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# Monomeric and Dinuclear Tungsten Carbyne Complexes Containing Benzyl, Allyl, and Alkenyl Carbyne Substituents

Alejandro E. Enriquez and Joseph L. Templeton*

*Department of Chemistry, University of North Carolina at Chapel Hill,*
*Chapel Hill, North Carolina 27599-3290*

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The phosphonium carbyne complexes $[Tp'(CO)_2W{\equiv}CPMe_2Ph]^+$ ($Tp'$ = hydridotris(3,5-dimethylpyrazolyl)borate) add the Grignard reagents $PhCH_2MgCl$ and $CH_2{=}CHCH_2MgCl$ at $C_\alpha$ to generate the zwitterionic carbene complexes $Tp'(CO)_2W{=}C(CH_2R)(Me_2Ph)$ ($R = Ph$, $CH{=}CH_2$) as intermediates which lose $PMe_2Ph$ to form neutral $Tp'(CO)_2W{\equiv}CCH_2R$ ($R = Ph$, $CH{=}CH_2$) carbyne complexes. Deprotonation of these carbyne complexes with strong base occurs at $C_\beta$ to form the reactive vinylidene anions $[Tp'(CO)_2W{=}C{=}C(H)(R)]^-$, which have been characterized by IR and NMR spectroscopy. The phenylvinylidene anion $[Tp'(CO)_2W{=}C{=}C(H)(Ph)]^-$ adds electrophiles at $C_\beta$, and the vinylvinylidene anion $[Tp'(CO)_2W{=}CCHCH{=}CH_2]^-$ reacts with MeI at $C_\beta$ to generate $Tp'(CO)_2W{\equiv}CCH(CH_3)(CH{=}CH_2)$. Treatment of this chiral carbyne complex with $^nBuLi$ generated the $[Tp'(CO)_2W{=}C{=}C(CH_3)CH{=}CH_2]^-$ anion, which reacts with MeI primarily at $C_\beta$ to form $Tp'(CO)_2W{\equiv}CC(CH_3)_2CH{=}CH_2$, although some methylation occurs at $C_\delta$ to generate the conjugated carbyne $Tp'(CO)_2W{\equiv}CC(CH_3){=}C(H)(CH_2CH_3)$. Isomerization of the allyl carbyne complex $Tp'(CO)_2W{\equiv}CCH_2CH{=}CH_2$ to a 4:1 mixture of *E* and *Z* vinyl carbyne $Tp'(CO)_2W{\equiv}CC(H){=}C(H)(CH_3)$ isomers was achieved through addition of $NEt_3$ to the allyl carbyne complex; the same mixture of isomers resulted from quenching a THF solution of $[Tp'(CO)_2W{=}C{=}CH(CH{=}CH_2)]^-$ with water. Quenching $[Tp'(CO)_2W{=}C{=}C(CH_3)CH{=}CH_2]^-$ with water generated $Tp'(CO)_2W{\equiv}CC(CH_3){=}C(H)(CH_3)$, the vinyl carbyne isomer of $Tp'(CO)_2W{\equiv}CC(H)(CH_3)CH{=}CH_2$. Parallels between organic nitriles ($N{\equiv}CR$) and the tungsten carbyne moiety ($W{\equiv}CR$) are evident in this work. Addition of $[Tp'(CO)_2W{\equiv}CPMe_2Ph]^+$ to the parent vinylvinylidene anion occurs at $C_\delta$ and forms a reactive zwitterionic phosphonium carbene intermediate that loses $PMe_2Ph$ to form the dinuclear bis(carbyne) compound $Tp'(CO)_2W{\equiv}CCH_2CH{=}CHC{\equiv}W(CO)_2Tp'$ as a 3.5:1 mixture of *E* and *Z* isomers. Deprotonation of $Tp'(CO)_2W{\equiv}CCH_2CH{=}CHC{\equiv}W(CO)_2Tp'$ forms the deep blue, anionic $[Tp'(CO)_2W{\equiv}CC(H)C(H)C(H)C{\equiv}W(CO)_2Tp']^-$ complex. The visible spectrum of this anion shows low-energy absorptions at 596 and 798 nm with extinction coefficients of approximately $8.0 \times 10^4\ cm^{-1}\ M^{-1}$.

## Introduction

Few general synthetic routes to transition-metal carbyne complexes have been developed.[1−4] Fischer prepared the first carbyne complexes by electrophilic abstraction of methoxide from a methoxymethylcarbene complex,[5] and oxide removal from acylmetalate complexes[6,7] is a similar route to carbyne complexes.[8,9] High-valent Schrock-type carbynes have been prepared by deprotonation of an alkylidene at $C_\alpha$, by oxidative addition of an alkylidene α-CH bond to a metal center,[10] and by metathesis between alkynes and ditungsten hexaalkoxides.[11,12] Proton addition to the $C_\beta$ site of acetylide, allenylidene, vinyl, and vinylidene complexes is also a versatile route to carbyne complexes.[1,2,13−18]

Construction of the metal−carbon triple bond in $Tp'(CO)_2M{\equiv}CCl$ (**1**; M = Mo, W) via oxidation of $[Et_4N]$-

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[1] Fischer, H.; Hofman, P.; Kreissl, F. R.; Schrock, R. R.; Schubert, U.; Weiss, K. *Carbyne Complexes*; VCH: New York, 1988.

[2] Kreissl, F. R. *Transition Metal Carbyne Complexes*; Kluwer: Boston, MA, 1993.

[3] Herndon, J. W. *Coord. Chem. Rev.* **1999**, *181*, 177−242.

[4] Herndon, J. W. *Coord. Chem. Rev.* **2000**, *209*, 387−451.

[5] Fischer, E. O.; Kreis, G.; Kreiter, C. G.; Müller, J.; Huttner, G.; Lorenz, H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 564−565.

[6] Fischer, H.; Fischer, E. O. *J. Organomet. Chem.* **1974**, *69*, C1−C3.

[7] Himmelreich, D.; Fischer, E. O. *Z. Naturforsch.* **1982**, *37B*, 1218.

[8] Mayr, A.; McDermott, G. A.; Dorries, A. M. *Organometallics* **1985**, *4*, 608−610.

