7418 J. Am. Chem. Soc. **1996,** *118,* 7418−7419

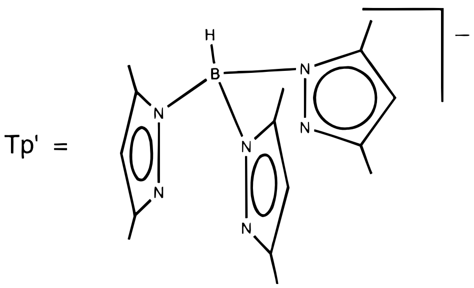
Dinuclear Molybdenum and Tungsten C_3-Bridged Complexes with Metal−Carbon Multiple Bonds

B. E. Woodworth and J. L. Templeton*

W. R. Kenan, Jr., Laboratory
Department of Chemistry
The University of North Carolina
Chapel Hill, North Carolina 27599-3290

Received March 22, 1996

Organometallic complexes with metal centers joined by C_n bridges, where $n = 1-6$ and 8, have been reported.[1−7] The recent review of hydrocarbon bridges in transition metal complexes by Beck is particularly relevant to the work described here.[7a] In this Communication we report the synthesis and characterization of complexes which have C_3 bridging units with metal−carbon triple bonds. In particular, methylene-bridged biscarbyne molecules serve as vehicles to prepare C_3-bridged complexes $Tp'(CO)_2Mo{\equiv}C\text{-}C{\equiv}CMo(O)_2Tp'$, $Tp'(CO)_2W{\equiv}CC{\equiv}CMo(O)_2Tp'$, and $Tp'(O)_2WC{\equiv}CC{\equiv}Mo(CO)_2Tp'$ (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate) as well as the ketone complex $Tp'(CO)_2W{\equiv}CC(O)C{\equiv}Mo(CO)_2Tp'$.



Examples of metals bridged by a C_3 unit have only recently been communicated.[3] Gladysz reported the synthesis of mixed-metal complexes with a C_3 bridge which takes advantage of the nucleophilic nature of $Cp^*(CO)_3ReC{\equiv}CLi$ and utilizes Fischer carbene to carbyne conversion chemistry.[3a] The C_3-bridged complex $[Cp^*(CO)_3ReC{\equiv}CC{\equiv}Mn(CO)_2Cp]^+[BF_4]^-$ also reflects a contribution from the cumulene resonance form $[Cp^*(CO)_3Re{=}C{=}C{=}C{=}Mn(CO)_2Cp]^+[BF_4]^-$.

A C_3 skeleton linking two metals can be assembled from complementary carbyne reagents. Metal vinylidene complexes $L_nM{=}C{=}CRR'$ are nucleophilic at the carbon β to the metal.[8] Deprotonation of $Tp'(CO)_2Mo{\equiv}CCH_3$ generates a vinylidene anion, observed by IR and NMR spectroscopies,[9] which reacts with electrophiles to yield derivative carbyne complexes.[10] Reaction of this molybdenum vinylidene anion with $Tp'(CO)_2Mo{\equiv}CCl$ (**1**),[11] known to undergo nucleophilic substitution of chloride,[10a] yields the yellow dimeric complex $Tp'(CO)_2Mo{\equiv}CCH_2C{\equiv}Mo(CO)_2Tp'$ (**2**)[12] (eq 1). Four metal−carbonyl stretches are observed in the IR spectrum (ν_{CO} = 2008, 1985, 1910, 1900 cm^{-1}). Diagnostic NMR signals include a singlet at 4.27 ppm (2 H, $-CH_2-$) in the ^1H NMR spectrum and signals at 284.7 ppm (t, $^2J_{CH}$ = 8 Hz, $Mo{\equiv}CCH_2C{\equiv}Mo$) and 68.5 ppm (t, $^1J_{CH}$ = 130 Hz, $Mo{\equiv}CCH_2C{\equiv}Mo$) in the ^{13}C NMR spectrum. A 2:1 NMR pattern for the Tp′ pyrazole rings reflects the presence of a molecular mirror plane.

$$\mathrm{Tp'(CO)_2M{\equiv}C\text{-}CH_3 + Tp'(CO)_2Mo{\equiv}C\text{-}Cl \xrightarrow[2)\ H^+]{1)\ KOBu^t} Tp'(CO)_2M{\equiv}C\text{-}CH_2\text{-}C{\equiv}Mo(CO)_2Tp'} \qquad (1)$$

