

## Stepwise Synthesis of ( $\equiv\text{CCH}_2\text{CH}_2\text{C}\equiv$ ), ( $\equiv\text{CCH}=\text{CHC}\equiv$ ), and ( $\equiv\text{CC}\equiv\text{CC}\equiv$ ) Bridges between Molybdenum or Tungsten Centers

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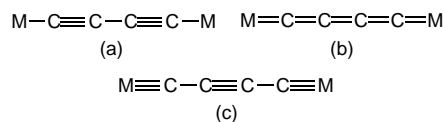
Received October 23, 1996

Hydrocarbon-bridged transition metal complexes have been beautifully reviewed by Beck.<sup>1</sup> Transition metal carbide bridges ( $\text{L}_n\text{M}(\text{C})_m\text{ML}_n$ ) are an important subset of hydrocarbon bridges.<sup>2</sup> Naked four-carbon bridges span the three forms depicted in Scheme 1;<sup>3</sup> most common is the diacetylene bridge a. Redox reactions of a and c have produced examples of the cumulene form b. Few examples of the biscarbyne  $\text{C}_4$ -bridging unit c have been reported. In this paper, we report a family of dinuclear biscarbyne complexes displaying  $\text{CH}_2\text{CH}_2$ ,  $\text{CH}=\text{CH}$ , and  $\text{C}\equiv\text{C}$  linkages.

Deprotonation of  $[\text{M}]\equiv\text{CCH}_3$  ( $[\text{M}] = \text{Tp}'(\text{CO})_2\text{Mo}$  (**1a**),  $\text{Tp}'(\text{CO})_2\text{W}$  (**1b**),  $\text{Tp}' = \text{hydridotris}(3,5\text{-dimethylpyrazolyl})\text{borate}$ ), at the carbon  $\beta$  to the metal, forms a vinylidene anion<sup>4a,5</sup>  $\{[\text{M}]=\text{C}=\text{CH}_2\}^-$  (eq 1) which has been shown to react with a variety of electrophiles.<sup>6</sup> Reaction with  $\text{Tp}'(\text{CO})_2\text{M}=\text{CCl}$  forms a  $\text{C}_3$  skeleton in  $[\text{M}]\equiv\text{CCH}_2\text{C}\equiv[\text{M}]$  products.<sup>7</sup> Green and co-workers observed that oxidation of an isoelectronic anionic metal vinylidene complex ( $[\text{Li}][\text{Cp}(\text{P}(\text{OMe})_3)_2\text{M}=\text{C}=\text{CH}'\text{Bu}]$ ), resulted in dimerization to form the neutral product  $[\text{Cp}^*(\text{P}(\text{OMe})_3)_2\text{M}=\text{CCH}'\text{Bu}]_2$ .<sup>6b</sup> Other examples of oxidative coupling reactions have been reported.<sup>8,3a</sup>

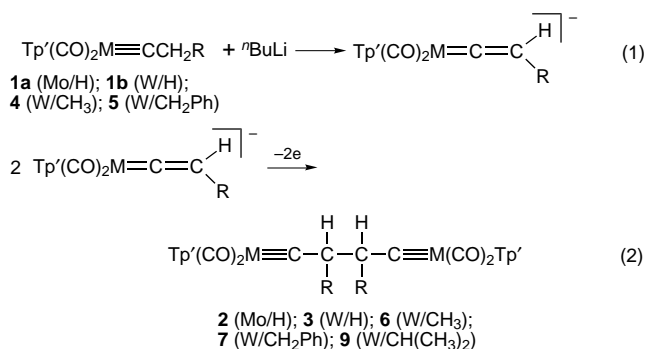
In an analogous reaction, oxidation of the parent vinylidene complex  $\{\text{Li}\}\{[\text{M}]=\text{C}=\text{CH}_2\}$  with ferrocenium, iodine, or nitrobenzene gives high yields of the bright yellow neutral dimer  $[\text{M}]\equiv\text{CCH}_2\text{CH}_2\text{C}\equiv[\text{M}]$  ( $\text{M} = \text{Mo}$ , **2**;<sup>9</sup>  $\text{W}$ , **3**<sup>10</sup>) (eq 2). The two methylene units in complex **2** are characterized by a singlet

### Scheme 1



at 3.10 ppm in the  $^1\text{H}$  NMR spectrum and a triplet of triplets at 46 ppm ( $^1J_{\text{CH}} = 133$  Hz,  $^2J_{\text{CH}} = 6$  Hz) in the  $^{13}\text{C}$  NMR spectrum. A 2:1 NMR pattern is observed for the dimethylpyrazole rings of the  $\text{Tp}'$  ligands.

