# Reactivity of the Tetrametallic Carbido Cluster $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right) \mathrm{WOs}_{3}\left(\mu_{4}-\mathrm{C}\right)(\mu-\mathrm{H})(\mathrm{CO})_{11}$ with Alkyne: Isomerization of an Allyl Fragment on a Tetrametallic Cluster Framework and Ring-Methyl Activation in the $\mathrm{C}_{5} \mathrm{Me}_{5}$ Ligand 

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#### Abstract

Treatment of the tetrametallic carbido-benzofuryl cluster $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right) \mathrm{WOs}_{3}\left(\mu_{4}-\mathrm{C}\right)(\mu-\mathrm{H})_{2}(\mu-$ $\left.\mathrm{C}_{8} \mathrm{H}_{6} \mathrm{O}\right)(\mathrm{CO})_{9}(\mathbf{1})$ with pressurized CO gas affords a carbido cluster $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right) \mathrm{WOs}_{3}\left(\mu_{4}-\mathrm{C}\right)(\mu-$ $\mathrm{H})(\mathrm{CO})_{11}(\mathbf{2})$ in nearly quantitative yield. The reactions of $\mathbf{2}$ with diisopropyl acetylenedicarboxylate (DPAD) are investigated. If complex 2 is first treated with Me3NO, the incorporation of DPAD at room temperature affords a cluster compound ( $\mathrm{C}_{5} \mathrm{Me}_{5}$ )$\mathrm{WOs}_{3}(\mathrm{CO})_{10}\left[\mathrm{C}_{3} \mathrm{H}\left(\mathrm{CO}_{2} \mathrm{Pri}\right)_{2}\right](3)$ in moderate yield, in which the allyl group is formed by hydride migration to the carbide. Complex $\mathbf{3}$ undergoes a facile metathesis to yield an isomer (4) with a different arrangement of the allyl $\mathrm{C}_{3}$ backbone. Upon thermolysis, complex $\mathbf{4}$ converts to a $\eta^{6}$-tetramethylfulvene complex $\left[\mathrm{C}_{5} \mathrm{Me}_{4}\left(\mathrm{CH}_{2}\right)\right] \mathrm{WO}_{3}(\mu-\mathrm{H})\left[\mathrm{C}_{3} \mathrm{H}\left(\mathrm{CO}_{2} \mathrm{Pr}^{\prime}\right)_{2}\right](\mathrm{CO})_{9}$ (5) by activation of a ring-methyl in the $\mathrm{C}_{5} \mathrm{Me}_{5}$ ligand and a trialkylidyne cluster $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right) \mathrm{WOs}_{3}\left(\mu_{3}-\right.$ $\mathrm{CH})\left(u_{3}-\mathrm{CCO}_{2} \mathrm{Pr}^{\mathrm{i}}\right)_{2}(\mathrm{CO})_{9}(\mathbf{6})$ by cleavage of two allyl $\mathrm{C}-\mathrm{C}$ bonds. The possible mechanism of their interconversion is discussed. If the reaction of the $\mathrm{Me}_{3} \mathrm{NO}$-activated complex $\mathbf{2}$ and DPAD is carried out in refluxing toluene, we obtained one more compound ( $\mathrm{C}_{5} \mathrm{Me}_{5}$ )$\mathrm{WOs}_{3}\left[\mathrm{CC}_{2}\left(\mathrm{CO}_{2} \mathrm{Pr}^{\mathrm{i}}\right)_{2} \mathrm{H}\right](\mathrm{CO})_{10}(7)$ in low yield, which appears to form through a secondary process involving hydride migration to the DPAD molecule instead.


The chemistry of carbido cluster complexes has devel oped in recent years to constitute a distinct research domain. ${ }^{1}$ For example, the early work of Bradley ${ }^{2}$ and Shriver ${ }^{3}$ on the reactivity of the $\mathrm{Fe}_{4}$ system illustrated that the exposed carbide participated in the $\mathrm{C}-\mathrm{C}$ and $\mathrm{C}-\mathrm{H}$ bond formation by addition of methanol, alkylation reagents, or acids. In the related $\mathrm{Ru}_{4}$ system, Lewis and J ohnson reported the first coupling reaction involving carbide and diphenylacetylene. ${ }^{4}$ These reactions are of noteworthy because they represent the key pathways for conversion of carbides to large hydrocarbon frag-

[^0]ments on catalytic surfaces. ${ }^{5}$ In a continuation of this type of investigation, our research group has discovered a reversible coupling between carbide and alkylidyne on metal cluster complexes, ${ }^{6}$ a heretofore unidentified reaction, but has been extensively discussed according to the conformity between ligated acetylides and carbidealkylidynes. ${ }^{7}$ In this paper, we report a high-yield method of generating the target carbido cluster compound $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right) \mathrm{WOs}_{3}\left(\mu_{4}-\mathrm{C}\right)(\mu-\mathrm{H})(\mathrm{CO})_{11}$ (2) and the subsequent reactivity study of this carbido cluster with an electron-deficient alkyne.
In addition, one product ( $\mathrm{C}_{5} \mathrm{Me}_{5}$ ) WOs $\mathrm{W}_{3}\left(\mathrm{CO}_{10}\left[\mathrm{C}_{3} \mathrm{H}\left(\mathrm{CO}_{2}-\right.\right.\right.$ $\left.\mathrm{Pr}^{\mathrm{i}}\right)_{2}$ ] (3) isolated from this coupling reaction, which contains a dimetallaallyl ligand, undergoes a series of rarely observed chemical transformations, involving cluster-assisted allyl metathesis, conversion of an $\eta^{5}$ $\mathrm{C}_{5} \mathrm{Me}_{5}$ to an $\eta^{6}$-tetramethylfulvene, and formation of three alkylidyneligands by cleavage of two $\mathrm{C}-\mathrm{C}$ bonds. Thus, the chemistry observed in the present study provides an ideal model to delineate various possible

[^1]reactions between carbide, hydride, and small unsaturated organic fragments and to interpret the novel reactivities for the allyl and the $\mathrm{C}_{5} \mathrm{Me}_{5}$ ligand of polynuclear cluster compounds.

## Experimental Section

General Information and Materials. Infrared spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ 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 J EOL-HX110 instrument operating in fast-atom bombardment modes (FAB). All reactions were performed under a nitrogen atmosphere using solvents dried with an appropriate reagent. The products were separated on commercially available preparative thin-layer chromatographic plates (Kieselgel $60 \mathrm{~F}_{254}, \mathrm{E} . \mathrm{Merck}$ ). Elemental analyses were performed at the NSC Regional Instrumentation Center at National Cheng Kung University, Tainan, Taiwan.

Synthesis of $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right) \mathrm{WOs}_{3}\left(\mu_{4}-\mathrm{C}\right)(\mu-\mathrm{H})(\mathrm{CO})_{11}$. A toluene solution ( 75 mL ) of $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right) \mathrm{WOs}_{3}\left(\mu_{4}-\mathrm{C}\right)\left(\mathrm{C}_{8} \mathrm{H}_{5} \mathrm{O}\right)(\mu-\mathrm{H})_{2}(\mathrm{CO})_{9}(\mathbf{1}$, $1.6 \mathrm{~g}, 1.26 \mathrm{mmol}$ ) was placed in a 100 mL stainless steel Parr high-pressure reactor. Then the reactor was charged with 650 psi of CO gas, and the solution was stirred at $135^{\circ} \mathrm{C}$ for 2 h . After the reactor was cooled to room temperature, the CO gas was released and the solvent was removed in vacuo. The orange residue was taken up in minimum amount of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and recrystallized in a mixture of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and methanol, giving 1.49 g of $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right) \mathrm{WOs}_{3}\left(u_{4}-\mathrm{C}\right)(u-\mathrm{H})(\mathrm{CO})_{11}(\mathbf{2}, 1.23 \mathrm{mmol}, 97 \%)$ as light orange crystalline materials.

