular structure and atomic labeling scheme of the complex CpWRu<sub>4</sub>(μ<sub>5</sub>-C)(μ-CPh)(μ-H)<sub>2</sub>(CO)<sub>11</sub> (**4**) with thermal ellipsoids shown at the 30% probability level.

**Chart 1**



Å), although the latter is slightly longer than that of the hydride-bridged Ru(3)–Ru(4) vector.

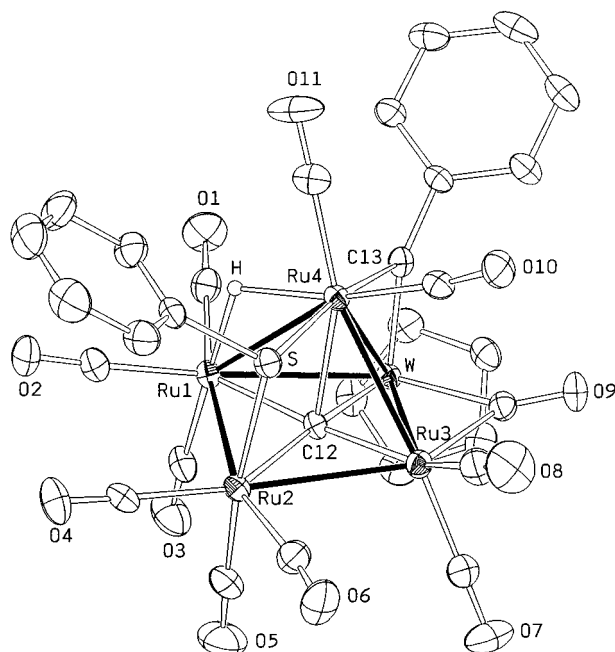
**Hydrogenation of 3.** Treatment of **3** with H<sub>2</sub> was carried out in an attempt to compare their reactivity with that of the pentametallic complexes **2**. Interestingly, the Cp derivative **3a** failed to afford any stable product, but the corresponding Cp\* complex **3b** reacted with H<sub>2</sub> under similar conditions to afford the hydrogenated product Cp\*WRu<sub>5</sub>(μ<sub>6</sub>-C)(μ-CPh)(μ-H)<sub>2</sub>(CO)<sub>13</sub> (**5**) in 68% yield. The identification of **5** was achieved using spectroscopic methods, of which the <sup>1</sup>H NMR spectrum showed a high-field signal at δ –16.72 (*J*<sub>WC</sub> = 77 Hz) corresponding to two W–H–Ru bridging hydride ligands. Moreover, the IR spectrum exhibits a ν(CO) pattern that is almost identical to that of the previously reported hydride complex Cp\*WRu<sub>5</sub>(μ<sub>6</sub>-C)(μ-CCH<sub>2</sub>Ph)(μ-H)<sub>2</sub>(CO)<sub>13</sub> (**6**, Chart 1),<sup>17</sup> obtained from direct hydrogenation of the carbido-acetylide complex Cp\*WRu<sub>5</sub>(μ<sub>5</sub>-C)(CCPh)(CO)<sub>13</sub>.

**Treatment of 2 with Thiophenol.** Reactions of **2a** or **2b** with thiophenol proceeded rapidly in refluxing toluene solution, affording two new cluster compounds, LWRu<sub>4</sub>(μ<sub>5</sub>-C)(μ-CPh)(μ-H)(μ-SPh)(CO)<sub>11</sub> (**7a**, L = Cp; **7b**, L = Cp\*). Complexes **7a** and **7b** were generated by 1:1 combination of the starting materials, as revealed by spectroscopic analysis and single-crystal X-ray diffraction study.