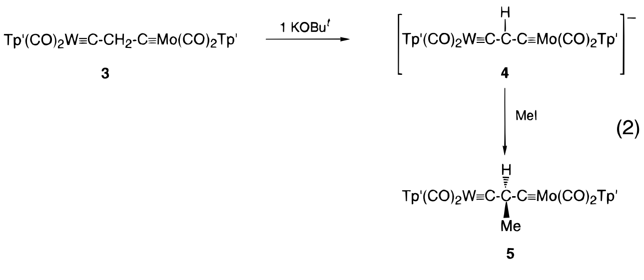
1

2, M = Mo
3, M = W

This simple synthetic route provides access to dinuclear complexes with different metals. Reaction of the tungsten vinylidene anion $[Tp'(CO)_2W{=}C{=}CH_2]^-$ with **1** forms a bright yellow, methylene-bridged complex, $Tp'(CO)_2W{\equiv}CCH_2C{\equiv}Mo(CO)_2Tp'$ (**3**)[13] (eq 1). Four carbonyl stretches are observed in the IR spectrum (ν_{CO} = 1986, 1973, 1894, 1878 cm^{-1}). There is a mirror plane of symmetry in the NMR spectra with distinct Tp′ signals for each half of the molecule. The $-CH_2-$ proton signal appears at 4.21 ppm ($^3J_{WH}$ = 7 Hz) while the methylene carbon resonates at 70 ppm (t, $^1J_{CH}$ = 129 Hz, $^2J_{WC}$ = 41 Hz). The $-CH_2-$ unit is relatively acidic[14] due to resonance stabilization of the anion.

$$\mathrm{Tp'(CO)_2W{\equiv}C\text{-}CH{=}C{=}\overset{-}{Mo}(CO)_2Tp'} \longleftrightarrow \mathrm{Tp'(CO)_2\overset{-}{W}{=}C{=}CH\text{-}C{\equiv}Mo(CO)_2Tp'}$$

Reaction of **3** with 1 equiv of $KOBu^t$ yields the $[Tp'(CO)_2W{\equiv}CCHC{\equiv}Mo(CO)_2Tp']^{1-}$ anion (**4**)[15] (eq 2) which can be observed in the ^{13}C NMR spectrum. The carbyne carbons appear as doublets at 313.7 and 298.1 ppm with $^2J_{CH}$ = 4.9 and 3.6 Hz, respectively. The central carbon is a doublet at 129.1 ppm



3 **4** **5**

(2)

---

[1] C₁ bridges: Beck, W.; Knauer, W.; Robl, C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 318−320. Etienne, M.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1991**, *113*, 2324−2325.

[2] C_2 bridges: Koutsantonis, G. A.; Selegue, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 2316−2317. Lemke, F. R.; Szalda, D. J.; Bullock, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 8466−8477. Ramsden, J. A.; Weng, W.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 5890−5891.

[3] C_3 bridges: (a) Weng, W.; Ramsden, J. A.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 3824−3825. (b) Weng, W.; Arif, A. M.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 891−892.

[4] C_4 bridges: (a) Wong, A.; Kang, P. C. W.; Tagge, C. D.; Leon, D. R. *Organometallics* **1990**, *9*, 1992−1994. (b) Fyfe, H. B.; Mlekuz, M.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1991**, 188−190. (c) Stang, P. J.; Tykwinski, R. *J. Am. Chem. Soc.* **1992**, *114*, 4411−4412. (d) Crescenzi, R.; Sterzo, C. L. *Organometallics* **1992**, *11*, 4301−4305. (e) Zhou, Y.; Seyler, J. W.; Weng, W.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 8509−8510. (f) Rappert, T.; Nürnberg, O.; Werner, H. *Organometallics* **1993**, *12*, 1359−1364. (g) Bruce, M. I.; Hinterding, P.; Tiekink, E. R. T.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1993**, *450*, 209−218. (h) Sonogashira, K.; Kataoka, S.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1978**, *160*, 319−327. (i) Le Narvor, N.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1993**, 357−359. (j) Seyler, J. W.; Weng, W.; Zhou, Y.; Gladysz, J. A. *Organometallics* **1993**, *12*, 3802−3804. (k) Le Narvor, N.; Toupet, L.; Lapinte, C. *J. Am. Chem. Soc.* **1995**, *117*, 7129−7138.