Spectral data for 2: MS (FAB, ${ }^{192}$ Os, $\left.{ }^{184} \mathrm{~W}\right) \mathrm{m} / \mathrm{z} 1216\left(\mathrm{M}^{+}\right)$. IR( $\mathrm{C}_{6} \mathrm{H}_{12}$ ): $v(\mathrm{CO}) 2086$ (s), 2057 (vs), 2043 (s), 2035 (s), 2009 (vs), 1987 (m, br), 1970 (vw), 1958 (m, br), 1930 (w, br), 1914 (vw, br), $1878(\mathrm{w}, \mathrm{br}) \mathrm{cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 293$ K): $\delta 2.06$ (s, 15H), -24.48 (s, 1H). ${ }^{13} \mathrm{C}$ NMR ( 100 MHz , $\left.\mathrm{CDCl}_{3}, 293 \mathrm{~K}\right): \operatorname{CO} \delta 212.6(2 \mathrm{C}, \mathrm{J} \mathrm{wc}=164 \mathrm{~Hz}), 178.8(3 \mathrm{C}$, br), 176.7 (2C), 174.1 (2C), 165.6 (2C); $\delta 340.3$ ( $\mu_{4}-\mathrm{C}, \mathrm{J}$ wc $=$ $104 \mathrm{~Hz}), 101.6\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right), 10.8(5 \mathrm{Me})$. Anal. Calcd for $\mathrm{C}_{22} \mathrm{H}_{16} \mathrm{O}_{11} \mathrm{Os}_{3} \mathrm{~W}: \mathrm{C}, 21.82 ; \mathrm{H}, 1.33$. Found: C, 21.61; $\mathrm{H}, 1.36$.

Reaction of 2 with DPAD. An acetonitrile solution (30 mL ) of freshly sublimed $\mathrm{Me}_{3} \mathrm{NO}$ ( $11.1 \mathrm{mg}, 0.148 \mathrm{mmol}$ ) was added dropwise to a mixture of $\mathrm{CH}_{2} \mathrm{Cl}_{2}(60 \mathrm{~mL})$, acetonitrile $(10 \mathrm{~mL})$, and $\mathbf{2}(150 \mathrm{mg}, 0.123 \mathrm{mmol})$. The addition of $\mathrm{Me}_{3}-$ NO caused the color of the solution to change from light yellow to orange. Two hours later, the solvents were removed in vacuo and the mixture was redissolved into 80 mL of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. DPAD ( $73 \mathrm{mg}, 0.37 \mathrm{mmol}$ ) was added to this $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution, and the resulting solution was stirred at room temperature for 20 h , until the color of solution changed from orange to dark red. The reaction mixture was then concentrated and separated by thin-layer chromatography. Devel opment with a $1: 1$ mixture of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and hexane produced a major red band, which was extracted from silica gel to yield 98 mg of $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right) \mathrm{WOs}_{3}\left[\mathrm{C}_{3} \mathrm{H}\left(\mathrm{CO}_{2} \mathrm{Pri}\right)_{2}\right](\mathrm{CO})_{10}(3,0.071 \mathrm{mmol}, 57 \%)$.

Spectral data for 3: MS (FAB, $\left.{ }^{192} \mathrm{Os},{ }^{184} \mathrm{~W}\right) \mathrm{m} / \mathrm{z} 1386\left(\mathrm{M}^{+}\right)$. IR ( $\mathrm{C}_{6} \mathrm{H}_{12}$ ): $v(\mathrm{CO}) 2074$ (s), 2008 (vs), 1999 ( s$), 1981$ (m), 1965 (m), 1942 (m), $1844(\mathrm{w}, \mathrm{br}) \mathrm{cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$, $293 \mathrm{~K}): \delta 7.97(\mathrm{~s}, 1 \mathrm{H}), 5.04\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CHMe}_{2}\right), 2.02(\mathrm{~s}, 15 \mathrm{H})$, $1.36(\mathrm{~d}, \mathrm{~J} \boldsymbol{\mathrm { H }} \mathrm{H}=6.2 \mathrm{~Hz}, 3 \mathrm{H}), 1.33(\mathrm{~d}, \mathrm{~J}$ нн $=6.3 \mathrm{~Hz}, 3 \mathrm{H}), 1.32(\mathrm{~d}$, $\left.\mathrm{J}_{\mathrm{H}}=6.2 \mathrm{~Hz}, 3 \mathrm{H}\right), 1.25(\mathrm{~d}, \mathrm{~J} \mathrm{H}=6.2 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 100 $\mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 293 \mathrm{~K}$ ): CO $\delta 230.8(\mathrm{~J} \mathrm{wc}=177 \mathrm{~Hz}), 218.1(\mathrm{~J} \mathrm{wc}$ $=139 \mathrm{~Hz}), 194.8,191.4,186.0,185.7(\mathrm{br}), 184.0,182.5,180.4$, 178.6 (br), 174.0 (br), 170.7; $\delta 126.8,119.9$ (CH), $105.8\left(\mathrm{C}_{5}\right.$ $\mathrm{Me}_{5}$ ), 102.9, 75.2 ( $\mathrm{CHMe}_{2}$ ), 70.9 ( $\mathrm{CHMe}_{2}$ ), 22.3 ( Me ), 22.0 $(2 \mathrm{Me}), 21.0(\mathrm{Me}), 10.3(5 \mathrm{Me})$. Anal. Calcd for $\mathrm{C}_{31} \mathrm{H}_{30} \mathrm{O}_{14}{ }^{-}$ $\mathrm{Os}_{3} \mathrm{~W}: ~ \mathrm{C}, 26.96 ; \mathrm{H}, 2.19$. Found: C, 27.34; H, 2.32.

Thermolysis of 3. A toluene solution ( 50 mL ) of $\mathbf{3}(50 \mathrm{mg}$, 0.036 mmol ) was heated at $90^{\circ} \mathrm{C}$ for 4 h , during which time the color changed from red to orange. The solvent was removed in vacuo, and the residue was taken up in minimum
amount of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and separated by thin-layer chromatography with a mixture of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and hexane (4:1), giving 5 mg of $\left(\mathrm{C}_{5}-\right.$ $\left.\mathrm{Me}_{5}\right) \mathrm{WOs}_{3}\left[\mathrm{C}_{3}\left(\mathrm{CO}_{2} \mathrm{Pr}^{\mathrm{i}}\right)_{2} \mathrm{H}\right](\mathrm{CO})_{10}(4,0.0036 \mathrm{mmol}, 10 \%), 5 \mathrm{mg}$ of $\left[\mathrm{C}_{5} \mathrm{Me}_{4}\left(\mathrm{CH}_{2}\right)\right] \mathrm{WOs}_{3}(\mu-\mathrm{H})\left[\mathrm{C}_{3} \mathrm{H}\left(\mathrm{CO}_{2} \mathrm{Pr}^{\mathrm{i}}\right)_{2}\right](\mathrm{CO})_{9}(5,0.0037 \mathrm{mmol}$, $10 \%)$, and 20 mg of $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right) \mathrm{WOs}_{3}\left(\mu_{3}-\mathrm{CH}\right)\left(\mu_{3}-\mathrm{CCO}_{2} \mathrm{Pr}^{\prime}\right)_{2}(\mathrm{CO})_{9}(6$, $0.015 \mathrm{mmol}, 41 \%)$.

Spectral data for 4: MS (FAB, ${ }^{192} \mathrm{Os}$, $\left.{ }^{184} \mathrm{~W}\right) \mathrm{m} / \mathrm{z} 1386\left(\mathrm{M}^{+}\right)$. IR ( $\mathrm{C}_{6} \mathrm{H}_{12}$ ): v(CO) 2077 (s), 2010 (vs), 1999 (s), 1966 (m), 1944 (m), $1830(\mathrm{w}, \mathrm{br}) \mathrm{cm}^{-1}$. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 293 \mathrm{~K}$ ): $\delta$ $8.72(\mathrm{~s}, 1 \mathrm{H}), 5.07\left(\mathrm{~m}, \mathrm{~J}\right.$ нн $\left.=6.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{CHMe}_{2}\right), 4.94(\mathrm{~m}, \mathrm{~J}$ нн $=6.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{CHMe}), 2.02(\mathrm{~s}, 15 \mathrm{H}), 1.39(\mathrm{~d}, \mathrm{~J}$ нн $=6.3 \mathrm{~Hz}$, $3 \mathrm{H}), 1.30(\mathrm{~d}, \mathrm{~J}$ нн $=6.2 \mathrm{~Hz}, 3 \mathrm{H}), 1.28(\mathrm{~d}, \mathrm{~J} \mathrm{H}=6.2 \mathrm{~Hz}, 3 \mathrm{H})$, 1.26 (d, J нн $=6.3 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 293$ $\mathrm{K}): ~ C O \delta 232.0(\mathrm{~J} \mathrm{wc}=176 \mathrm{~Hz}), 217.7(\mathrm{~J} \mathrm{wc}=138 \mathrm{~Hz}), 193.3$, 189.8, 185.6 (br), 184.6, 183.4, 182.7, 179.1, 177.6 (br), 176.8, 173.2 (br); $\delta 130.7,118.6$ (CH), $105.7\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right), 96.9,74.9$ ( $\mathrm{CHMe}_{2}$ ), 69.7 ( $\mathrm{CHMe}_{2}$ ), $21.8(\mathrm{Me}), 21.7(\mathrm{Me}), 21.6(\mathrm{Me}), 21.1$ (Me), 10.0 ( 5 Me ). Anal. Cal cd for $\mathrm{C}_{31} \mathrm{H}_{30} \mathrm{O}_{14} \mathrm{Os}_{3} \mathrm{~W}: \mathrm{C}, 26.96$; $\mathrm{H}, 2.19$. Found: C, 27.37; H, 2.32.