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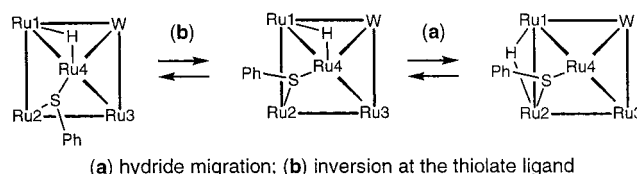


**Figure 4.** Molecular structure and atomic labeling scheme of the complex  $\text{CpWRu}_4(\mu_5\text{-C})(\mu\text{-CPh})(\mu\text{-H})(\mu\text{-SPh})(\text{CO})_{11}$  (**7a**) with thermal ellipsoids shown at the 30% probability level.

Crystals of **7a** suitable for X-ray diffraction study were obtained from slow diffusion of hexane into a  $\text{CH}_2\text{-Cl}_2$  solution. The molecular structure is presented in Figure 4, showing a wingtip-bridged butterfly geometry, with the alkylidyne and the hydride being associated with the W–Ru(4) hinge and the Ru(1)–Ru(4) edge, respectively, while the thiolate ligand is found to span the Ru(2)–Ru(4) vector with distance of 3.4186(8) Å. All other metal–metal distances are in the range 2.8030(7)–2.9321(7) Å, but the Ru(2)–Ru(4) distance is obviously too long to permit any significant interaction, a consequence of the lone pair donation from the thiolate ligand to the Ru metal atom. The analogous wingtip-bridged butterfly framework has been noted in several  $\text{Ru}_5$  carbido compounds prepared by addition of thiophenol or even silane to the parent carbido cluster  $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{15}$ .<sup>18</sup> The Ru–S distances (2.441(1) and 2.477(2) Å) observed in **7a** are slightly longer than the Ru–S distances (2.389 and 2.391 Å) in the cluster  $\text{Ru}_3(\mu\text{-H})(\mu\text{-SEt})(\text{CO})_{10}$ ,<sup>19</sup> where the thiolate ligand is associated with the Ru–Ru edge that also supports the hydride. Concomitant with the lengthening of the Ru–S distances is a much wider Ru–S–Ru angle of 88.09(5)° observed in **7a**, indicating a greater flexibility in the bonding of the thiolate ligand.

Although the X-ray structure of **7a** seems rather simple, its behavior in solution is more complicated, showing coexistence of two easily interconvertible isomers. This is evident by observation of two broadened  $^1\text{H}$  NMR hydride resonance signals at  $\delta$  –16.58 and –17.09 for **7a** and at  $\delta$  –16.34 and –16.94 for **7b** with a relative ratio of 1:4 at room temperature. For complex **7a**, these hydride signals coalesce and merge to form a

### Scheme 3



(a) hydride migration; (b) inversion at the thiolate ligand

very broad signal upon raising the temperature to 323 K. On the other hand, these hydride signals sharpen substantially as the temperature is lowered, suggesting a slowing of the mutual exchange in solution.

We speculate that this exchange process is probably caused by hydride migration from the Ru(1)–Ru(4) edge to the nearby Ru(1)–Ru(2) edge (Scheme 3), as the related hydride emigrational exchange in solution has already been well documented in hydride cluster chemistry.<sup>20</sup> The Ru(1)–Ru(2) edge is chosen as the new site for the hydride because it is geometrically close to the Ru(1)–Ru(4) edge and thus will give the lowest activation barrier for hydride migration. Moreover, the second possibility involves flipping of the bridging thiolate ligand, which would also generate two interchangeable structural isomers with the phenyl group pointing either *syn* or *anti* to the bridging hydride. This second hypothesis is supported by observation of both the *syn* and the *anti* isomers for the diiron thiolate complex  $[\text{Fe}(\mu\text{-SR})(\text{CO})_3]_2$ , R = Me or Ph, of which the isomerization in solution is caused by a similar ligand movement involving the thiolates.<sup>21</sup> Currently, our spectroscopic data are in agreement with both possibilities, and thus additional experimentation is needed in order to fully differentiate them.