[9] McDermott, G. A.; Dorries, A. M.; Mayr, A. *Organometallics* **1987**, *6*, 925−931.

[10] Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210−3222.

[11] Listemann, M. L.; Schrock, R. R. *Organometallics* **1985**, *4*, 74−83.

[12] Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6806−6815.

[13] Kim, H. P.; Angelici, R. J. *Adv. Organomet. Chem.* **1987**, *27*, 51−111.

[14] Mayr, A.; Hoffmeister, H. *Adv. Organomet. Chem.* **1991**, *32*, 227−324.

[15] Pourreau, D. B.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1985**, *24*, 249−352.

[16] Buhro, W. E.; Chisholm, M. H. *Adv. Organomet. Chem.* **1987**, *27*, 311−369.

[17] Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds*; Wiley: New York, 1988.

[18] Engel, P. F.; Pfeffer, M. *Chem. Rev.* **1995**, *95*, 2281−2309.

10.1021/om010549m CCC: \$22.00
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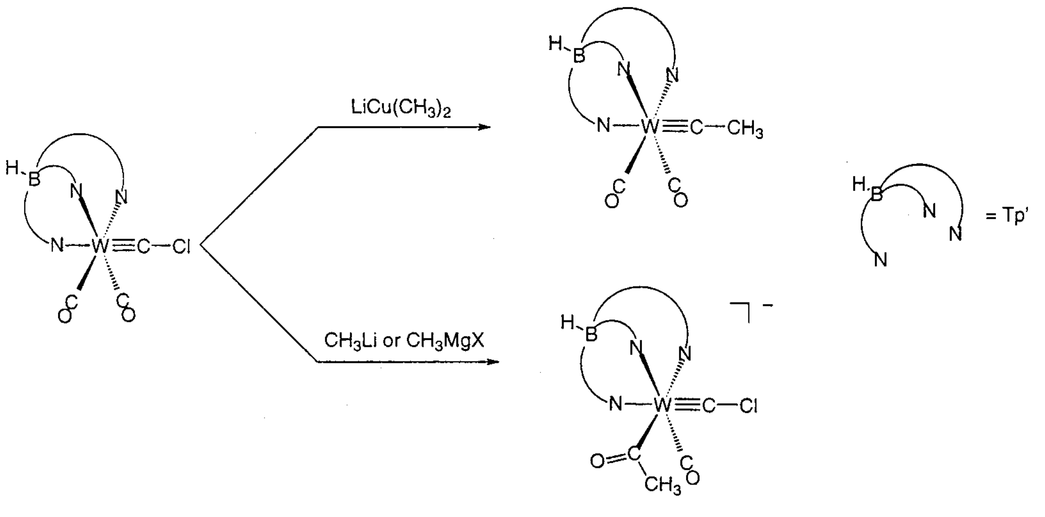
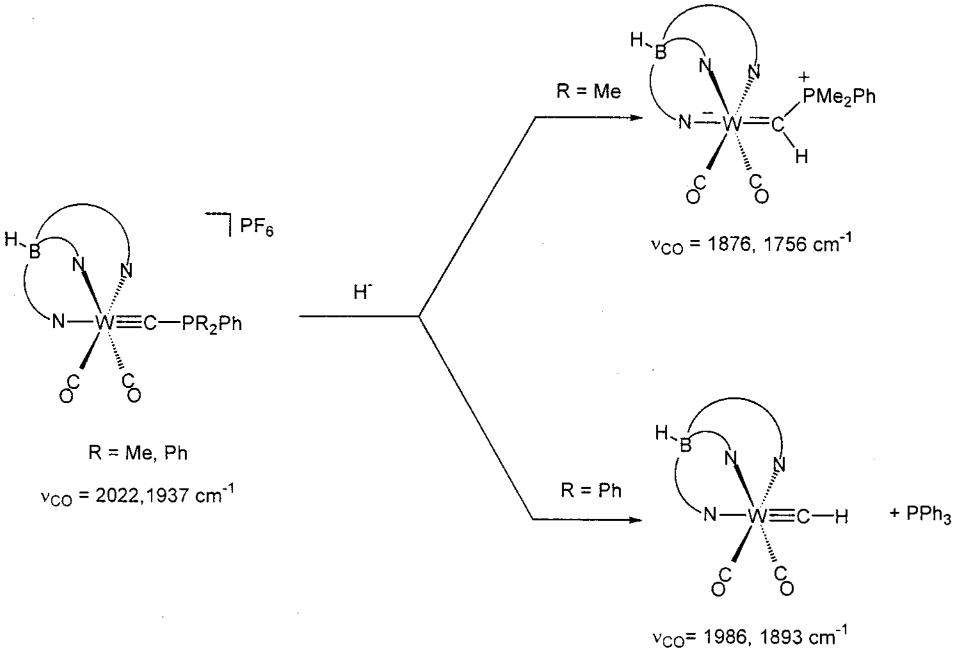
**Scheme 1. Reactivity of $Tp'(CO)_2W{\equiv}CCl$ with Organometallic Methyl Reagents**



**Scheme 2. Reactivity of $[Tp'(CO)_2W{\equiv}CPR_2Ph][PF_6]$ Phosphonium Carbyne Complexes**



$[Tp'(CO)_3M]$ with $[ArN_2][BF_4]$ in $CH_2Cl_2$ is unique.[19,20] Lalor's chlorocarbyne complex has been used to prepare numerous heteroatom-substituted carbyne complexes.[21−23] Treatment of the chlorocarbyne monomer with $LiCuMe_2$ provides $Tp'(CO)_2W{\equiv}CCH_3$ (**2**),[24] but reaction of $Tp'(CO)_2W{\equiv}CCl$ with either methyllithium or methyl Grignard reagents leads to nucleophilic attack at a carbonyl ligand to form the anionic acyl complex $[Tp'(CO)(CH_3(O)C)\ W{\equiv}CCl]^-$ instead (Scheme 1).