[5] C_5 bridges: Weng, W.; Bartik, T.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2199−2202.

[6] C_6 and C_8 bridges: (a) Brady, M.; Weng, W.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1994**, 2655−2656. (b) Coat, F.; Lapinte, C. *Organometallics* **1996**, *15*, 477−479.

[7] General references: (a) Beck, W.; Niemer, B.; Wieser, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 923−949. (b) Lang, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 547−550.

[8] Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59−128.

[9] Brower, D. C.; Stoll, M.; Templeton, J. L. *Organometallics* **1989**, *8*, 2786−2792.

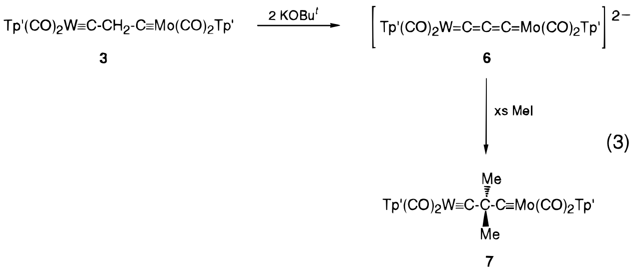
[10] (a) Chaona, S.; Lalor, F. J.; Ferguson, G.; Hunt, M. M. *J. Chem. Soc., Chem. Commun.* **1988**, 1606−1608. (b) Beevor, R. G.; Freeman, M. J.; Green, M.; Morton, C. E.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, 68−70.

[11] Desmond, T.; Lalor, F. J.; Ferguson, G.; Parvez, M. *J. Chem. Soc., Chem. Commun.* **1983**, 457−459.

[12] $Tp'(CO)_2Mo{\equiv}CCH_2C{\equiv}Mo(CO)_2Tp'$ (2). Yield: 68%. IR (KBr): 2008, 1985, 1910, 1900 cm^{-1} (ν_{Mo-CO}). ^1H NMR (250 MHz, $CDCl_3$): δ 4.27 (s, 2 H, CCH_2C). ^{13}C NMR (100.56 MHz, $CDCl_3$): δ 284.7 (t, $^2J_{CH}$ = 8 Hz, $Mo{\equiv}C-$), 225.1 (s, $MoC{\equiv}O$), 68.5 (t, $^1J_{CH}$ = 130 Hz). Anal. Calcd for $B_2C_{37}H_{46}N_{12}Mo_2O_4$: C, 47.46; H, 4.95; N, 17.95. Found: C, 47.63; H, 4.99; N, 17.73.

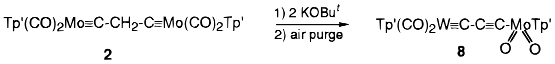
with $^1J_{\mathrm{CH}} = 152$ Hz. Addition of MeI to this anion yields the monomethylated product $\mathrm{Tp'(CO)_2W{\equiv}CCH(Me)C{\equiv}Mo(CO)_2Tp'}$ (**5**)[16] (eq 2). The added methyl appears as a doublet at 1.7 ppm, and the methine proton is a quartet at 4.2 ppm in the ^{1}H NMR spectrum ($^3J_{\mathrm{HH}} = 7$ Hz); disruption of the mirror symmetry leads to six unique signals for the aromatic Tp′ pyrazole protons, and all of the Tp′ methyl signals are also distinct.

Surprisingly, 2 equiv of KOBu^t removes both protons from the bridging carbon to form a dianion, $\mathrm{[Tp'(CO)_2W{=}C{=}C{=}C{=}Mo(CO)_2Tp']^{2-}}$ (**6**)[17] (eq 3). In the ^{1}H NMR spectrum (THF-d^8), two distinct sets of Tp′ signals are observed with retention of a molecular mirror plane. The ^{13}C NMR spectrum supports the dianion assignment with metal-bound carbon resonances at 238.4, 234.4, 230.4, and 226.9 ppm (s, W=*C*=C, Mo=*C*=C, W*C*≡O and Mo*C*≡O) along with the central carbon at 153.8 ppm (s, W=C=*C*=C=Mo). Acid regenerates starting material while addition of excess MeI yields the dimethylated complex $\mathrm{Tp'(CO)_2W{\equiv}CC(Me)_2C{\equiv}Mo(CO)_2Tp'}$ (**7**)[18] (eq 3). There is a mirror plane of symmetry evident in the NMR spectra with the central methyls appearing at 1.78 ppm in the ^{1}H NMR spectrum and at 27.3 ppm (qq, $^1J_{\mathrm{CH}} = 130$ Hz, $^2J_{\mathrm{CH}} = 4$ Hz, CC(CH$_3$)$_2$C) in the ^{13}C NMR spectrum. The central carbon resonates at 75.6 ppm (C*C*(Me)$_2$C) while carbyne signals appear at 298 (s, Mo≡*C*−) and 295 (s, $^1J_{\mathrm{WC}} = 195$ Hz, W≡*C*−).