### Discussion

Treatment of acetylide cluster **1** with  $\text{Ru}_3(\text{CO})_{12}$  affords the  $\text{WRu}_4$  and  $\text{WRu}_5$  carbido-alkylidyne clusters **2** and **3** in moderate yields (Scheme 1). The  $\text{WRu}_4$  complex **2** is an intermediate en route to the larger  $\text{WRu}_5$  cluster **3**, as both complexes can be obtained in good yields by heating **2** with  $\text{Ru}_3(\text{CO})_{12}$  in refluxing heptane or toluene solution.

The key feature in this unique chemical transformation is the acetylide C–C bond cleavage, which is somewhat related to that of the butterfly  $\text{WOs}_3$  acetylide cluster  $\text{Cp}^*\text{WOs}_3(\text{CO})_{11}(\text{C}_2\text{Ph})$ , prepared by direct coupling of **1b** and the triosmium complex  $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ .<sup>22</sup> Although we were unable to isolate the respective  $\text{WOs}_4$  or  $\text{WOs}_5$  carbido clusters upon addition of excess osmium reagent  $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$  during its synthesis, treatment of the  $\text{WOs}_3$  acetylide complex with decarbonylation reagent  $\text{Me}_3\text{NO}$ , followed by heating in toluene, gave rise to the formation of a related C–C bond cleavage product,  $\text{Cp}^*\text{WOs}_3(\mu_4\text{-C})(\mu\text{-CPh})(\text{CO})_{10}$ , in good yield, suggesting that cleavage of the acetylide

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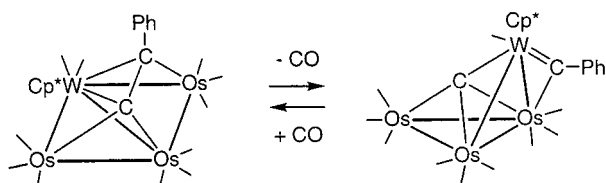
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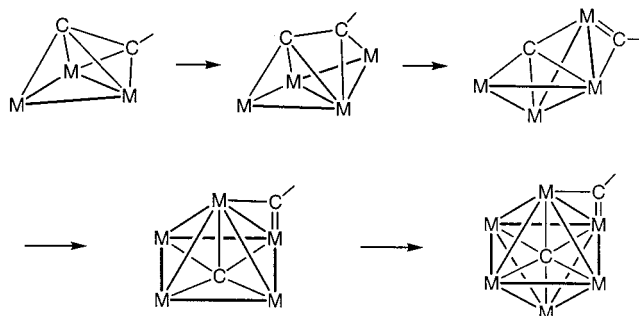
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Scheme 4



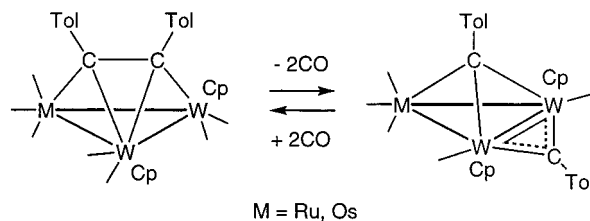
Scheme 5



C–C bond is possible through the assistance of only four transition-metal atoms (Scheme 4).<sup>23</sup> On the basis of this observation, we propose that the transformations **1** → **2** → **3** may involve a transient formation of the tetrametallic complex  $\text{LWRu}_3(\text{C}_2\text{Ph})(\text{CO})_{11}$  via addition of one  $\text{Ru}(\text{CO})_3$  fragment. Then cleavage of the C–C bond became feasible on the tetrametallic framework to give an analogous carbido-alkylidyne intermediate,  $\text{LWRu}_3(\mu_4\text{-C})(\mu\text{-CPh})(\text{CO})_{10}$ , which then combined with an additional  $\text{Ru}(\text{CO})_n$  fragment through cluster expansion to afford the complexes **2** and **3** in sequence. For these cluster expansion and acetylide C–C bond cleavage reactions, the gradual change of the metal and carbon skeleton is schematically depicted in Scheme 5.