The cationic phosphonium carbyne complexes $[Tp'(CO)_2W{\equiv}CPMe_3]^+$, $[Tp'(CO)_2W{\equiv}CPMe_2Ph]^+$, and $[Tp'(CO)_2W{\equiv}CPPh_3]^+$ can be prepared by treating $Tp'(CO)_2W{\equiv}CCl$ with the corresponding phosphine.[22] These phosphonium carbynes are susceptible to nucleophilic attack by hydride donors to form $Tp'(CO)_2W{=}C(PMe_2R)(H)$ (R = Me, Ph) carbene complexes (Scheme 2). [25] The triphenylphosphonium derivative $[Tp'(CO)_2W{\equiv}CPPh_3]^+$ forms $Tp'(CO)_2W{=}C(PPh_3)(H)$ en route to the parent methylidyne complex $Tp'(CO)_2W{\equiv}CH$.[26]

An extension of this synthetic methodology using phosphonium carbyne reagents to prepare carbyne complexes containing either a benzyl group or an allyl group bound to the carbyne carbon is described here. Deprotonation of these complexes produces reactive vinylidene anions that allow access to (1) the new alkyl carbynes $Tp'(CO)_2W{\equiv}CC(R)(R')(R'')$ ($R = H$, $R' = CH_3$, $R'' = C_6H_5$, $C_2H_3$; $R = R' = CH_3$, $R'' = C_6H_5$, $C_2H_3$), (2) the simple vinyl carbynes $Tp'(CO)_2W{\equiv}CC(R){=}C(H)$-

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(19) Lalor, F. J.; Desmond, T. J.; Cotter, G. M.; Shanahan, C. A.; Ferguson, G.; Parvez, M.; Ruhl, B. *J. Chem. Soc., Dalton Trans.* **1995**, 1709−1726.

(20) Desmond, T.; Lalor, F. J.; Ferguson, G.; Parvez, M. *J. Chem. Soc., Chem. Commun.* **1983**, 457−459.

(21) Choana, S.; Lalor, F. J.; Ferguson, G.; Hunt, M. M. *J. Chem. Soc., Chem. Commun.* **1988**, 1606−1608.

(22) Jamison, G. M.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 1954−1959.

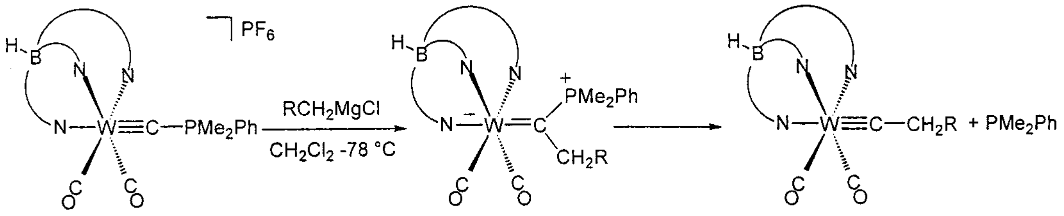
(23) Etienne, M.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1991**, *113*, 2324−2325.

(24) Woodworth, B. E.; Frohnapfel, D. S.; White, P. S.; Templeton, J. L. *Organometallics* **1998**, *17*, 1655−1662.

(25) Bruce, A. E.; Gamble, A. S.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1987**, *6*, 1350−1352.

(26) Enriquez, A.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 4992−5002.

**Scheme 3. Preparation of Benzyl- and Allyl-Substituted Carbyne Complexes**



**3**; $\nu_{CO}$ = 2023,1938 cm$^{-1}$

**4a**, R = Ph; $\nu_{CO}$ = 1864, 1733 cm$^{-1}$

**4b**, R = vinyl; $\nu_{CO}$ = 1865, 1743 cm$^{-1}$

**5**, R = Ph; $\nu_{CO}$ = 1972, 1880 cm$^{-1}$

**6**, R = vinyl; $\nu_{CO}$ = 1971, 1878 cm$^{-1}$

**Table 1. Selected $^{13}$C NMR Data[a] for Monomeric Tp′(CO)$_2$WC$_\alpha$C$_\beta$C$_\gamma$C$_\delta$ Complexes**

| complex | C$_\alpha$ | C$_\beta$ | C$_\gamma$ | C$_\delta$ | CO |
|---|---|---|---|---|---|
| [W]═CCH$_2$Ph (**5**)[b] | 287, $^1J_{WC} = 189$ | 57.5, $^1J_{CH} = 127$, $^2J_{WC} = 39$ | | | 223, $^1J_{WC} = 166$ |
| [W]═CCH$_2$CH═CH$_2$ (**6**)[b] | 288, $^1J_{WC} = 191$ | 56.0, $^1J_{CH} = 127$, $^2J_{WC} = 37$ | 132, $^1J_{CH} = 160$ | 117, $^1J_{CH} = 150$ | 223, $^1J_{WC} = 170$ |
| K{[W]═C═C(H)(Ph)} (**8**)[c] | 322, $^1J_{WC} = 162$ | 114, $^1J_{CH} = 148$, $^2J_{WC} = 36$ | | | 236, $^1J_{WC} = 174$ |
| K{[W]═C═CHCH═CH$_2$} (**9**)[c] | 326, $^1J_{WC} = 162$ | 116, $^1J_{CH} = 149$, $^2J_{WC} = 37$ | 135, $^1J_{CH} = 146$ | 95, $^1J_{CH} = 151$ | 238, $^1J_{WC} = 173$ |
| [W]═CC(H)(Me)(Ph) (**10**)[b] | 293, $^1J_{WC} = 189$ | 61.0, $^1J_{CH} = 127$, $^1J_{CH} = 37$ | | | 223.9, $^1J_{WC} = 166$;<br>223.7, $^1J_{WC} = 166$ |
| [W]═CC(Me)$_2$(Ph) (**11**)[d] | 298 | 59.4, $^2J_{WC} = 34$ | | | 225, $^1J_{WC} = 166$ |
| [W]═CC(H)(Me)CH═CH$_2$ **(12)**[d] | 293, $^1J_{WC} =188$ | 59.3, $^1J_{CH} = 115$, $^2J_{WC} = 37$ | 139, $^1J_{CH} = 155$ | 114, $^1J_{CH} = 154$ | 225, $^1J_{WC} = 166$;<br>224, $^1J_{WC} = 166$ |
| [W]═CC(Me)$_2$CH═CH$_2$ **(13)**[d] | 296 | 58.6 | 143, $^1J_{CH} = 166$ | 111, $^1J_{CH} = 155$ | 225, $^1J_{WC} = 166$ |
| [W]═CCH═C(H)(CH$_3$) (**15-*E***)[b] | 280, $^1J_{WC} = 183$ | 142, $^1J_{CH} = 153$, $^2J_{WC} = 44$ | 138, $^1J_{CH} = 156$ | 18.3, $^1J_{CH} = 127$ | 223, $^1J_{WC} = 170$ |
| [W]═CCH═C(H)(CH$_3$) (**15-*Z***)[b] | 281,$^1J_{WC} =183$ | 140, $^1J_{CH} = 154$, $^2J_{WC} = 42$ | 136, $^1J_{CH} = 156$ | 16.0, $^1J_{CH} = 125$ | 225, $^1J_{WC} = 166$ |
| [W]═CC(Me)═C(H)(CH$_3$) (**16**-*E*)[d] | 285.2 | 148.2 | 131, $^1J_{CH} = 155$ | under Tp′ | 225 |
| [W]═CC(Me)═C(H)(CH$_3$) (**16**-*Z*)[d] | 284.5 | 146.5 | 130, $^1J_{CH} = 155$ | under Tp′ | 226 |