Similar reactivity is seen with substituted carbyne reagents of the type  $[\text{W}]\equiv\text{CCH}_2\text{R}$  ( $\text{R} = \text{CH}_3$ , **4**;  $\text{CH}_2\text{Ph}$ , **5**)<sup>11</sup> which, upon deprotonation and oxidation, also form bright yellow dimers  $[\text{W}]\equiv\text{CCHRCHRC}\equiv[\text{W}]$  ( $\text{R} = \text{CH}_3$ , **6**;<sup>12</sup>  $\text{CH}_2\text{Ph}$ , **7**<sup>13</sup>) (eq 2). Two diastereomers, meso and dl pairs, are observed for **6** and **7**, reflecting the presence of two stereogenic carbon centers. The sterically demanding isopropyl carbyne  $[\text{W}]\equiv\text{CCH}(\text{CH}_3)_2$  (**8**<sup>14</sup>) can also be deprotonated; oxidation forms  $[\text{W}]\equiv\text{CC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{C}\equiv[\text{W}]$  (**9**<sup>14</sup>). In all cases, the metal-carbon triple bond is retained in the  $[\text{M}]\equiv\text{C}$  units linked by a saturated bridge.



Dimeric complexes containing two metal alkylidyne units linked by a  $\text{CH}=\text{CH}$  group have been reported by Schrock.  $\text{LMo}\equiv\text{CCH}=\text{CHC}\equiv\text{MoL}$  ( $\text{L} = (\text{R}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}$ ) was formed by coupling of the parent acetylides,<sup>15a</sup> and  $(^t\text{BuO})_3\text{W}\equiv\text{C}-\text{CH}=\text{CHC}\equiv\text{W}(\text{O}^t\text{Bu})_3$  was synthesized by metathesis of an alkylidyne complex with an enediyne.<sup>15b</sup> An example of a biscarbyne with a substituted unsaturated bridge is  $\text{Cp}(\text{CO})_2\text{Cr}\equiv\text{CC}(\text{Ph})=\text{C}(\text{Ph})\text{C}\equiv\text{Cr}(\text{CO})_2\text{Cp}$ , which is believed to be formed through a complex redox cycle.<sup>16</sup> Also of note is the biscarbene complex  $\text{Cp}'(\text{CO})_2\text{Mn}=\text{C}(\text{OEt})\text{CH}_2\text{CH}_2(\text{OEt})\text{C}=\text{Mn}$

(10) For  $\text{Tp}'(\text{CO})_2\text{W}\equiv\text{CCH}_2\text{CH}_2\text{C}\equiv\text{W}(\text{CO})_2\text{Tp}'$  (**3**): yield = 90%; IR (KBr) 1963, 1867  $\text{cm}^{-1}$  ( $\nu_{\text{WC}=\text{O}}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.05 (s, 4 H,  $-\text{CH}_2\text{CH}_2-$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  289.9 (s,  $^1J_{\text{WC}} = 180$  Hz,  $\text{W}=\text{C}-$ ), 47.9 (tt,  $^1J_{\text{CH}} = 130$  Hz,  $^2J_{\text{CH}} = 6$  Hz,  $^2J_{\text{WC}} = 40$  Hz,  $-\text{CH}_2\text{CH}_2-$ ).

(11) See Supporting Information for complete details of synthesis and characterization along with crystal structure data.