Spectral data for 5: MS (FAB, $\left.{ }^{192} \mathrm{Os},{ }^{184} \mathrm{~W}\right) \mathrm{m} / \mathrm{z} 1358\left(\mathrm{M}^{+}\right)$. IR ( $\mathrm{C}_{6} \mathrm{H}_{12}$ ): $v(\mathrm{CO}) 2087$ (s), 2065 (vs), 2027 (vs), 2012 (s), 1996 (m), 1981 (w), 1972 (w), 1954 (m), 1840 (s), 1694 (m, br) cm ${ }^{-1}$. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 293 \mathrm{~K}$ ): $\delta 8.77$ (s, 1H), 5.04 (m, $2 \mathrm{H}, \mathrm{CHMe}_{2}$ ), $3.85(\mathrm{~d}, \mathrm{~J} \boldsymbol{\mathrm { H }} \mathrm{=}=3.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.36(\mathrm{~s}, 3 \mathrm{H}), 2.27(\mathrm{~d}$, $\left.\mathrm{J}_{\mathrm{H}}=3.2 \mathrm{~Hz}, 1 \mathrm{H}\right), 2.05(\mathrm{~s}, 3 \mathrm{H}), 1.61(\mathrm{~s}, 3 \mathrm{H}), 1.37(\mathrm{~d}, \mathrm{~J}$ нн $=6.4$ $\mathrm{Hz}, 3 \mathrm{H}), 1.32(\mathrm{~d}, \mathrm{~J} \boldsymbol{\mu}=6.3 \mathrm{~Hz}, 6 \mathrm{H}), 1.29(\mathrm{~d}, \mathrm{~J} \boldsymbol{\mathrm { h }} \mathrm{H}=6.1 \mathrm{~Hz}$, 3H), $0.80(\mathrm{~s}, 3 \mathrm{H}),-20.28(\mathrm{~s}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CD}_{2^{-}}$ $\mathrm{Cl}_{2}, 293 \mathrm{~K}$ ): CO $\delta$ 194.6, 185.2, 184.5, 183.1, 182.5, 176.6, $176.3,175.8,175.4,168.2,167.5 ; \delta 133.8,133.3,128.1(\mathrm{CH})$, 123.6 ( $\mathrm{C}_{5}$-ring), 117.6 ( $\mathrm{C}_{5}$-ring), 113.2 ( $\mathrm{C}_{5}$-ring), 99.2 ( $\mathrm{C}_{5}$-ring), 99.0 ( $\mathrm{C}_{5}$-ring), 70.5 ( $\mathrm{CHMe}_{2}$ ), 70.3 ( $\mathrm{CHMe}_{2}$ ), $56.8\left(\mathrm{CH}_{2}\right), 22.8$ ( Me ), $22.5(\mathrm{Me}), 22.3(2 \mathrm{Me}), 19.8(\mathrm{Me}), 13.4(\mathrm{Me}), 9.1(\mathrm{Me}), 8.8$ (Me). Anal. Calcd for $\mathrm{C}_{30} \mathrm{H}_{30} \mathrm{O}_{13} \mathrm{Os}_{3} \mathrm{~W}$ : C, 26.63; H, 2.23. Found: C, 27.19; H, 2.31.

Spectral data for 6: MS (FAB, $\left.{ }^{192} \mathrm{Os},{ }^{184} \mathrm{~W}\right) \mathrm{m} / \mathrm{z} 1358\left(\mathrm{M}^{+}\right)$. IR ( $\mathrm{C}_{6} \mathrm{H}_{12}$ ): v(CO) 2089 (m), 2058 (vs), 2011 (m), 1997 (s), 1981 (m), 1971 (w), $1671(\mathrm{vw}) \mathrm{cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$, $293 \mathrm{~K}): \delta 8.37(\mathrm{~s}, \mathrm{~J} \mathbf{w н}=32 \mathrm{~Hz}, 1 \mathrm{H}), 5.02(\mathrm{~m}, \mathrm{~J}$ нн $=6.3 \mathrm{~Hz}$, $2 \mathrm{H}), 2.04(\mathrm{~s}, 15 \mathrm{H}), 1.34(\mathrm{~d}, \mathrm{~J} \boldsymbol{\text { нн }}=6.3 \mathrm{~Hz}, 12 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (100 $\left.\mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 293 \mathrm{~K}\right): \delta 182.7\left(2 \mathrm{CO}_{2} \mathrm{Pr}^{i}, \mathrm{~J} w \mathrm{wc}=26 \mathrm{~Hz}\right), 172.0$ (br, 3CO), 171.3 (6C, CO), 157.5 ( $\mu_{3}-\mathrm{CH}$, J wc $=102 \mathrm{~Hz}$ ), 156.1 ( $2 \mathrm{C}, \mu_{3}-\mathrm{C}, \mathrm{J}$ wc $=105 \mathrm{~Hz}$ ), $109.0\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right), 69.8(2 \mathrm{CHMe}), 22.0$ ( 4 Me ), $10.4(5 \mathrm{Me})$. Anal. Calcd for $\mathrm{C}_{30} \mathrm{H}_{30} \mathrm{O}_{13} \mathrm{Os}_{3} \mathrm{~W}: \mathrm{C}, 26.63$; H, 2.23. Found: C, 27.14; H, 2.30.

Reaction of $\mathbf{2}$ with DPAD, Second Method. An acetonitrile solution ( 30 mL ) of freshly sublimed $\mathrm{Me}_{3} \mathrm{NO}(23.5 \mathrm{mg}$, 0.33 mmol ) was added dropwise to a mixture of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ (60 mL ), acetonitrile ( 10 mL ), and complex 2 ( $250 \mathrm{mg}, 0.206 \mathrm{mmol}$ ) over a period of 2 h . The sol vent was removed under vacuum, the mixture was redissolved into 75 mL of toluene. After the addition of DPAD ( $103 \mu \mathrm{~L}$ ), the mixture was heated at $110^{\circ} \mathrm{C}$ for 5 min . The solution was then removed under vacuum, and the residue was separated by thin-layer chromatography. Development with a $1: 1$ mixture of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and hexane produced four bands, which were extracted from silica gel to yield 9 mg of $4(0.006 \mathrm{mmol}, 3 \%), 25 \mathrm{mg}$ of $5(0.018 \mathrm{mmol}$, $9 \%), 6 \mathrm{mg}$ of $6(0.004 \mathrm{mmol}, 2 \%)$, and 15 mg of brown ( $\mathrm{C}_{5}{ }^{-}$ $\left.\mathrm{Me}_{5}\right) \mathrm{WOs}_{3}\left[\mathrm{CC}_{2}\left(\mathrm{CO}_{2} \mathrm{Pr}^{2}\right)_{2} \mathrm{H}\right](\mathrm{CO})_{10}(\mathbf{7}, 0.011 \mathrm{mmol}, 5 \%)$.