[a] NMR data obtained at room temperature unless otherwise noted. Chemical shifts are reported in ppm and coupling constants in Hz. Some tungsten satellites were too weak to observe. [b] In CD$_2$Cl$_2$. [c] In THF-$d_8$. [d] In C$_6$D$_6$.

(CH$_3$) (R = H, CH$_3$), and (3) a dinuclear C$_5$H$_4$ bridged bis(carbyne) complex, Tp′(CO)$_2$W≡CCH$_2$CH═CHC≡W(CO)$_2$Tp′.

## Results and Discussion

**Synthesis of Tp′(CO)$_2$W≡CCH$_2$R (R = C$_6$H$_5$ (5), CH═CH$_2$ (6)).** Addition of PhCH$_2$MgCl or H$_2$C═CHCH$_2$MgCl to a red solution of [Tp′(CO)$_2$W≡CPMe$_2$Ph][PF$_6$] (**3**) resulted in a blue-green solution with IR absorptions for the two CO ligands near 1864 and 1738 cm$^{-1}$ assigned to the zwitterionic carbene intermediate Tp′(CO)$_2$W═C(PMe$_2$Ph)(CH$_2$R) (**4**), shown in Scheme 3. The analogous but more robust Tp′(CO)$_2$W═CH(PMe$_3$) complex has been previously reported.[25] Alumina chromatography and removal of PMe$_2$Ph as [PMe$_3$Ph][I] following treatment with MeI provided Tp′(CO)$_2$W≡CH$_2$R (R = Ph (**5**), vinyl (**6**)) in good yield (Scheme 3).

The $^1$H NMR spectrum of benzyl carbyne **5** displays a 2:1 pattern for the Tp′ methine protons and a 6:3:6:3 pattern for the Tp′ methyl resonances, indicating a molecular mirror plane. A singlet at 3.82 ppm has tungsten satellites ($^3J_{WH}$ = 7 Hz) that are diagnostic for the methylene hydrogens on C$_\beta$. The $^1$H NMR spectrum for the allyl carbyne complex Tp′(CO)$_2$W≡C$_\alpha$C$_\beta$H$_2$C$_\gamma$H═C$_\delta$H$_2$ **(6)** displays a similar pattern for the Tp′ ligand resonances, with additional signals due to the allyl fragment. The methylene hydrogens on C$_\beta$ for **6** resonate as a doublet at 3.28 ppm ($^3J_{HH}$ = 7 Hz, $^3J_{WH}$ = 7 Hz). The olefinic hydrogen on C$_\gamma$ is assigned to a doublet of doublet of triplets at 5.95 ppm ($^3J_{HH(trans)}$ = 17 Hz, $^3J_{HH(cis)}$ = 10 Hz, $^3J_{HH(vicinal)}$= 7 Hz). Signals for the two terminal olefinic hydrogens on C$_\delta$ appear as multiplets at 5.11 and 5.02 ppm. The $^{13}$C NMR spectra of complexes **5** and **6** both show resonances near 288 ppm ($^1J_{WC} \approx 190$ Hz) for the carbyne carbon (C$_\alpha$) and ~57 ppm ($^2J_{WC} \approx 38$ Hz) for C$_\beta$. These $^{13}$C NMR signals mimic values for C$_\alpha$ and C$_\beta$ for related alkyl carbynes.[24,26] Additional resonances at 132 and 117 ppm correspond to C$_\gamma$ and C$_\delta$, respectively, of the allyl carbyne backbone in complex **6** (Table 1).

**Deprotonation/Alkylation Reactions of Tp′(CO)$_2$W≡CCH$_2$Ph (5) and Tp′(CO)W≡CCH$_2$CH═CH$_2$ (6).** Vinylidene ligands are susceptible to electrophilic attack at the $\beta$-carbon to form carbyne derivatives.[27] Green and co-workers reported carbyne−vinylidene−carbyne interconversions for Cp(P(OMe)$_3$)$_2$Mo≡CCH$_2{}^t$Bu based on deprotonation and addition of an electrophile,[28−31] and

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(27) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197−257.