(12) For  $\text{Tp}'(\text{CO})_2\text{W}\equiv\text{CCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{C}\equiv\text{W}(\text{CO})_2\text{Tp}'$  (**6**): yield = 91%; IR (KBr) 1969, 1866  $\text{cm}^{-1}$  ( $\nu_{\text{WC}=\text{O}}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) isomer 1  $\delta$  3.54 (m, 2 H,  $\text{CCH}(\text{CH}_3)$ ), 1.43 (m, 6 H,  $\text{CCH}(\text{CH}_3)\text{C}$ ), isomer 2  $\delta$  2.85 (m, 2 H,  $\text{CCH}(\text{CH}_3)$ ), 1.48 (m, 6 H,  $\text{CCH}(\text{CH}_3)$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) isomer 1  $\delta$  298.0 (s,  $\text{W}=\text{C}-$ ), 56.7 ( $\text{W}=\text{CCH}(\text{CH}_3)$ ), 16.93 ( $\text{CCH}(\text{CH}_3)$ ); isomer 2:  $\delta$  297.7 ( $\text{W}=\text{C}-$ ), 58.7 ( $\text{W}=\text{CCH}(\text{CH}_3)$ ), 18.86 ( $\text{CCH}(\text{CH}_3)$ ).

(13) For  $\text{Tp}'(\text{CO})_2\text{W}\equiv\text{CCH}(\text{CH}_2\text{Ph})\text{CH}(\text{CH}_2\text{Ph})\text{C}\equiv\text{W}(\text{CO})_2\text{Tp}'$  (**7**): yield = 82%; IR (KBr) 1964, 1869  $\text{cm}^{-1}$  ( $\nu_{\text{WC}=\text{O}}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) isomer 1  $\delta$  7.08–6.80 (m, 10 H,  $-\text{CH}_2\text{C}_6\text{H}_5$ ), 3.70–2.75 (m, 6 H,  $\text{CCH}(\text{CH}_2\text{Ph})$ ); isomer 2  $\delta$  6.93–6.91 (m, 10 H,  $-\text{CH}_2\text{C}_6\text{H}_5$ ), 3.70–2.70 (m, 6 H,  $\text{CCH}(\text{CH}_2\text{Ph})$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) isomer 1  $\delta$  297.6 ( $\text{W}=\text{C}-$ ), 64.03 ( $\text{W}=\text{CCH}(\text{CH}_2\text{Ph})$ ), 35.39 ( $\text{W}=\text{CCH}(\text{CH}_2\text{Ph})$ ), isomer 2  $\delta$  297.6 (s,  $\text{W}=\text{C}-$ ), 64.60 ( $\text{W}=\text{CCH}(\text{CH}_2\text{Ph})$ ), 39.13 ( $\text{W}=\text{CCH}(\text{CH}_2\text{Ph})$ ).

(14) For  $\text{Tp}'(\text{CO})_2\text{W}\equiv\text{CC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{C}\equiv\text{W}(\text{CO})_2\text{Tp}'$  (**9**): yield = 54%; IR (KBr) 1963, 1864  $\text{cm}^{-1}$  ( $\nu_{\text{WC}=\text{O}}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.59 (s, 12 H,  $-\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2-$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  303.4 ( $\text{W}=\text{C}-$ ), 62.6 ( $-\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2-$ ), 25.2 ( $-\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{C}-$ ).

(15) (a) Shih, K.-Y.; Schrock, R. R.; Kempe, R. *J. Am. Chem. Soc.* **1994**, *116*, 8804–8805. (b) Krouse, S. A.; Schrock, R. R. *J. Organomet. Chem.* **1988**, *355*, 257–265.

(16) Ustynyuk, N. A.; Vinogradova, V. N.; Andrianov, V. G.; Sturchkov, Yu. T. *J. Organomet. Chem.* **1984**, *268*, 73–78.

(1) Beck, W.; Niemer, B.; Wieser, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 923–1110.

(2) (a) Bunz, U. H. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 969–971. (b) Lang, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 547–550. (c) Chisholm, M. H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 673–674.

(3) For example, see: (a) Le Narvor, N.; Toupet, L.; Lapinte, C. *J. Am. Chem. Soc.* **1995**, *117*, 7129–7138. (b) Weng, W.; Bartik, T.; Brady, M.; Bartik, B.; Ramsden, J. A.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1995**, *117*, 11922–11931. (c) Zhou, Y.; Seyler, J. W.; Weng, W.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 8509–8510. (d) Bruce, M. I.; Hinterding, P.; Tiekink, E. R. T.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1993**, *450*, 209–218. (e) Crescenzi, R.; Lo Sterzo, C. *Organometallics* **1992**, *11*, 4301–4305. (f) Stang, P. J.; Tykwinski, R. *J. Am. Chem. Soc.* **1992**, *114*, 4411–4412. (g) Wong, A.; Kang, P. C. W.; Tagge, C. D.; Leon, D. R. *Organometallics* **1990**, *9*, 1992–1994.