Spectral data for 7: MS (FAB, $\left.{ }^{192} \mathrm{Os},{ }^{184} \mathrm{~W}\right) \mathrm{m} / \mathrm{z} 1386\left(\mathrm{M}^{+}\right)$. IR ( $\mathrm{C}_{6} \mathrm{H}_{12}$ ): v(CO) 2076 (s), 2040 (s), 2018 (vs), 2003 (s), 1979 (m), 1965 (w), 1831 (w,br), 1718 (m) cm ${ }^{-1}$. ${ }^{1} \mathrm{H}$ NMR ( 300 MHz , $\left.\mathrm{CD}_{2} \mathrm{Cl}_{2}, 293 \mathrm{~K}\right): \delta 5.27(\mathrm{~m}, \mathrm{~J}$ нн $=6.2 \mathrm{~Hz}, 1 \mathrm{H}), 5.03(\mathrm{~m}, \mathrm{~J}$ нн $=$ $6.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.82(\mathrm{~s}, 1 \mathrm{H}), 2.01(\mathrm{~s}, 15 \mathrm{H}), 1.38(\mathrm{~d}, \mathrm{~J} \boldsymbol{\mathrm { H }}=6.2 \mathrm{~Hz}$, $3 \mathrm{H}), 1.35\left(\mathrm{~d}, \mathrm{~J}_{\text {нн }}=6.2 \mathrm{~Hz}, 3 \mathrm{H}\right), 1.21\left(\mathrm{~d}, \mathrm{~J}_{\text {нн }}=6.2 \mathrm{~Hz}, 3 \mathrm{H}\right)$, $1.17(\mathrm{~d}, \mathrm{~J} \boldsymbol{\mathrm { H }} \mathrm{~J}=6.2 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 293$ $\mathrm{K}): \mathrm{CO} \delta 216.7(\mathrm{~J} \mathrm{wc}=161 \mathrm{~Hz}), 216.5(\mathrm{~J} \mathrm{wc}=166 \mathrm{~Hz}), 184.8$, 181.6 (3С), 181.0, 178.6 (3C), 172.5, 168.2; $\delta 285.7(\mathrm{~J} \mathrm{wc}=110$ $\mathrm{Hz}), 110.0,105.1\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right), 72.1\left(\mathrm{CHMe}_{2}\right), 69.4\left(\mathrm{CHMe}_{2}\right), 22.9$ (CH), 22.3 (Me), $22.2(\mathrm{Me}), 22.1(2 \mathrm{Me}), 11.3$ ( 5 Me ). Anal. Calcd for $\mathrm{C}_{31} \mathrm{H}_{30} \mathrm{O}_{14} \mathrm{Os}_{3} \mathrm{~W}$ : $\mathrm{C}, 26.96 ; \mathrm{H}, 2.19$. Found: C, 27.35; H, 2.23.

Table 1. X-ray Structural Data of Complexes 3-7a

| compound | 3 | 4 | 5 | 6 | 7 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| formula | $\mathrm{C}_{31} \mathrm{H}_{30} \mathrm{O}_{14} \mathrm{Os}_{3} \mathrm{~W}$ | $\mathrm{C}_{31} \mathrm{H}_{30} \mathrm{O}_{14} \mathrm{Os}_{3} \mathrm{~W}$ | $\mathrm{C}_{30} \mathrm{H}_{30} \mathrm{O}_{13} \mathrm{Os}_{3} \mathrm{~W}$ | $\mathrm{C}_{30} \mathrm{H}_{30} \mathrm{O}_{13} \mathrm{Os}_{3} \mathrm{~W}$ | $\mathrm{C}_{31} \mathrm{H}_{30} \mathrm{O}_{14} \mathrm{Os}_{3} \mathrm{~W}$ |
| mol wt | 1381.0 | 1381.01 | 1353.0 | 1353.0 | 1424.12 |
| cryst syst | monoclinic | orthorhombic | triclinic | orthorhombic | triclinic |
| space group | $\mathrm{P} 2_{1 / \mathrm{c}}$ | Pca21 | P $\overline{1}$ | Pnma | P $\overline{1}$ |
| a ( $\AA$ ) | 17.928(4) | 19.789(4) | 9.492(2) | 19.272(4) | 10.423(2) |
| b ( $\AA$ ) | 20.112(3) | 9.373(4) | 12.216(2) | 18.303(3) | 18.606(3) |
| $c(\AA)$ | 20.160(5) | 19.068(3) | 15.287(4) | 9.565(3) | 18.667(3) |
| $\alpha$ (deg) |  |  | 80.27(2) |  | 92.89(2) |
| $\beta$ (deg) | 90.72(3) |  | 79.56(2) |  | 90.25(2) |
| $\gamma$ (deg) |  |  | 84.79(2) |  | 94.44(2) |
| volume ( $\AA^{3}$ ) | 7269(3) | 3537(2) | 1714.9(7) | 3374(1) | 3605(1) |
| Z | 8 | 4 | 2 | 4 | 4 |
| $\mathrm{D}_{\mathrm{c}}\left(\mathrm{g} / \mathrm{cm}^{3}\right)$ | 2.524 | 2.594 | 2.618 | 2.664 | 2.545 |
| F (000) | 4998 | 2499 | 1220 | 2443 | 2499 |
| $2 \theta$ (max) | 50.0 | 55.0 | 45.0 | 55.0 | 45 |
| h, k, I ranges | $\begin{aligned} & -21 \text { to } 21,0 \text { to } 23, \\ & 0 \text { to } 23 \end{aligned}$ | $\begin{aligned} & 0 \text { to } 25,0 \text { to } 12, \\ & 0 \text { to } 24 \end{aligned}$ | $\begin{aligned} & -10 \text { to } 10,0 \text { to } 13, \\ & -15 \text { to } 16 \end{aligned}$ | $\begin{aligned} & 0 \text { to } 25,0 \text { to } 23, \\ & 0 \text { to } 12 \end{aligned}$ | $\begin{aligned} & -11 \text { to } 11,0 \text { to } 20, \\ & -20 \text { to } 20 \end{aligned}$ |
| cryst size, mm | $0.20 \times 0.50 \times 0.60$ | $0.13 \times 0.25 \times 0.14$ | $0.02 \times 0.10 \times 0.15$ | $0.05 \times 0.25 \times 0.35$ | $0.20 \times 0.25 \times 0.40$ |
| $\mu(\mathrm{MoK} \alpha), \mathrm{cm}^{-1}$ | 137.5 | 141.4 | 145.7 | 148.1 | 138.62 |
| transmission; max, min | 1.000, 0.245 | 1.000, 0.415 | 1.000, 0.479 | 1.000, 0.395 | 1.000, 0.629 |
| no. of data in refinement | 7114 with $\mathrm{I} \geq 2 \sigma(\mathrm{l})$ | 3308 with $\mathrm{I} \geq 2 \sigma(\mathrm{l})$ | 2893 with $\mathrm{I} \geq 2 \sigma(\mathrm{I})$ | 2603 with $\mathrm{I} \geq 2 \sigma(\mathrm{l})$ | 6389 with $\mathrm{I} \geq 2 \sigma(\mathrm{l})$ |
| no. of atoms and params | 158, 884 | 79, 442 | 76, 425 | 43, 224 | 158, 884 |
| weight modifier, g | 0.019 | 0.0001 | 0.0001 | 0.0001 | 0.0001 |
| $\max \Delta / \sigma$ ratio | 0.002 | 0.031 | 0.0045 | 0.003 | 0.014 |
| $\mathrm{R}_{\mathrm{F}} ; \mathrm{R}_{\mathrm{w}}$ | 0.050; 0.042 | 0.039; 0.039 | 0.036; 0.034 | 0.038; 0.040 | 0.032; 0.030 |
| GOF | 1.46 | 1.49 | 1.21 | 1.48 | 1.19 |
| D-map, max/min e/ $\AA^{3}$ | 3.52/-2.23 | 3.30/-1.93 | 1.38/-1.70 | 1.24/-1.59 | 0.91/-0.87 |

a Features common to all determinations: Nonius CAD-4 diffractometer, $\lambda(\operatorname{MoK} \alpha)=0.7107 \AA$. Minimized function: $\sum\left(w \mid F_{o}-F_{c}{ }^{2}\right)$. Weighting scheme: $\mathrm{w}^{-1}=\sigma^{2}\left(\mathrm{~F}_{\mathrm{o}}\right)+|\mathrm{g}| \mathrm{F}_{0}{ }^{2} ; \mathrm{GOF}=\left[\Sigma \mathrm{w}\left|\mathrm{F}_{\mathrm{o}}-\mathrm{F}_{\mathrm{c}}\right|^{2} /\left(\mathrm{N}_{\mathrm{o}}-\mathrm{N}_{\mathrm{v}}\right)\right]^{1 / 2}\left(\mathrm{~N}_{\mathrm{o}}=\right.$ number of observations; $\mathrm{N}_{\mathrm{v}}=$ number of variables $)$.
Table 2. Selected Bond Distances ( $\boldsymbol{A}$ ) and Angles
(deg) of $\mathbf{3}^{\mathbf{a}}$

X-ray Crystallography. The X-ray diffraction measurements were carried out on a Nonius CAD-4 diffractometer at room temperature. Lattice parameters were determined from 25 randomly selected high-angle reflections. Three standard reflections were monitored every 3600 s. Nosignificant change in intensity ( $\leq 2 \%$ ) 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 by using the NRCC-SDP-VAX package. All of the non-hydrogen atoms had anisotropic temperature factors, while the hydrogen atoms of the organic substituents were placed at the calculated positions with $U_{H}=U_{C}+0.1$. The crystallographic refinement parameters of complexes 3-7 are given in Table 1, while their selected bond distances and angles are presented in Tables 2-6.