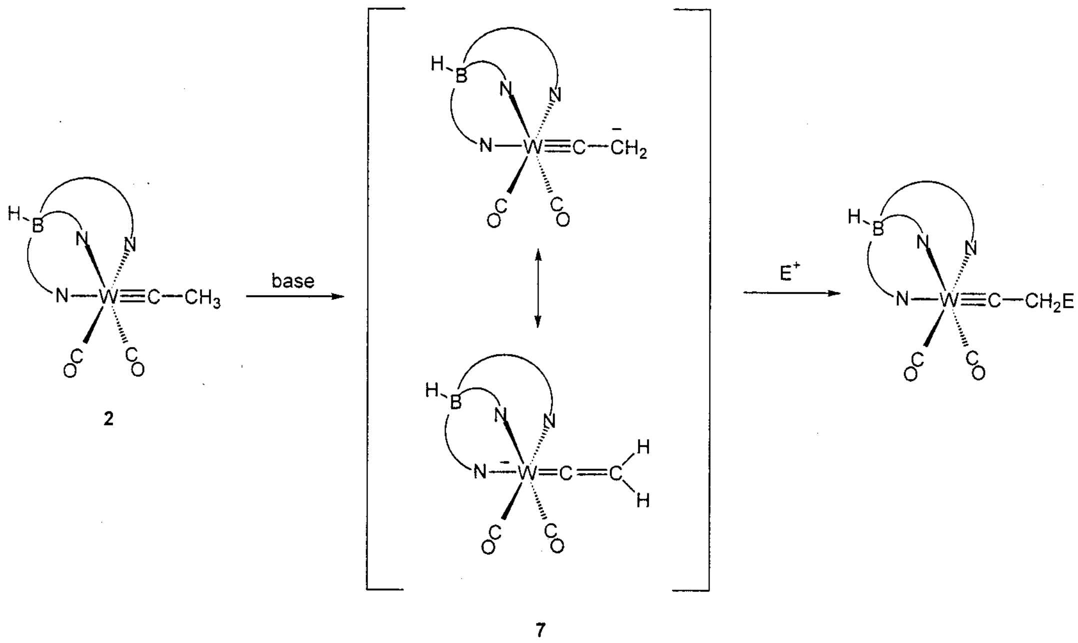
(28) Beevor, R. G.; Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1983**, 673−675.

(29) Beevor, R. G.; Freeman, M. J.; Green, M.; Morton, C. E.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, 68−70.

(30) Beevor, R. G.; Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1987**, 1319−1328.

(31) Beevor, R. G.; Freeman, M. J.; Green, M.; Morton, C. E.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1991**, 3021−3030.

**Scheme 4. Derivatization of a Methylcarbyne Complex**

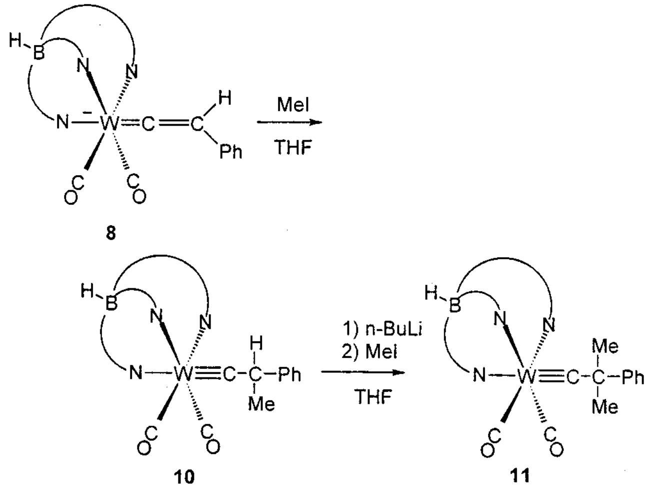


vinylidene to carbyne transformations have also been reported in other systems.[32−38] The methylcarbyne complex $Tp'(CO)_2W{\equiv}CCH_3$ can be deprotonated at $C_\beta$ to form the vinylidene anion $[Li][Tp'(CO)_2W{=}C{=}CH_2]$ (**7**), which adds electrophiles at $C_\beta$ (Scheme 4).[24]

Benzyl carbyne **5** and allyl carbyne **6** can be deprotonated by either $^{n}$BuLi or KO$^{t}$Bu to generate anionic vinylidene complexes. Both $[Tp'(CO)_2W{=}C{=}C(H)(Ph)]^-$ (**8**) and $[Tp'(CO)_2W{=}C{=}C(H)(CH{=}CH_2)]^-$ (**9**) have been characterized by infrared and NMR spectroscopy. A decrease in the CO stretching frequencies from $\nu_{CO}$ 1972, 1880 cm$^{-1}$ to $\nu_{CO}$ 1880, 1698 cm$^{-1}$ is observed when a THF solution of phenyl carbyne **5** is deprotonated with $^{n}$BuLi. This shift to lower metal carbonyl stretching frequencies reflects increased electron density on the metal in phenylvinylidene anion **8**. The $^1$H and $^{13}$C NMR spectra of **8** were obtained by dissolving solid KO$^{t}$Bu and benzylcarbyne **5** in THF-$d_8$. The key resonance in the $^1$H NMR spectrum of phenylvinylidene complex **8** is a singlet at 4.42 ppm with tungsten satellites ($^3J_{WH} = 5.6$ Hz) for the hydrogen attached to $C_\beta$. Carbon-13 signals at 322 ppm ($^1J_{WC} = 162$ Hz) and 114 ppm ($^2J_{WC} = 36$ Hz) for $C_\alpha$ and $C_\beta$ clearly indicate the presence of a vinylidene ligand. Both $^1$H and $^{13}$C spectra indicate that the molecule has mirror symmetry on the NMR time scale; therefore, the plane of the C(H)(Ph) moiety must bisect the angle between the two carbonyl ligands if the molecule is static.

The anionic vinylvinylidene complex **9** displays spectroscopic characteristics similar to those of the phenylvinylidene complex **8**. The $^1$H NMR spectrum of **9** shows separate signals for each hydrogen of the $[Li][Tp'(CO)_2W{=}C_\alpha{=}C_\beta HC_\gamma H{=}C_\delta H_2]$ vinylvinylidene backbone. The hydrogen on $C_\beta$ resonates as a doublet at 4.49 ppm ($^3J_{HH} = 10$ Hz). The hydrogen attached to $C_\gamma$ resonates downfield as a doublet of triplets at 6.60 ppm ($^3J_{HH(trans)} = 16$ Hz; $^3J_{HH(cis)} = {}^3J_{HH(vicinal)} = 10$ Hz). Each of the terminal vinylic hydrogens on $C_\delta$ appears as a doublet of doublets, one at 4.27 ppm ($^3J_{HH} = 16$ Hz, $^2J_{HH}$(geminal) = 2 Hz) and the other at 3.71($^3J_{HH} = 10$ Hz, $^2J_{HH}$(geminal) = 2 Hz). The $^{13}$C NMR spectrum of **9** shows $C_\alpha$ at 326 ppm with $^1J_{WC} = 162$ Hz, while $C_\beta$ resonates at 116 ppm with $^2J_{WC} = 37$ Hz. The signals for $C_\gamma$ and $C_\delta$ appear at 135 and 95 ppm, respectively.