(4) (a) Brower, D. C.; Stoll, M.; Templeton, J. L. *Organometallics* **1989**, *8*, 2786–2792. (b) McDermott, G. A.; Dorries, A. M.; Mayr, A. *Organometallics* **1987**, *6*, 925–931. An improved synthesis of **1** has been achieved. **1** was synthesized from the reaction of  $\text{Tp}'(\text{CO})_2\text{WCCl}^{\text{tBu}}$  with 0.5 equiv of  $\text{LiMe}_2\text{Cu}$  in THF (72% yield).<sup>11</sup> (c) Desmond, T.; Lalor, F. J.; Ferguson, G.; Parvez, M. *J. Chem. Soc., Chem. Commun.* **1983**, 457–459.

(5) For reviews of vinylidene chemistry, see: (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59–128. (b) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197–257.

(6) (a) Chaona, S.; Lalor, F. J.; Ferguson, G.; Hunt, M. M. *J. Chem. Soc., Chem. Commun.* **1988**, 1606–1608. (b) Beevor, R. G.; Freeman, M. J.; Green, M.; Morton, C. E.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, 68–70. (c) Jamison, G. M.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 1954–1959.

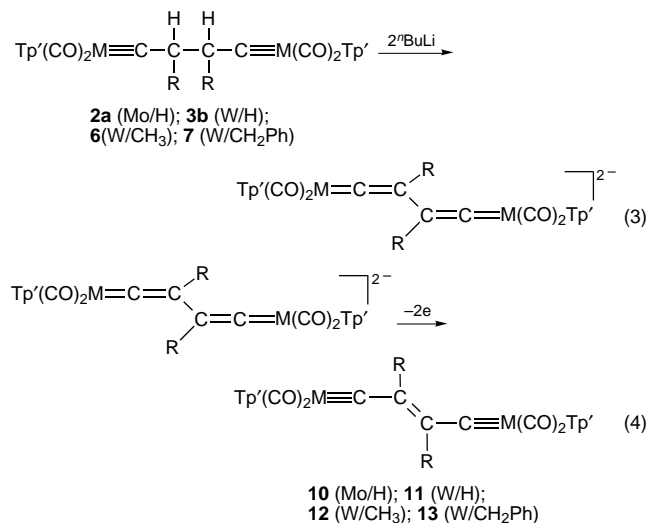
(7) Woodworth, B. E.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 7418–7419.

(8) (a) Rabier, A.; Lugan, N.; Mathieu, R.; Geoffroy, G. L. *Organometallics* **1994**, *13*, 4676–4678. (b) Le Narvor, N.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1993**, 357–359. (c) Iyer, R. S.; Selegue, J. P. *J. Am. Chem. Soc.* **1987**, *109*, 910–911.

(9) For  $\text{Tp}'(\text{CO})_2\text{Mo}\equiv\text{CCH}_2\text{CH}_2\text{C}\equiv\text{Mo}(\text{CO})_2\text{Tp}'$  (**2**): yield = 72%; IR (KBr) 1976, 1879  $\text{cm}^{-1}$  ( $\nu_{\text{MoC}=\text{O}}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.10 (s, 4 H,  $-\text{CH}_2\text{CH}_2-$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  300.7 (s,  $\text{Mo}=\text{C}-$ ), 46.0 (tt,  $^1J_{\text{CH}} = 133$  Hz,  $^2J_{\text{CH}} = 7$  Hz,  $-\text{CH}_2\text{CH}_2-$ ).