## Results

Synthesis and Characterization of Carbido Cluster 2. The target carbido carbonyl complex $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)$ -$\mathrm{WOs}_{3}\left(\mu_{4}-\mathrm{C}\right)(\mu-\mathrm{H})(\mathrm{CO})_{11}$ (2), which possesses a wingtip W atom, a multisite bound carbide, and a hydride spanning the Os-Os hinge, was obtained in nearly quantitative yield from treatment of butterfly carbidobenzofuryl cluster $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right) \mathrm{WOs}_{3}(\mu 4-\mathrm{C})(\mu-\mathrm{H})_{2}\left(\mu-\mathrm{C}_{8} \mathrm{H}_{6} \mathrm{O}\right)$ -

Table 3. Selected Bond Distances ( $\AA$ ) and Angles
(deg) of $4^{a}$

| $\mathrm{W}-\mathrm{Os}(1)$ | $2.863(1)$ | $\mathrm{W}-\mathrm{Os}(3)$ | $2.900(1)$ |
| :--- | :---: | :--- | :--- |
| $\mathrm{Os}(1)-\mathrm{Os}(2)$ | $2.768(1)$ | $\mathrm{Os}(1)-\mathrm{Os}(3)$ | $2.796(1)$ |
| $\mathrm{Os}(2)-\mathrm{Os}(3)$ | $2.850(1)$ | $\mathrm{W}-\mathrm{O}(11)$ | $2.21(1)$ |
| $\mathrm{Os}(1)-\mathrm{C}(15)$ | $2.22(2)$ | $\mathrm{Os}(3)-\mathrm{C}(15)$ | $2.11(2)$ |
| $\mathrm{Os}(1)-\mathrm{C}(16)$ | $2.33(2)$ | $\mathrm{Os}(1)-\mathrm{C}(17)$ | $2.30(2)$ |
| $\mathrm{Os}(2)-\mathrm{C}(17)$ | $2.07(2)$ | $\mathrm{C}(14)-\mathrm{C}(15)$ | $1.48(3)$ |
| $\mathrm{C}(15)-\mathrm{C}(16)$ | $1.40(3)$ | $\mathrm{C}(16)-\mathrm{C}(17)$ | $1.44(3)$ |
| $\mathrm{C}(14)-\mathrm{O}(11)$ | $1.24(2)$ |  |  |
| $\angle \mathrm{W}-\mathrm{O}(11)-\mathrm{C}(14)$ | $117(1)$ | $\angle \mathrm{C}(14)-\mathrm{C}(15)-\mathrm{C}(16)$ | $114(2)$ |
| $\angle \mathrm{C}(15)-\mathrm{C}(16)-\mathrm{C}(17)$ | $118(2)$ | $\angle \mathrm{C}(16)-\mathrm{C}(17)-\mathrm{C}(18)$ | $113(2)$ |
| $\angle \mathrm{W}-\mathrm{C}(9)-\mathrm{O}(9)$ | $174(2)$ | $\angle \mathrm{W}-\mathrm{C}(10)-\mathrm{O}(10)$ | $165(2)$ |

a Esd in parentheses.
Table 4. Selected Bond Distances ( $\AA$ ) and Angles (deg) of $5^{a}$

| $\mathrm{W}-\mathrm{Os}(1)$ | $2.926(1)$ | $\mathrm{W}-\mathrm{Os}(2)$ | $2.676(1)$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{W}-\mathrm{Os}(3)$ | $2.962(1)$ | $\mathrm{Os}(1)-\mathrm{Os}(2)$ | $2.865(1)$ |
| $\mathrm{Os}(1)-\mathrm{Os}(3)$ | $2.910(1)$ | $\mathrm{Os}(2)-\mathrm{Os}(3)$ | $2.852(1)$ |
| $\mathrm{W}-\mathrm{C}(14)$ | $2.16(2)$ | $\mathrm{W}-\mathrm{C}(15)$ | $2.33(2)$ |
| $\mathrm{W}-\mathrm{C}(16)$ | $2.22(2)$ | $\mathrm{Os}(1)-\mathrm{C}(14)$ | $2.18(2)$ |
| $\mathrm{Os}(3)-\mathrm{C}(16)$ | $2.14(2)$ | $\mathrm{W}-\mathrm{C}(21)$ | $2.34(2)$ |
| $\mathrm{W}-\mathrm{C}(22)$ | $2.17(2)$ | $\mathrm{W}-\mathrm{C}(23)$ | $2.30(2)$ |
| $\mathrm{W}-\mathrm{C}(24)$ | $2.48(2)$ | $\mathrm{W}-\mathrm{C}(25)$ | $2.53(2)$ |
| $\mathrm{W}-\mathrm{C}(27)$ | $2.32(2)$ |  |  |
| $\angle \mathrm{C}(13)-\mathrm{C}(14)-\mathrm{C}(15)$ | $113(1)$ | $\angle \mathrm{C}(14)-\mathrm{C}(15)-\mathrm{C}(16)$ | $119(1)$ |
| $\angle \mathrm{C}(15)-\mathrm{C}(16)-\mathrm{C}(17)$ | $109(1)$ | $\angle \mathrm{W}-\mathrm{C}(22)-\mathrm{C}(27)$ | $77(1)$ |
| E Esd in parentheses. |  |  |  |

$(\mathrm{CO})_{9}(\mathbf{1})$ with pressurized CO gas ( $50 \mathrm{~atm}, 135^{\circ} \mathrm{C}, 2$ h). ${ }^{8}$ (Scheme 1) The identification of $\mathbf{2}$ was achieved by routine spectroscopic methods. Solution infrared spectroscopy shows that the pattern of the CO stretching peaks is similar to that of the structurally characterized carbido cluster complex $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right) \mathrm{WR} \mathrm{u}_{3}\left(\mu_{4}-\mathrm{C}\right)(\mu-\mathrm{H})(\mathrm{CO})_{11} .{ }^{9}$ The ${ }^{1} \mathrm{H}$ NMR spectrum exhibits the presence of a high-

[^2]Scheme 1

(1)

(2)
field hydride signal at $\delta-24.48$, together with the sharp signal at $\delta-2.06$ due to the $\mathrm{C}_{5} \mathrm{Me}_{5}$ ligand. In addition, the ${ }^{13} \mathrm{C}$ NMR spectrum gives one W -CO signal at $\delta$ $212.6(2 \mathrm{C}, \mathrm{J} \mathrm{wc}=164 \mathrm{~Hz})$ and four Os-CO signals at $\delta$ 178.8 (3C, br), 176.7 (2C), 174.1 (2C), 165.6 (2C). The broad signal at $\delta 178.8$ is assigned to the CO ligands of the unique $\mathrm{Os}(\mathrm{CO})_{3}$ vertex at the wingtip position, while the observation of three more $\mathrm{Os}-\mathrm{CO}$ signals with ratio of 2:2:2 is consistent with the formation of a timeaveraged mirror plane which bisects the whole molecule. The final confirmation comes from the detection of a downfield signal at $\delta 340.3$ with $\mathrm{J} \mathrm{wc}=104 \mathrm{~Hz}$, which unambiguously suggests the existence of the $\mu_{4}$-carbide ligand.