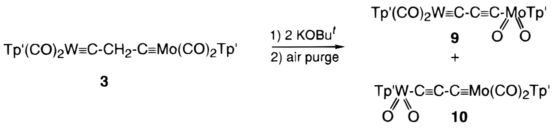
(3)

Treating **2** with 2 equiv of KOBu^t followed by exposure to air yields the green mixed-valent dimer $\mathrm{Tp'(CO)_2Mo{\equiv}CC{\equiv}CMo(O)_2Tp'}$ (**8**)[19] (eq 4). Here a Mo(II) metal center is connected to a Mo(VI) metal center through a $\mathrm{C_3}$ bridge. Carbonyl stretching frequencies are $\nu_{\mathrm{Mo-CO}} = 1983$ and 1897 cm^{-1}, and metal−oxo stretches are at $\nu_{\mathrm{Mo=O}} = 928$ and 895 cm^{-1}. Two distinct sets of Tp′ signals, each indicating a mirror plane, are observed in the ^{1}H and ^{13}C NMR spectra. Signals at 252.8 (Mo≡*C*−) and 122.7 and 113.9 (Mo≡C*C*≡*C*Mo) ppm in the ^{13}C NMR spectrum characterize this $\mathrm{C_3}$ bridge.

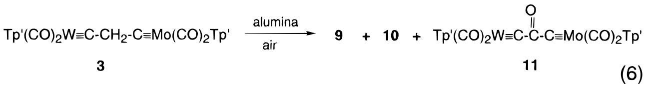


(4)

Similarly, in the presence of base, **3** can be oxidized with air to form two new bimetallic complexes which can be separated by column chromatography (eq 5). The major product is $\mathrm{Tp'(CO)_2W{\equiv}CC{\equiv}CMo(O)_2Tp'}$ (**9**),[20] a green solid which is brown in solution. Carbonyl stretching frequencies are $\nu_{\mathrm{W-CO}} = 1971$ and 1877 cm^{-1}, and metal-oxo stretches come at $\nu_{\mathrm{Mo=O}} = 925$ and 892 cm^{-1}. In the ^{13}C NMR spectrum, signals at 246 ppm (W≡*C*−) and 130 and 120 ppm (W≡C*C*≡*C*Mo) mimic the dimolybdenum ^{13}C NMR chemical shifts. A minor product in this reaction is $\mathrm{Tp'(O)_2WC{\equiv}CC{\equiv}Mo(CO)_2Tp'}$ (**10**)[21] (green, $\nu_{\mathrm{Mo-CO}} = 1985$, 1904 cm^{-1}, $\nu_{\mathrm{W=O}} = 947$, 904 cm^{-1}). Oxidation of **3** with air during chromatography on alumina also leads to the formation of minor amounts of **9** and **10** along with a small amount of a third product, the ketone-bridged complex $\mathrm{Tp'(CO)_2W{\equiv}CC(O)C{\equiv}Mo(CO)_2Tp'}$ (**11**)[22] (green, $\nu_{\mathrm{CO}} = 2016$, 1991, 1928, 1906 cm^{-1}) (eq 6). A signal at 183 ppm in the ^{13}C NMR is diagnostic for the ketone.[23] In a more rational synthesis, ketone **11** was prepared by reaction of **6** with 2-(phenylsulfonyl)-3-phenyloxaziridine[24] followed by treatment with HCl. Oxidation of the methylene bridge to a ketone is possible due to activation by the flanking carbyne units.



(5)



(6)

High-yield formation of $\mathrm{Tp'(CO)_2M{\equiv}CCH_2C{\equiv}Mo(CO)_2Tp'}$ provides an exciting generator for derivative dinuclear chemistry with three carbon atoms linking two metals.