(CO)<sub>2</sub>Cp'. When reacted with <sup>n</sup>BuLi followed by CuI, the dimer undergoes oxidation to form a conjugated bridge in Cp'-(CO)<sub>2</sub>Mn=C(OEt)CH=CH(OEt)C=Mn(CO)<sub>2</sub>Cp'.<sup>8a</sup>

We have been able to form a conjugated linkage between low oxidation state metal centers by stepwise oxidation of the saturated bridges. Addition of 2 equiv of <sup>n</sup>BuLi to complex **2**, **3**, **6**, or **7** forms an orangish-red THF solution, presumably the dianions {Li}<sub>2</sub>{[M]=C=CRCR=C=[M]} (eq 3). These resonance stabilized anionic vinylidene intermediates can be oxidized with ferrocenium, iodine, or nitrobenzene to give unsaturated bridges between the two carbyne fragments [M]=CCR=CRC=[M] (eq 4).<sup>17-20</sup>



NMR data for **10** includes an olefinic resonance at 6.49 ppm (CH=CH) in the <sup>1</sup>H NMR spectrum and resonances at 285 ppm (Mo≡C) and 141 ppm (dd, <sup>1</sup>J<sub>CH</sub> = 161 Hz, <sup>2</sup>J<sub>CH</sub> = 6.5 Hz, CH=CH) in the <sup>13</sup>C NMR spectrum. Dark red X-ray quality crystals of **12** were obtained from CH<sub>2</sub>Cl<sub>2</sub>/pentane, and the structure is shown in Figure 1. This dimer has an inversion center with a trans configuration of metal centers about the olefinic bridge. Bond distances for the bridging unit are consistent with the biscarbyne formulation: W≡C (1.808 Å), C—C (1.450 Å), and C=C (1.36 Å).<sup>11</sup>

Lapinte reported the radical coupling of Cp\*(dppe)FeC≡CH using ferrocenium hexafluorophosphate to form [Cp\*(dppe)Fe=C=CHCH=C=Fe(dppe)Cp\*](PF<sub>6</sub>)<sub>2</sub>. Deprotonation yielded the neutral, 1,3-diyne C<sub>4</sub>-bridged complex Cp\*(dppe)FeC≡C—C≡CFe(dppe)Cp\*.<sup>3a</sup> Gladysz formed C<sub>4</sub>-bridged complexes by

(17) For [Tp'(CO)<sub>2</sub>Mo≡CCH=CHC≡Mo(CO)<sub>2</sub>Tp'] (**10**): yield = 85%; IR (KBr) 1991, 1973, 1890 cm<sup>-1</sup> (ν<sub>MoC=O</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 6.49 (s, 2H, -CH=CH-); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 285.0 (Mo≡C-), 141.0 (-CH=CH-).

(18) For [Tp'(CO)<sub>2</sub>W≡CCH=CHC≡W(CO)<sub>2</sub>Tp'] (**11**): yield = 82%; IR (KBr) 1977, 1956, 1869 cm<sup>-1</sup> (ν<sub>WC=O</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 6.63 (s, 2H, -CH=CH-); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 276.4 (W≡C-), 144.6 (-CH=CH-).

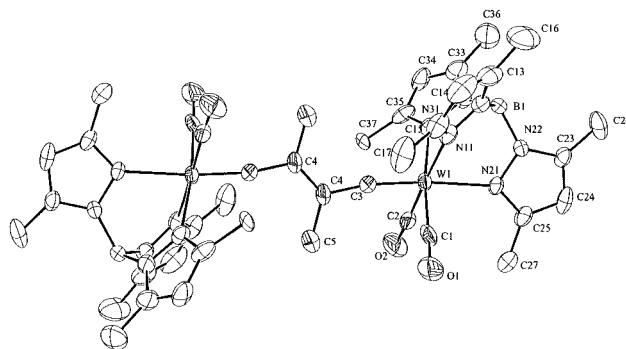
(19) For [Tp'(CO)<sub>2</sub>W≡CC(CH<sub>3</sub>)=C(CH<sub>3</sub>)C≡W(CO)<sub>2</sub>Tp'] (**12**): yield = 34%; IR (KBr) 1957, 1869 cm<sup>-1</sup> (ν<sub>WC=O</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.92 (6 H, -C(CH<sub>3</sub>)=C-); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 283.2 (W≡C-), 148.3 (-C(CH<sub>3</sub>)=C(CH<sub>3</sub>)-), 17.09 (-C(CH<sub>3</sub>)=C(CH<sub>3</sub>)-).

(20) For [Tp'(CO)<sub>2</sub>W≡CC(CH<sub>2</sub>Ph)=C(CH<sub>2</sub>Ph)C≡W(CO)<sub>2</sub>Tp'] (**13**): IR (KBr) 1963, 1875 cm<sup>-1</sup> (ν<sub>WC=O</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.10 (s, 5 H, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 3.84 (s, 4H, CH<sub>2</sub>Ph); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 283.2 (W≡C-), 151.9 (C=C), 37.5 (CH<sub>2</sub>Ph).