Reaction of 2 with Alkyne. Complex 2 showed poor reactivity with diiisopropyl acetylenedi carboxylate (DPAD) in toluene solution at reflux, and we only obtained the recovery of starting material under this condition. However, when the carbido cluster 2 was first treated with excess anhydrous $\mathrm{Me}_{3} \mathrm{NO}$ in a mixed solution of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and acetonitrile, the addition of DPAD gave a red product $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right) \mathrm{WOs}_{3}(\mathrm{CO})_{10}\left[\mathrm{C}_{3} \mathrm{H}\left(\mathrm{CO}_{2} \mathrm{Pr}^{1}\right)_{2}\right]$ (3) in $57 \%$ yield (room temperature, 20 h ). The stoichiometry of $\mathbf{3}$ was initially confirmed by FAB mass analysis, which exhibited a parent ion at $\mathrm{m} / \mathrm{z} 1386$, showing a formula of $\mathrm{C}_{31} \mathrm{H}_{30} \mathrm{O}_{14} \mathrm{Os}_{3} \mathrm{~W}$. In addition, disappearance of the hydride signal and occurrence of a sharp singlet at $\delta 7.97$ in the ${ }^{1} \mathrm{H}$ NMR spectrum suggests the formation of a CH fragment, accompanying coordination of the DPAD molecule. The X-ray diffraction study was then carried out to reveal the molecular structure of this addition product.

[^3] Chem. Soc., Dalton Trans. 1990, 3033.


Figure 1. Molecular structure and atomic labeling scheme of the complex $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right) \mathrm{WOs}_{3}(\mathrm{CO})_{10}\left[\mathrm{C}_{3} \mathrm{H}\left(\mathrm{CO}_{2} \mathrm{Pri}_{2}\right]\right.$ (3), with thermal ellipsoids shown at the $30 \%$ probability level.

Crystals of $\mathbf{3}$ contains two crystallographically distinct but structurally similar molecules in the asymmetric unit. A perspective view of one mol ecule is depicted in Figure 1, which consists of a butterfly arrangement of metal atoms and a dihedral angle of $153.85(4)^{\circ}$. The W atom is located at a wingtip position, while the other vertex is occupied by two $\mathrm{Os}(\mathrm{CO})_{3}$ units and one Os$(\mathrm{CO})_{2}$ unit, the latter is located at a hinge site. The carbon atom $\mathrm{C}(11)$, which is derived from the carbido ligand of $\mathbf{2}$, is now coupled with hydride and DPAD to form a dimetallaallyl fragment with two relatively short $\sigma$-bonds $(\mathrm{Os}(1)-\mathrm{C}(13)=2.13(2) \AA$ and $\mathrm{Os}(3)-\mathrm{C}(11)=$ $2.14(2) \AA$ ) and three slightly longer $\pi$-interactions (2.23(2) $-2.30(2) \AA$ ) to the $\mathrm{Os}(\mathrm{CO})_{2}$ group. Moreover, the carbonyl oxygen atom of one carboxylate fragment is coordinated to the W atom with a distance 2.20(1) $\AA$, forming a ligand to metal dative bond in a manner similar to the complexes bearing carboxylate-substituted hydrocarbon ligands. ${ }^{10}$ If we consider that this $\mathrm{C}=\mathrm{O} \rightarrow \mathrm{W}$ interaction donates two electrons to the cluster core, then the molecule contains 62 val ence electrons, which is typical for tetrametallic complexes with five metal metal bonds.
The reactivity of $\mathbf{3}$ is of noteworthy. Thermolysis of 3 in toluene at $90^{\circ} \mathrm{C}$ for 4 h afforded three complexes $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right) \mathrm{WOs}_{3}\left(\mathrm{CO}_{1}{ }_{10}\left[\mathrm{C}_{3}\left(\mathrm{CO}_{2} \mathrm{Pri}\right)_{2} \mathrm{H}\right](4),\left[\mathrm{C}_{5} \mathrm{Me}_{4}\left(\mathrm{CH}_{2}\right)\right]-\right.$ $\mathrm{WOs}_{3}(\mu-\mathrm{H})\left[\mathrm{C}_{3} \mathrm{H}\left(\mathrm{CO}_{2} \mathrm{Pr}^{\mathrm{i}}\right)_{2}\right](\mathrm{CO})_{9}(5)$, and $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right) \mathrm{WOS}_{3}\left(\mu_{3}-\right.$ $\mathrm{CH})\left(u_{3}-\mathrm{CCO}_{2} \mathrm{Pri}_{2}\right)_{2}(\mathrm{CO})_{9}(6)$ in $10 \%, 10 \%$, and $41 \%$ yields, respectively (Scheme 2). The time sequence of their formation is obtained by monitoring their individual reactivity. These investigations include heating a toluene solution of $\mathbf{4}$ at reflux for 2 h , which afforded a mixture 5 and $\mathbf{6}$ in $11 \%$ and $65 \%$ yields, while heating 5 under analogous conditions gave only 6 in $28 \%$ yield. Thus, these results clearly suggest that $\mathbf{4}$ is the kinetic product while $\mathbf{6}$ is the most stable, thermodynamic

[^4]Scheme 2

(2)

## DPAD


(3) $\mathrm{R}=\mathrm{Pr}$


(8)

(5)

(6)
product of these thermally induced isomerization reactions.

The characterization of $\mathbf{4}$ is first provided by the IR $\nu$ (CO) spectrum. In solution, complex 4 gives a CO stretching pattern identical to that of $\mathbf{3}$, suggesting that it is a structural isomer of $\mathbf{3}$. Furthermore, the ${ }^{13} \mathrm{C}$ NMR spectrum exhibits a very similar spectral pattern for the allyl fragment and CO ligands, while the ${ }^{1} \mathrm{H}$ NMR spectrum shows a CH signal shifting to a downfield position at $\delta 8.72$. On the basis of these observations, a structure with the CH fragment located at the middle of dimetallaallyl fragment is envisaged. In fact, a single-crystal X-ray diffraction study confirmed this proposal. As can be seen from the ORTEP diagram shown in Figure 2 and the selected distances listed in Table 3, the overall molecular geometry of 4, which comprises the nearly planar $\mathrm{WOs}_{3}$ framework and the expected allyl fragment, $\mathrm{CRCHCR}\left(\mathrm{R}=\mathrm{CO}_{2} \mathrm{Pr} \mathrm{r}^{\mathrm{i}}\right.$ ), with one carbonyl oxygen atom coordinated to the ( $\mathrm{C}_{5} \mathrm{Me}_{5}$ ) W$(\mathrm{CO})_{2}$ fragment, is essentially identical to that of complex $\mathbf{3}$ discussed earlier.
For complex 5, the ${ }^{1} \mathrm{H}$ NMR spectrum shows the expected CH grouping and two isopropyl signals for the allyl fragment $\mathrm{CRCHCR}, \mathrm{R}=\mathrm{CO}_{2} \mathrm{Pr}$. However, the sharp signal of the $\mathrm{C}_{5} \mathrm{Me}_{5}$ ligand is now replaced by four methyl signals at $\delta 3.36,2.05,1.61$, and 0.80 , two doublets at $\delta 3.85$ and $2.27(\mathrm{~J} \mathrm{HH}=3.2 \mathrm{~Hz})$ due to an exocydic $\mathrm{CH}_{2}$ group, and a hydride signal at $\delta-20.28$. Such a dramatic change of the ${ }^{1} \mathrm{H}$ NMR spectral pattern strongly suggests that one methyl group of the $\mathrm{C}_{5} \mathrm{Me}_{5}$ ligand has undergone a $\mathrm{C}-\mathrm{H}$ activation reaction to produce one hydride, one methylene, and four inequivalent methyl functional groups, giving the formation of tetramethylfulvene group. Accordingly, the ${ }^{13} \mathrm{C}$ NMR


Figure 2. Molecular structure and atom labeling scheme of the complex $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right) \mathrm{WOs}_{3}(\mathrm{CO})_{10}\left[\mathrm{C}_{3}\left(\mathrm{CO}_{2} \mathrm{Pr}\right)_{2} \mathrm{H}\right](4)$, with thermal ellipsoids shown at the $30 \%$ probability level.