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

Supporting Information Available: Experimental details and characterization data for the compounds described in the text (7 pages). See any current masthead page for ordering and Internet access instructions.

JA960940C

---

(13) $\mathrm{Tp'(CO)_2W{\equiv}CCH_2C{\equiv}Mo(CO)_2Tp'}$ (**3**). Yield: 58%. IR (KBr): 1986, 1973, 1894, 1878 cm^{-1}. (ν_{CO}). ^{1}H NMR (250 MHz, CDCl$_3$): δ 4.21 (s, 2 H, $^3J_{\mathrm{WH}} = 7$ Hz, C*C*H_2C). ^{13}C NMR (100.56 MHz, CDCl$_3$): δ 287.5 (s, Mo≡*C*−), 273.5 (s, W≡*C*−), 225.0 (s, Mo*C*≡O), 223.2 (s, W*C*≡O), 70.1 (t, $^1J_{\mathrm{CH}} = 129$ Hz, $^2J_{\mathrm{WC}} = 41$ Hz, C*C*H$_2$C). Anal. Calcd for $\mathrm{B_2C_{37}H_{46}N_{12}MoO_4W}$: C, 43.39; H, 4.53; N, 16.41. Found: C, 43.50; H, 4.51; N, 16.31.

(14) The −CH$_2$− protons of **4** in the presence of Et$_3$N exchanged with added D$_2$O to give −CD$_2$− within 15 min.

(15) $\mathrm{[K][Tp'(CO)_2W{\equiv}CCHC{\equiv}Mo(CO)_2Tp']}$ (**4**). ^{13}C NMR (100.56 MHz, THF, C$_6$D$_6$): δ 313.7 (d, $^2J_{\mathrm{CH}} = 4.9$ Hz, Mo≡*C*−) 298.1 (d, $^2J_{\mathrm{CH}} = 3.6$ Hz, W≡*C*−), 231.4 (s,$^1J_{\mathrm{WC}} = 172$ Hz, W*C*≡O), 229.6 (s, Mo*C*≡O), 129.1 (d, $^1J_{\mathrm{CH}} = 152$ Hz, C*C*HC).

(16) $\mathrm{Tp'(CO)_2W{\equiv}CCH(CH_3)C{\equiv}Mo(CO)_2Tp'}$ (**5**). Yield: 27%. IR (KBr): 1982, 1968, 1886, 1874 cm^{-1} (ν_{CO}). ^{1}H NMR (250 MHz, CD$_2$Cl$_2$): δ 4.25 (q, 1 H, $^3J_{\mathrm{HH}} = 7$ Hz, $^3J_{\mathrm{WH}} = 4$ Hz, CC*H*(CH$_3$)C), 1.70 (d, 3 H, $^3J_{\mathrm{HH}} = 7$ Hz, CCH(C*H*$_3$)C); ^{13}C NMR (100.56 MHz, CD$_2$Cl$_2$): δ 294.6 (s, Mo≡*C*−), 281.0 (s, W≡*C*−), 226.6, 225.3, 224.5, 223.3 (s, 2 W*C*≡O, 2 Mo*C*≡O), 74.3 (dq, $^1J_{\mathrm{CH}} = 129$ Hz, $^3J_{\mathrm{CH}} = 5$ Hz, $^2J_{\mathrm{WC}} = 38$ Hz, C*C*H(CH$_3$)C); the added methyl signal appears with the Tp′ methyls between 17.4 and 12.8 ppm.

(17) $\mathrm{[K]_2[Tp'(CO)_2W{=}\mathbf{C}{=}C{=}C{=}Mo(CO)_2Tp']}$ (**6**). ^{13}C NMR (100.56 MHz, THF, C$_6$D$_6$): δ 238.4, 234.4, 230.4, 226.9 (s, W=*C*−, Mo=*C*−, W*C*≡O, Mo*C*≡O), 153.8 (s, Mo=C=*C*=C=W).