(21) For [K]<sub>2</sub>[Tp'(CO)<sub>2</sub>Mo=C=C=C=C=Mo(CO)<sub>2</sub>Tp'] (**14**): <sup>13</sup>C NMR (THF/C<sub>6</sub>D<sub>6</sub>) δ 279.8 (Mo=C=), 258.2 (Mo=C=C=).

(22) For [Tp'(CO)<sub>2</sub>Mo=CC=CC=Mo(CO)<sub>2</sub>Tp'] (**15**): IR (KBr) 2004, 1977, 1901 cm<sup>-1</sup> (ν<sub>MoC=O</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 248.9 (Mo≡C-), 107.0, (-C=C-).

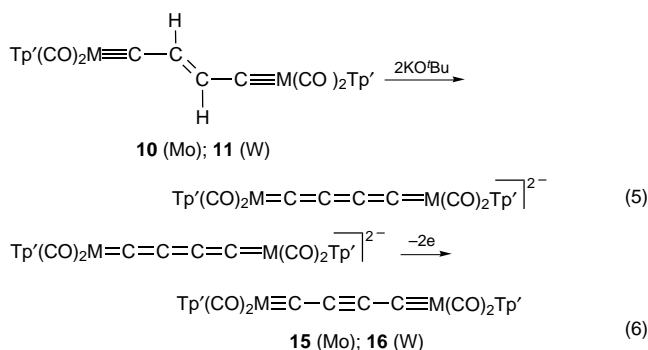
(23) For [Tp'(CO)<sub>2</sub>W≡CC=CC=W(CO)<sub>2</sub>Tp'] (**16**): IR (KBr) 1987, 1958, 1878 cm<sup>-1</sup> (ν<sub>WC=O</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 243.7 (W≡C-), 88.0 (-C=C-).



**Figure 1.** ORTEP diagram of Tp'(CO)<sub>2</sub>W≡CC(CH<sub>3</sub>)=C(CH<sub>3</sub>)C≡W(CO)<sub>2</sub>Tp' (**12**).

oxidative coupling of two ruthenium ethynyl monomers and then removed two electrons to form a cumulene dication.<sup>3c</sup> We have been able to form a biscarbyne C<sub>4</sub>-bridged dimer directly from the parent olefin complexes **10** and **11**.

Both olefinic hydrogens can be removed from the parent olefin complexes **10** and **11** to form a dianion with a cumulene-like bridge (eq 5). In an NMR experiment, dark green complex **10** and 2 equiv of KO<sup>t</sup>Bu in THF formed an intensely colored blue-green solution. Formation of a dianionic, C<sub>4</sub>-cumulene



bridge was evident in the <sup>13</sup>C NMR spectrum. Resonances at 280 and 258 ppm (singlets, Mo=C=C=C=C=Mo) along with resonances indicating a single Tp' ligand environment with a mirror plane of symmetry characterize the {K}<sub>2</sub>{[Mo]=C=C=C=C=[Mo]}<sup>21</sup> (**14**) product. Oxidation of this dianion yields the neutral C<sub>4</sub>-bridged dimer, [Mo]=CC=CC=[Mo]<sup>22</sup> (eq 6). Carbon-13 resonances at 249 ppm (Mo≡C) and 107 ppm (C≡C) characterize the C<sub>4</sub> bridge.

We have been able to access the unusual M=CC=CC=M framework<sup>23</sup> by stepwise proton removal and subsequent oxidation to effect net dihydrogen removal from the original -CH<sub>2</sub>CH<sub>2</sub>- linkage to form -CH=CH- and -C≡C- tethers between the two robust metal carbyne moieties. The role of the metal centers in housing the negative charges at the intermediate dianion stage is essential to the oxidation sequence that we have achieved.

**Acknowledgment.** We thank the Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences (DE-FG02-96ER14608) and the National Science Foundation (CHE-9208207) for generous support of this work.

**Supporting Information Available:** Complete crystallographic data for **12**, experimental details, and characterization data for the compounds described in the text (15 pages). See any current masthead page for ordering and Internet access instructions.

JA963662Q