Figure 3. Molecular structure and atomic label ing scheme of the complex $\left[\mathrm{C}_{5} \mathrm{Me}_{4}\left(\mathrm{CH}_{2}\right)\right] \mathrm{WOs}_{3}(\mu-\mathrm{H})\left[\mathrm{C}_{3}\left(\mathrm{CO}_{2} \mathrm{Pri}\right)_{2} \mathrm{H}\right](\mathrm{CO})_{9}$ (5), with thermal ellipsoids shown at the 30\% probability level.
spectrum exhibits five signals in the range $\delta 123.6$ 99.0, which are assigned to the five inner carbon atoms derived from the $\mathrm{C}_{5} \mathrm{Me}_{5}$ ligand, one methylene carbon signal at $\delta 56.8$, and three more methyl signals at $\delta 22.8$, 22.5 , and 22.3 with a ratio of $1: 1: 2$. Thus, the singlecrystal X-ray diffraction analysis was carried out to confirm the bonding of this tetramethylfulvene group.
As indicated in Figure 3, the metal framework adopts a tetrahedral geometry with the $\mathrm{W}-\mathrm{Os}(2)$ edge (2.676(1) $\AA$ ) being the shortest within the molecule. In addition, the methylene carbon atom $\mathrm{C}(27)$ is coordinated to the W metal atom. The disposition of the $\mathrm{C}_{5}$ ring and the exocyclic $\mathrm{CH}_{2}$ arm is related to that found for the monometallic $\eta^{6}$-tetramethylfulvene complexes reported. ${ }^{11}$ Other important features involve the allyl group $\mu_{3}-\mathrm{CRCHCR}, \mathrm{R}=\mathrm{CO}_{2} \mathrm{Pr}$, which is coordinated to a $\mathrm{WOs}_{2}$ metal triangle and possesses two $\mathrm{CO}_{2} \mathrm{Pr}{ }^{\mathrm{i}}$ substituents at both terminal positions. The hydride ligand, although not located on the electron density


Figure 4. M olecular structure and atom labeling scheme of the complex $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right) \mathrm{WOs}_{3}\left(\mu_{3}-\mathrm{CH}\right)\left(\mu_{3}-\mathrm{CCO}_{2} \mathrm{Pri}_{2}(\mathrm{CO})_{9}(\mathbf{6})\right.$, with thermal ellipsoids shown at the 30\% probability level.
map, is believed to associate with the Os-Os vector below the allyl ligand, as the corresponding $\mathrm{Os}(1)-\mathrm{Os}-$ (3) distance (2.910(1) $\AA$ ) is significantly longer that the other Os-Os distances, $\mathrm{Os}(1)-\mathrm{Os}(2)=2.865(1) \AA$ and $\mathrm{Os}(2)-\mathrm{Os}(3)=2.852(1) \AA$, of the tetrahedral cluster skeleton.

On the other hand, the ${ }^{13} \mathrm{C}$ NMR spectrum of 6 shows two alkylidyne $\mathrm{C}_{\alpha}$ signals at $\delta 157.5(\mathrm{~J}$ wc $=102 \mathrm{~Hz})$ and $156.1(\mathrm{~J} \mathrm{wc}=105 \mathrm{~Hz})$ in a ratio of 1:2, although the observed chemical shifts are moved to the high-field region with respect to that reported for the $\mu_{3}$-alkylidyne ligand. ${ }^{12}$ The result of the X-ray diffraction study, which is in accordance with the ${ }^{13} \mathrm{C}$ NMR data, reveals a butterfly framework with a dihedral angle of 100.33$(2)^{\circ}$, the existence of three alkylidyne ligands, and a crystallographical imposed mirror plane, passing the $\mathrm{W}-\mathrm{Os}(1)$ hinge and bisecting the molecule (Figure 4). The Os(2)-Os(2) distance (3.253(1) $\AA$ ) is fully compatible with the prediction based on the cluster valenceelectron counting ( 62 electrons). The equivalent alkylidyne fragments, each carries a $\mathrm{CO}_{2} \mathrm{Pr}^{i}$ fragment, are located at the outer face of each $\mathrm{WOs}_{2}$ wing. The unique methylidyne ligand, which lies on the mirror plane, spans the hinge W atom and the wingtip Os atoms. Thus, the observed structure is related to that of the trialkylidyne complex $\mathrm{CpWOs}_{3}\left(\mu_{3}-\mathrm{CTol}\right)_{3}(\mathrm{CO})_{9}$ prepared by Park and co-workers. ${ }^{13}$ Interestingly, the $\mathrm{W}-\mathrm{C}_{\alpha}$ distances $(\mathrm{W}-\mathrm{C}(6)=1.98(2) \AA$ and $\mathrm{W}-\mathrm{C}(7)=2.00(1)$ $\AA$ ) of the alkylidyne ligands are equal within the experimental errors. Thus, it suggests that the steric interaction between the $\mathrm{C}_{5} \mathrm{Me}_{5}$ ligand and the $\mathrm{CO}_{2} \mathrm{Pr}^{\mathrm{i}}$ substituent is about the same as that to the methylidyne hydrogen atom.

[^5]

Figure 5. Molecular structure and atom labeling scheme of the complex $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right) \mathrm{WOs}_{3}\left[\mathrm{CC}_{2}\left(\mathrm{CO}_{2} \mathrm{Pr}^{1}\right)_{2} \mathrm{H}\right](\mathrm{CO})_{10}$ (7), with thermal ellipsoids shown at the 30\% probability level.

## Chart 1


(7) $\mathrm{R}=\mathrm{CO}_{2} \mathrm{Pr}$

$L=C p, C_{5} \mathrm{Me}_{5} ; R=\mathrm{H}, \mathrm{Me}, \mathrm{Ph}$

Generation of a Vinyl Alkylidyne Cluster. To explore the other less probable reaction route occurring between the carbide and alkyne, we examined the reaction of the acetonitrile-substituted complex $\mathbf{2}$ with DPAD in refluxing toluene solution. It is noteworthy that in addition to the previously mentioned complexes 4, 5, and 6, we isolated one more cluster complex ( $\mathrm{C}_{5}$ $\left.\mathrm{Me}_{5}\right) \mathrm{WOs}_{3}\left[\mathrm{CC}_{2}\left(\mathrm{CO}_{2} \mathrm{Pr}^{\mathrm{i}}\right)_{2} \mathrm{H}\right](\mathrm{CO})_{10}$ (7) in low yield, Chart 1. This newly isolated complex shows a parent molecular ion at $\mathrm{m} / \mathrm{z}$ 1386, which is identical to that of the allyl complexes $\mathbf{3}$ and $\mathbf{4}$, suggesting the retention of the $\mathrm{WOs}_{3}(\mathrm{CO})_{10}$ framework and the incorporation of one DPAD unit. The ${ }^{1} \mathrm{H}$ NMR spectrum of 7 exhibits the expected signals for the $\mathrm{C}_{5} \mathrm{Me}_{5}$ and two isopropyl groups and a sharp signal at $\delta 2.82$ attributable to the CH proton. This ${ }^{1} \mathrm{H}$ NMR data is in accordance with the hydride migration to either the carbide atom or the DPAD fragment. Furthermore, the ${ }^{13} \mathrm{C}$ NMR spectrum exhibits two W-bound CO ligands at $\delta 216.7$ (J wc $=161$ $\mathrm{Hz})$ and $216.5(\mathrm{~J}$ wc $=166 \mathrm{~Hz})$ and a downfield quaternary carbon signal at $\delta 285.7$ with J wc $=110 \mathrm{~Hz}$, which is believed to be due to the $\alpha$-carbon of a substituted alkylidyne functional group. In addition, this carbon atom is probably linked to the DPAD molecule but not the hydrideligand, as observed in 3, because it gave no J ch coupling. Therefore, these NMR spectral data implicate the formation of a different hydrocarbon ligand for 7, and the single-crystal X-ray crystal structural analysis was examined to establish its identity.