**Scheme 5. Reactivity of Phenylvinylidene Anions toward Iodomethane**



Quenching the resonance-stabilized anionic complex **8** with either water or HCl regenerates the benzyl carbyne complex **5**. Treatment of a THF solution of **8** at −78 °C with MeI provides the chiral carbyne complex $Tp'(CO)_2W{\equiv}CC(H)(Me)(Ph)$ (**10**). The $^1$H NMR spectrum of **10** displays unique resonances for each of the Tp′ methine hydrogens and methyl groups due to the

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(32) Nickias, P. N.; Selegue, J. P.; Young, B. A. *Organometallics* **1988**, *7*, 2248−2250.

(33) Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1987**, *109*, 1401−1407.

(34) Carvalho, M. F. N. N.; Henderson, R. A.; Pombeiro, A. J. L.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1989**, 1796−1797.

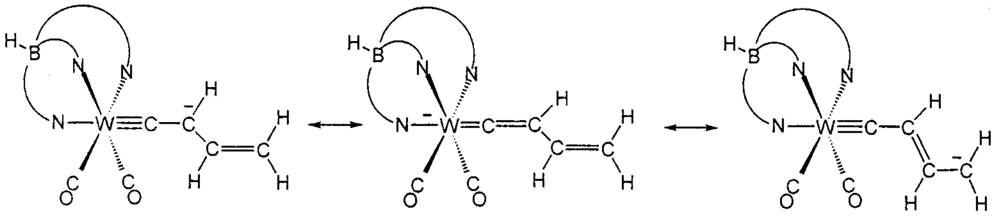
(35) Carvalho, M. F. N. N.; Almeida, S. S. P. R.; Pombeiro, A. J. L.; Henderson, R. A. *Organometallics* **1997**, *16*, 5441−5448.

(36) Pombeiro, A. J. L.; Hills, A.; Hughes, D. L.; Richards, R. L. *J. Organomet. Chem.* **1988**, *352*, C5−C7.

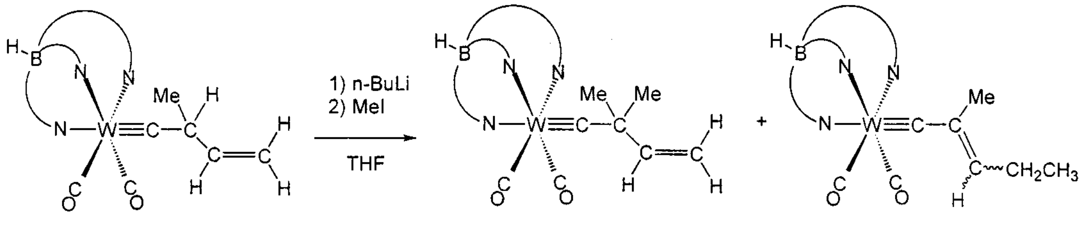
(37) Höhn, A.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 737−738.

(38) Höhn, A.; Werner, H. *J. Organomet. Chem.* **1990**, *382*, 255−272.

**Scheme 6. Resonance Structures of Vinylvinylidene Complex 9**



**Scheme 7. Reactivity of Vinylvinylidene Anions toward Iodomethane**



12 13 14 1:1 *E*:*Z*

presence of a stereogenic $\beta$-carbon. The hydrogen attached to $C_\beta$ appears at 3.94 ppm as a quartet with tungsten satellites ($^3J_{HH} = 7$ Hz, $^3J_{WH} = 7$ Hz), and the $C_\beta$ methyl group appears as a doublet at 1.67 ppm. The $^{13}C$ NMR spectrum of **10** displays a resonance at 293 ppm ($^1J_{WC} = 189$ Hz) for $C_\alpha$ and a resonance at 61 ppm with tungsten satellites ($^2J_{WC} = 37$ Hz) for $C_\beta$. Complex **10** undergoes deprotonation and methylation at $C_\beta$ to produce the $C_s$-symmetric complex $Tp'(CO)_2W{\equiv}CC(CH_3)_2Ph$ (**11**) (Scheme 5).

**Addition of Electrophiles to Vinylvinylidene $[Tp'(CO)_2W{=}C{=}C(H)(CH{=}CH_2)]^-$ (9).** Unlike the phenylvinylidene anion, where electrophilic addition to the phenyl group would destroy the aromaticity, electrophilic addition to the $C_\delta$ carbon at the terminal end of the resonance-stabilized vinylvinylidene anion **9** (Scheme 6) offers two attractive features: (1) the tungsten−carbon triple bond and the resulting olefin double bond are in conjugation and (2) a more highly substituted olefin forms relative to the parent allyl carbyne complex **6**.

Treatment of vinylvinylidene anion **9** with iodomethane provides $Tp'(CO)_2W{\equiv}CC(H)(Me)\text{-}CH{=}CH_2$ (**12**). A stereogenic center at $C_\beta$ of **12** is reflected in the NMR spectra. The methyl group attached to $C_\beta$ resonates at 1.37 ppm ($^3J_{HH} = 7$ Hz). Couplings between the hydrogen attached to $C_\beta$ and both the methyl group and the vicinal olefinic proton are identical ($^3J_{HH} = 7$ Hz), and tungsten satellites with $^3J_{WH} = 7$ Hz can also be observed for the $C_\beta$ proton at 3.34 ppm. The olefinic protons appear at 5.98, 5.06, and 5.00 ppm. The $^{13}C$ NMR spectrum of **12** shows separate resonances for the two diastereotopic carbonyl ligands at 225 and 224 ppm. The carbyne carbon $C_\alpha$ appears at 293 ppm with $^1J_{WC} = 188$ Hz, while $C_\beta$ resonates at 59.3 ppm with $^2J_{WC} = 37$ Hz. The signals for $C_\gamma$ and $C_\delta$ appear at 139 and 114 ppm, respectively (Table 1).