(18) $\mathrm{Tp'(CO)_2W{\equiv}CC(CH_3)_2C{\equiv}Mo(CO)_2Tp'}$ (**7**). Yield: 52%; IR (KBr): 1985, 1970, 1893, 1874 cm^{-1} (ν_{CO}). ^{1}H NMR (250 MHz, CDCl$_3$): δ 1.78 (s, 6 H, CC(C*H*$_3$)$_2$C); ^{13}C NMR (100.56 MHz, CDCl$_3$): δ 298 (s, Mo≡*C*−), 285 (s, $^1J_{\mathrm{WC}} = 195$ Hz, W≡*C*−), 226 (s, Mo*C*≡O), 224 (s, $^1J_{\mathrm{WC}} = 170$ Hz, W*C*≡O), 75.6 (m, C*C*(Me)$_2$C), 27.3 (qq, $^1J_{\mathrm{CH}} = 130$ Hz, $^3J_{\mathrm{CH}} = 4$ Hz). Anal. Calcd for $\mathrm{B_2C_{39}H_{50}N_{12}MoO_4W}$: C, 44.51; H, 4.79; N, 15.97. Found: C, 44.57; H, 4.80; N, 15.86.

(19) $\mathrm{Tp'(CO)_2Mo{\equiv}CC{\equiv}CMo(O)_2Tp'}$ (8). Yield: 84%. IR (KBr): 1983, 1897 cm^{-1} ($\nu_{\mathrm{Mo-CO}}$), 928, 895 cm^{-1} ($\nu_{\mathrm{Mo=O}}$). ^{13}C NMR (100.56 MHz, CDCl$_3$): 252.8 (s, Mo≡*C*−), 228.1 (s, Mo*C*O), 122.7, 113.9 (s, Mo*C*≡*C*C≡Mo). Anal. Calcd for $\mathrm{B_2C_{35}H_{44}N_{12}Mo_2O_4}$: C, 46.18; H, 4.87; N, 18.46. Found: C, 46.42; H, 4.94; N, 18.19.

(20) $\mathrm{Tp'(CO)_2W{\equiv}CC{\equiv}CMo(O)_2Tp'}$ (**9**). Yield: 69%. IR (KBr): 1971, 1877 cm^{-1} ($\nu_{\mathrm{W-CO}}$), 925, 892 cm^{-1} ($\nu_{\mathrm{Mo=O}}$). ^{13}C NMR (100.56 MHz, CDCl$_3$): δ 246 (s, W≡*C*−), 226 (s, $^1J_{\mathrm{WC}} = 160$ Hz,W*C*≡O), 129.9, 120.1 (s, Mo*C*≡*C*C≡W). Anal. Calcd for $\mathrm{B_2C_{35}H_{44}N_{12}MoO_4W}$: C, 42.11; H, 4.44; N, 16.84. Found: C, 42.16; H, 4.47; N, 16.64.

(21) $\mathrm{Tp'(O)_2WC{\equiv}CC{\equiv}Mo(CO)_2Tp'}$ (**10**). Yield: 5%. IR (KBr): 1985, 1904 cm^{-1} ($\nu_{\mathrm{Mo-CO}}$), 947, 904 cm^{-1} ($\nu_{\mathrm{W=O}}$). ^{13}C NMR (100.56 MHz, CDCl$_3$): δ 253 (s, Mo≡*C*−), 228 (s, Mo*C*O), 124.4, 119.9 (s, W*C*≡*C*C≡Mo).

(22) $\mathrm{Tp'(CO)_2W{\equiv}CC(O)C{\equiv}Mo(CO)_2Tp'}$ (**11**). Yield: 17% (with the Davis oxaziridine reagent). IR (KBr): 2016, 1991, 1928, 1906 cm^{-1} (ν_{CO}). ^{13}C NMR (100.56 MHz, CDCl$_3$): δ 282.3, 274.3 (s, W≡*C*− and Mo≡*C*−), 227.0 (s, Mo*C*O), 225.7 (s, $^1J_{\mathrm{WC}} = 162$ Hz, W*C*O), 183.3 (s, C*C*(=O)C). Anal. Calcd for $\mathrm{B_2C_{37}H_{44}N_{12}MoO_5W}$: C, 42.80; H, 4.27; N, 16.19. Found: C, 42.67; H, 4.27; N, 16.07.

(23) Stretches $\nu_{\mathrm{C\equiv C}}$ for **8**, **9**, and **10** and $\nu_{\mathrm{C=O}}$ for **11** were not observed upon inspection of the infrared spectra.

(24) Davis, F. A.; Stringer, O. D. *J. Org. Chem.* **1982**, *47*, 1774−1775.