As indicated in Figure 5, the cluster core consists of a tetrahedral geometry composed by two $\mathrm{Os}(\mathrm{CO})_{3}$, one $\mathrm{Os}(\mathrm{CO})_{2}$, and one $\mathrm{W}(\mathrm{CO})_{2}$ metal vertex. The W -Os distances are about equal (2.920(1)-2.963(1) Å), while the $\mathrm{Os}(1)-\mathrm{Os}(2)$ distance $(2.745(1) \AA \AA)$ is slightly shorter

Scheme 3

then the other two Os-Os distances (2.819(1) and 2.852(1) Å). The variation of the metal-metal distances is normal and falls within the expected range for the 60electron, saturated $\mathrm{WOs}_{3}$ cluster compound. The alkylidyne carbon atom $\mathrm{C}(11)$, which is obviously derived from the carbide ligand of $\mathbf{2}$, resides on the $\mathrm{W}-\mathrm{Os}(1)-$ $\mathrm{Os}(3)$ metal triangle and is linked to a vinyl fragment $\mathrm{C}(16)-\mathrm{C}(17)$ with two $\mathrm{CO}_{2} \mathrm{Pr}$ i substituents located at the cis-position. This vinyl group, produced by the coupling of DPAD and the hydride, is further coordinated to the unique $\operatorname{Os}(\mathrm{CO})_{2}$ vertex with slightly elongated bond lengths $(\mathrm{Os}(1)-\mathrm{C}(16)=2.16(2) \AA$ and $\mathrm{Os}(1)-\mathrm{C}(17)=$ 2.25(1) Å). If we ignored this secondary olefinic $\pi$-interaction, the overall molecular geometry is analogous to that of the structurally characterized alkylidyne compounds $\mathrm{LWOs}_{3}\left(\mu_{3}-\mathrm{CR}\right)(\mathrm{CO})_{11}\left(\mathrm{~L}=\mathrm{Cp}\right.$ and $\mathrm{C}_{5} \mathrm{Me}_{5} ; \mathrm{R}$ $=$ Tol and H$),{ }^{14}$ which all possess a normal face-bridging alkylidyne ligand and three $\mathrm{Os}(\mathrm{CO})_{3}$ metal vertexes at the basal positions of the cluster.

## Discussion

We have developed a convenient and high-yield preparative route to the carbido cluster $\mathbf{2}$ from carbidobenzofuryl cluster 1, a product which is initially prepared from acetylide complexes $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right) \mathrm{WOs}_{3}\left(\mathrm{CCCH}_{2^{-}}\right.$ $\mathrm{OPh})(\mathrm{CO})_{11}$. If we take this into consideration, the formation of $\mathbf{2}$ goes through the novel acetylide C-C bond cleavage to afford a carbide and alkylidyne (Scheme 3). The alkylidyne then isomerizes to give a benzofuryl substituent through a complex isomerization process involving sequential $\mathrm{C}-\mathrm{H}$ bond activation, orthometalation, and $\mathrm{C}-\mathrm{C}$ bond formation. Eventually, the removal of the benzofuryl substituent (probably as benzofuran) from the $\mathrm{WOs}_{3}$ frame is effected by treatment with CO under pressure. This extraordinary reaction is parallel to the CO disproportionation reaction that has been widely applied for the synthesis of many group 8 carbido carbonyl clusters. ${ }^{15}$

The reactivity of $\mathbf{2}$ with an electron-deficient al kyne, DPAD, was then examined. It appears that the addition

[^6]Scheme 4


Chart 2

(9)
of $\mathrm{Me}_{3} \mathrm{NO}$ is essential to lower the reaction barrier and to provide a potential coordination site for the incoming DPAD. F or the reaction carried out at room temperature, we isolated the allyl cluster $\mathbf{3}$ as the major product, suggesting that the hydride migration to the carbide is an important key step (pathway A of Scheme 4). The hydride migration to the carbide atom has been observed in the related carbido complex $\mathrm{Ru}_{4}\left(\mu_{4}-\mathrm{C}\right)(\mu-\mathrm{H})_{2^{-}}$ $(\mathrm{CO})_{12}$, in which the reversible hydride migration between the Ru-Ru and Ru-C(carbide) edges has been confirmed by a variable-temperature ${ }^{1} \mathrm{H}$ NMR study. ${ }^{16}$ The resulting methylidyne ligand then reacts with the DPAD to afford the allyl ligand observed in 3, for which the reaction is akin to those documented for other alkylidyne clusters and many alkynes. ${ }^{17}$ Unfortunately, a simultaneous coupling of carbide, hydride, and DPAD or other possibilities cannot be satisfactorily ruled out at present.

Furthermore, if the reaction was executed in refluxing toluene, one additional cluster product 7 was isolated in lower yield. This result suggests the occurrence of a second, less favorable pathway which involves the hydride migration to the coordinated DPAD instead (pathway B of Scheme 4). Again, the timing of the $C-C$ bond formation between the carbide and DPAD molecule in 7, with respect to the hydride migration to DPAD, is uncertain based on our present experimental evidences.
The isolation of the allyl complex 3 provides a good opportunity to examine several important cluster reactions involving (i) allyl metathesis, (ii) cluster core rearrangement, and (iii) competitive $\mathrm{C}-\mathrm{H}$ or $\mathrm{C}-\mathrm{C}$ bond activation (Scheme 2). The conversion from complex 3 to its isomer $\mathbf{4}$ is best understood by cleavage of the allyl the $\mathrm{C}-\mathrm{C}$ bond to give transient alkyne and alkylidyne fragments, followed by alkyne rotation and regeneration of the $\mathrm{C}-\mathrm{C}$ bond. We believe that the latent unsaturation required for the $\mathrm{C}-\mathrm{C}$ bond cleavage is provided by lifting the weak $\mathrm{C}=\mathrm{O} \rightarrow \mathrm{W}$ dative interaction of the $\mathrm{CO}_{2^{-}}$ Pri substituent, as this isomerization proceeded with no loss of CO ligand and because the reaction is not affected

[^7]by exposing it to a CO atmosphere. The driving force of the isomerization is also deduced, which is believed to be the steric repulsion between the $\mathrm{CO}_{2} \mathrm{Pr}^{\mathrm{i}}$ substituents of the allyl ligand, as these functional groups are further away from each other in 4 and heating of a solution of $\mathbf{4}$ produces no detectable amount of the more congested precursor 3.

Moreover, extensive heating of the allyl complex 4 in refluxing toluene solution led to the formation of a mixture of 5 and $\mathbf{6}$ (Scheme 2). Their formation can be visualized by, first, generation of an unsaturated, tetrahedral allyl intermediate complex (8) through removal of one CO ligand from the W atom. This hypothesis is further supported by the isolation of a structurally characterized, highly reactive Cp compound, $\left.\mathrm{CpWOs}_{3}\left(\mathrm{C}_{3} \mathrm{Me}_{2} \mathrm{Tol}\right) \mathrm{CO}\right)_{9}$ (9) Chart 2, which contains only 58 cluster valence electrons. ${ }^{18}$ We believe that the unsaturated nature of $\mathbf{8}$ would induce the $\mathrm{C}-\mathrm{H}$ activation at a methyl group of the nearby $\mathrm{C}_{5} \mathrm{Me}_{5}$ ligand, giving the formation of tetramethylfulvene and a bridging hydride, as observed in 5. On the other hand, the same unsaturated cluster core would also promote the cleavage of allyl C-C bonds, affording the observed butterfly cluster 6, which possesses three triply bridging alkylidyne ligands. Interestingly, the $\mathrm{C}-\mathrm{H}$ bond activation of the methyl group is partially reversible as thermolysis of $\mathbf{5}$ gives the production of $\mathbf{6}$ in low yield.

[^8]This conversion is best understood in terms of the regeneration of the intermediate 8, which is then converted to complex 6 via the allyl $\mathrm{C}-\mathrm{C}$ bond cleavage reaction discussed earlier.

## Summary

In summary, our studies provide a further example for the possible formation of a $\mathrm{C}-\mathrm{C}$ bond between the carbide and alkyne and have shown that the cluster complexes formed can undergo facile conversion involving allyl metathesis, $\mathrm{C}-\mathrm{C}$ bond cleavage, and other parallel processes such as $\mathrm{C}-\mathrm{H}$ bond activation of a ring methyl in the $\mathrm{C}_{5} \mathrm{Me}_{5}$ ligand. The key intermediate is the tetrahedral complex 6, which possesses an unsaturated cluster core with only 58 cluster valence electrons. A related investigation on the addition of alkenes to the carbido cluster 2, which also shows the formation of a similar intermediate, will be described in the future.

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Supporting Information Available: X-ray structural data including tables of bond distances, atomic coordinates, and thermal parameters for complexes 3-7 (32 pages). Ordering information is given on any current masthead page.


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