The W atom appears to play an important role in activation of the acetylide C–C bond, since the resulting alkylidyne ligand in **2** and **3** is always coordinated to the W atom and produced a thermodynamically stable W–C multiple bonding, which is characterized by the short alkylidyne W–C distances detected in solid state. This observation probably suggests that the formation of a stable W–C bond could be one of the main driving forces of the reaction, in addition to the involvement of  $\text{M} \rightarrow \pi^*$  charge transfer from the relatively electropositive W atom to the resulting alkylidyne ligands.<sup>24</sup> In good agreement with our experimental finding, Shapley and co-workers have reported that heating the related alkyne complex  $\text{CpWOS}_3(\mu\text{-H})(\text{C}_2\text{Ph}_2)(\text{CO})_{10}$  affords the scission product  $\text{CpWHO}_3(\mu_3\text{-CPh})_2(\text{CO})_9$ ,<sup>25</sup> while the alkyne clusters  $\text{Cp}_2\text{W}_2\text{M}(\text{C}_2\text{Tol}_2)(\text{CO})_7$  also undergo facile alkyne C–C bond scission to produce the bis-alkylidyne clusters  $\text{Cp}_2\text{W}_2\text{M}(\mu\text{-CR})(\mu_3\text{-CR})(\text{CO})_5$ ,  $\text{M} = \text{Ru, Os}$ ;  $\text{R} = \text{Tol}$  (Scheme 6).<sup>26</sup> As anticipated, the alkylidyne ligands of all scission products are found to associate with the W atom. In contrast, for the corre-

Scheme 6



sponding homometallic complexes, which are best represented by the group 8 acetylide complex  $\text{M}_3(\mu\text{-H})(\text{C}_2\text{Ph})(\text{CO})_{10}$  and alkyne complexes  $\text{M}_3(\text{C}_2\text{Ph}_2)(\text{CO})_{10}$ ,  $\text{M} = \text{Ru}$  and  $\text{Os}$ ,<sup>27</sup> no comparable C–C bond cleavage has been observed even under extensive heating in solution. Moreover, in the case of  $\text{Os}_3(\text{C}_2\text{Ph}_2)(\text{CO})_{10}$ , formation of the highly reactive metal complex  $\text{Os}_3(\text{C}_2\text{Ph}_2)(\text{CO})_9$  with alkyne adapting the  $\mu_3\text{-}\eta^2$  ( $\perp$ ) configuration was noted upon removal of one CO ligand,<sup>28</sup> showing a preferred reaction pathway for the cluster skeletal rearrangement over the occurrence of the proposed alkyne C–C bond scission. Thus, the chemistry of  $\text{M}_3(\mu\text{-H})(\text{C}_2\text{Ph})(\text{CO})_{10}$  and  $\text{M}_3(\text{C}_2\text{Ph}_2)(\text{CO})_{10}$ ,  $\text{M} = \text{Ru}$  and  $\text{Os}$ , serves as a good contrasting example to those of W-containing acetylide and alkyne cluster complexes, in which scission of the C–C bond has more or less become a typical reaction pattern.

The cleavage of the C–C bond can be easily reversed in this system. Thus, treatment of **3** with pressurized CO (14 atm) in toluene at 80 °C afforded **1** in 94% yield. Also, treatment of **2** with CO under similar conditions also produced **1**. It is interesting to notice that the degradation of **3** does not stop at the stage of the pentametallic complexes **2**, but proceeds all the way to the parent acetylide complexes **1** and regeneration of the C–C linkage. This reactivity pattern is in sharp contrast to the relative inertness of the analogous homometallic carbido cluster  $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{15}$ , which is found to be stable in 80 atm of CO atmosphere at 90 °C.<sup>29</sup> This observation suggests that the concomitant presence of an alkylidyne moiety in complexes **2** and **3** will make the formation of the original acetylide ligand much more favored. On the other hand, in the absence of the alkylidyne ligand, the carbide ligand would only react with CO to afford a more unstable  $\text{C}=\text{C}=\text{O}$  ketenylidene fragment. As Shriver and Shapley have independently demonstrated formation of the ketenylidene fragment from a carbide atom in the trimetallic system,<sup>30</sup> it is possible that, despite of the inertness of  $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{15}$ , excessive heating could eventually lead to formation of such ketenylidene species, if it was stable under the experimental conditions.