The major product obtained following deprotonation and methylation of **12** was $Tp'(CO)_2W{\equiv}CC(Me)_2CH{=}CH_2$ (**13**). The $^1H$ NMR spectrum of **13** reveals a molecular mirror plane and classic vinyl group doublets of doublets for each of the three vinylic protons. Discernible signals for a minor product in the $^1H$ NMR spectrum of **13** are triplets ($J_{HH} = 8$ Hz) of approximately equal intensity at 5.95 and 5.47 ppm, quintets of equal intensity at 2.34 and 1.78 ppm ($J_{HH} = 8$ Hz), a broad singlet at 1.86 ppm, and triplets of equal intensity at 0.80 and 0.76 ppm ($J_{HH} = 8$ Hz). We tentatively assign this minor product as a 1:1 mixture of *E* and *Z* isomers of $Tp'(CO)_2W{\equiv}CC(Me){=}C(H)(CH_2CH_3)$ (**14**). Complex **14** probably forms because the tertiary site ($C_\beta$) of the vinylidene anion $[Li][Tp'(CO)_2W{=}C_\alpha{=}C_\beta(Me)C_\gamma H{=}C_\delta H_2]$ is hard to access, and some $C_\delta$ addition occurs by default. The orange powder obtained contained 76% **13**, 12% **14-*Z***, and 12% **14-*E*** by NMR integration (Scheme 7).

**Vinyl Carbyne Formation.** Alkenyl carbynes have been described by several groups. Kolobova prepared $[Cp(CO)_2Mn{\equiv}CCH{=}CR_2][X]$ complexes by protonation of $Cp(CO)_2Mn{=}C{=}C{=}CR_2$ allenylidene complexes at $C_\beta$,[39] and analogous manganese derivatives have been prepared by Geoffroy.[40,41] One route to osmium alkenyl carbyne complexes involves treating dihydridoosmium(IV) complexes with alkynols.[42,43] Protonation of an osmium allenylidene at $C_\beta$ provides $[Cp(P^iPr_3)(Cl)Os{\equiv}CCH{=}CPh_2][BF_4]$,[44] and dehydration of the appropriate precursor complex provides $(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2(H)Os{\equiv}CCH{=}C(Me)(R)$.[45] Most germane to this report are osmium and rhodium alkenyl carbyne complexes derived from unsaturated vinylvinylidene complexes, $L_nM{=}C{=}CHC(CH_3){=}CH_2$ (M = Os, Rh), by protonation to form cationic osmium[46,47] and rhodium[48] alkenyl carbyne derivatives.

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(39) Kolobova, N. E.; Ivanov, L. L.; Zhvanko, O. S.; Khitrova, O. M.; Batsanov, A. S.; Struchkov, Y. T. *J. Organomet. Chem.* **1984**, *262*, 39−47.

(40) Terry, M. R.; Kelley, C.; Lugan, N.; Geoffroy, G. L. *Organometallics* **1993**, *12*, 3607−3617.

(41) Kelley, C.; Lugan, N.; Terry, M. R.; Geoffroy, G.; Haggerty, B. S.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 6735−6749.

(42) Weber, B.; Steinert, P.; Windmüller, B.; Wolf, J.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1994**, 2595−2596.

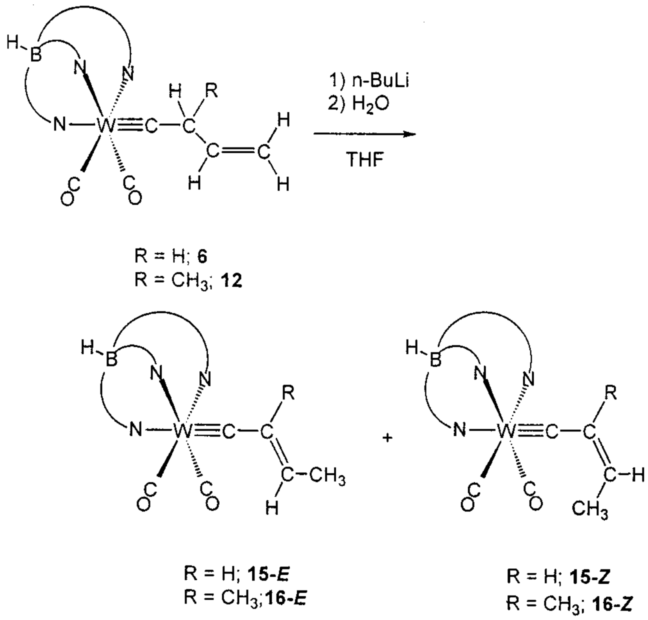
(43) Espuelas, J.; Esteruelas, M.; Lahoz, F. J.; Oro, L.; Ruiz, N. *J. Am. Chem. Soc.* **1993**, *115*, 4683−4689.

(44) Crochet, P.; Esteruelas, M.; López, A. M.; Ruiz, N.; Tolosa, J. *Organometallics* **1998**, *17*, 3479−3486.

(45) Buil, M. L.; Esteruelas, M. A.; García-Yebra, C.; Gutiérrez-Puebla, E.; Olívan, M. *Organometallics* **2000**, *19*, 2184−2193.

(46) Esteruelas, M. A.; López, A. M.; Ruiz, N.; Tolosa, J. I. *Organometallics* **1997**, *16*, 4657−4667.