To further explore the chemical reactivity of these newly prepared carbido-alkylidyne complexes, hydro-

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generation of complexes **2** and **3** was examined, and our results showed that the final product depended to some extent on the ancillary ligand of the W atom. Thus, hydrogenation of the Cp complex **2a** gave the dihydride complex **4**, in which one CO ligand on the apical Ru center was replaced by two bridging hydride ligands. On the other hand, treatment of the Cp\* complex **2b** with hydrogen has failed to afford any isolable product. It appears to us that the Cp\* ligand on the W atom has reduced the reactivity with respect to hydrogen coordination, but such change is not discernible upon treatment with the more reactive thiophenol molecule, as we have rapidly obtained the addition products **7a** and **7b** from both complexes **2a** and **2b** upon heating.

In addition, the pattern of hydrogenation reaction was reversed for the octahedral WRu<sub>5</sub> complexes **3**. Treatment of the Cp complex **3a** with H<sub>2</sub> has produced no isolated product, but reaction with the corresponding Cp\* complex **3b** has led to the isolation of complex **5**. Moreover, the hydride ligands of **5** are associated with the W–Ru edges at *trans*-dispositions, but it is in sharp contrast with that of **4**, in which the hydride ligands are located at two nearby Ru–Ru edges. The tendency for formation of W–H–Ru hydrides in the Cp\* complex **5** is parallel to the observation of solution equilibration involving hydride complexes LWOs<sub>3</sub>(μ-H)(CO)<sub>12</sub> and LWOs<sub>3</sub>(μ-H)<sub>3</sub>(CO)<sub>11</sub>, L = Cp and Cp\*.<sup>31</sup> In the latter systems, changing the ancillary ligand from Cp to Cp\* on the W atom has caused the hydride to migrate from the Os–Os edge to the W–Os edge within the coordination sphere, as revealed by both X-ray structural determination and VT <sup>1</sup>H NMR studies. This site preference of the hydride ligand is undoubtedly associated with both steric and electron-donating capabilities of the methyl groups of the Cp\* ligand.

### Conclusion

We have developed a new and high-yield method in preparing the W–Ru carbido-alkylidyne clusters **2** and

**3** via reversible cleavage of the acetylide C–C bond. The possible reaction mechanism, which may include the formation of a tetrametallic acetylide scission product, has been proposed according to the chemistry documented for the related W–Os complexes. Moreover, our data reveal that even the ancillary ligand on the W atom would be a contributing factor in determining their fundamental characteristics such as reactivity pattern. Accordingly, reaction of **2a** with H<sub>2</sub> gives the dihydride complex **4**, and treatment of both complexes **2a** and **2b** with thiophenol affords the thiolate complexes **7a** and **7b** by concurrent elimination of CO and Ru–Ru bond cleavage. The reactions of **3** with hydrogen are in contrast with that occurring in complexes **2**, and only the Cp\* derivative complex **5** is obtained in high yield.

Finally, the hydride ligands of both complexes **4** and **5** can be easily removed by passage of CO into the solution during heating, whereas complexes **7** show formation of two interconvertible isomers due to the hydride migration or inversion of the phenylthiolate group within the cluster framework. Formation of the alkylidene fragment μ-CHPh via hydride transfer to the alkylidyne carbon atom was not observed under all conditions, despite the fact that this reaction pattern has been established for the cluster complexes possessing an alkylidyne ligand.<sup>32</sup>

**Acknowledgment.** We thank the National Science Council of the Republic of China for financial support (Grant No. NSC 86-2113-M007-035).

**Supporting Information Available:** X-ray crystallographic file (CIF) for **2a**, **3a**, **4**, and **7a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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