**Scheme 8. Synthesis of Vinyl Carbyne Complexes**



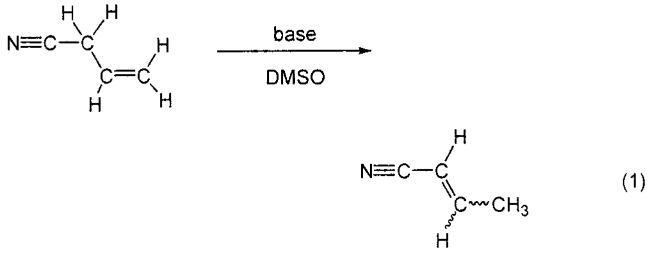
R = H; **6**
R = CH$_3$; **12**

R = H; **15-*E***
R = CH$_3$;**16-*E***

R = H; **15-*Z***
R = CH$_3$; **16-*Z***

Fischer prepared cyclopentenyl carbyne derivatives from the corresponding carbene complexes via his classic carbyne synthetic methodology.[49] Tungsten alkenyl carbyne complexes containing a methylenecycloalkane substituent have been prepared by protonation at C$_\delta$ of alkenyl−vinylidene complexes.[50−53] The noncyclic alkenyl carbyne complex Tp′(CO)$_2$W≡CCH=C(H)(Ph) has been prepared by elimination of water from Tp′(CO)$_2$W≡CCH$_2$C(H)(Ph)(OH).[24]

Conversion of the allyl carbyne complex **6** to its conjugated vinyl isomer Tp′(CO)$_2$W≡CC(H)=C(H)(CH$_3$)-(**15**) was achieved by treating **6** with 10 mol % triethylamine. Treating vinylvinylidene anion **9** with water also yields **15**. Both routes provide **15** as a 4:1 mixture of *E* and *Z* isomers (Scheme 8). Treating the vinylvinylidene anion **9** in THF solution at −78 °C with HCl etherate generates a 1:1 mixture of allyl carbyne **6** and vinyl carbyne **15** (8:1 *E*:*Z*) isomers. These data suggest that C$_\beta$ of **9** is the site of kinetic reactivity, but reversible deprotonation reactions ultimately led to the thermodynamically favored vinyl carbyne product. The conversion of allyl carbyne **6** to the *E* and *Z* vinyl carbyne mixture of **15** can be compared to the base-catalyzed isomerization of 3-butenenitrile to an *E* and *Z* mixture of crotonitrile (eq 1).[54,55] The analogy between transition-metal carbene complexes and esters set forth by Fischer[56−58] appears to have a corollary that relates the transition metal carbyne complexes described here to nitriles.



(1)

The $^1$H NMR spectrum of vinylcarbyne **15** reveals a resonance for the hydrogen on C$_\beta$ of the *E* isomer as a doublet at 6.17 ppm with a typical trans $^3J_{\mathrm{HH}} = 16$ Hz coupling to the hydrogen on C$_\gamma$ at 6.22 ppm. The olefinic protons for the minor *Z* isomer appear at 6.15 and 5.57 ppm and display a characteristic $^3J_{\mathrm{HH(cis)}} = 11$ Hz coupling. The methyl hydrogens on C$_\delta$ for the *E* isomer appear as a doublet at 1.30 ppm ($^3J_{\mathrm{HH}} = 5$ Hz), while the signal for the minor *Z* isomer appears as a doublet of doublets at 1.83 ppm ($^3J_{\mathrm{HH}} = 7$ Hz and $^4J_{\mathrm{HH}} = 2$ Hz). The $^{13}$C NMR spectrum of the **15-*E*** and **15-*Z*** mixture locates the C$_\beta$ sp$^2$ carbon resonances ~90 ppm further downfield than the signal for the C$_\beta$ sp$^3$ carbon of the parent allyl carbyne isomer **6**. The *E* isomer C$_\beta$ signal at 142 ppm is flanked by tungsten satellites with $^2J_{\mathrm{WC}} = 44$ Hz. The companion resonance for **15-*Z*** appears at 140 ppm.

When $^n$BuLi was added to vinyl carbyne **15** before addition of HCl, a 1:1 mixture of allyl carbyne **6** and starting vinylcarbyne complex **15** was obtained. Quenching the same anion with MeI provides methylvinylcarbyne complex **12** (the same product obtained from deprotonation/methylation of allyl carbyne **6**), as well as unidentified products. These reactions (Scheme 9) prove that the terminal methyl group (C$_\delta$) of vinyl carbyne **15** is acidic and a methyl proton can be removed by $^n$BuLi to generate vinylvinylidene anion **9** (Scheme 6).

Complex **12** was converted to its vinyl carbyne isomer by deprotonation with $^n$BuLi, quenching with water, and purification on alumina (Scheme 8). This reaction sequence provides Tp′(CO)$_2$W≡CC(Me)=C(H)(Me) (**16**), predominantly as the *E* isomer. We have assigned the connectivity of the major product as the *E* isomer because the terminal methyl hydrogens, which appear as a doublet at 1.31 ppm, have almost the same chemical shift as the terminal methyl hydrogens in **15-*E***. The other key resonance for **16-*E***, a downfield quartet at 6.02 ppm for the hydrogen attached to C$_\gamma$, is also comparable to the analogous resonance of **15-*E***. A trace amount of **16-*Z*** was also observed, as signals for the terminal methyl group and the olefinic proton on C$_\gamma$ of **16-*Z*** appear as a doublet at 1.72 ppm and quartet at 5.5 ppm, respectively. When the spectrum of the same sample was obtained 1 day later, the signals for **16-*Z*** had increased significantly and a 1.7:1 ratio of **16-*E*** and **16-*Z*** was observed.

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(47) Crochet, P.; Esteruelas, M. A.; López, A. M.; Martínez, M.; Oliván, M.; Oñate, E.; Ruiz, N. *Organometallics* **1998**, *17*, 4500−4509.

(48) Rappert, T.; Nürnberg, O.; Mahr, N.; Wolf, J.; Werner, H. *Organometallics* **1992**, *11*, 4156−4164.

(49) Fischer, E. O.; Wagner, W. R.; Kreissl, F. R.; Neugebauer, D. *Chem. Ber.* **1979**, *112*, 1320−1328.

(50) Zhang, L.; Gamasa, M. P.; Gimeno, J.; Carbajo, R. J.; Lopez-Ortiz, F. *Organometallics* **1996**, *15*, 4274−4284.

(51) Zhang, L.; Gamasa, M. P.; Gimeno, J.; Galindo, A.; Mealli, C.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* **1997**, *16*, 4099−4108.

(52) Zhang, L.; Gamasa, M. P.; Gimeno, J.; Carbajo, R.; Lopez-Ortiz, F.; GuedesdaSilva, M. F. C.; Pombeiro, A. J. L. *Eur. J. Inorg. Chem.* **2000**, 341−350.

(53) Zhang, L.; Gamasa, M. P.; Gimeno, J.; GuedasdaSilva, M. F. C.; Pombeiro, A. J. L.; Graiff, C.; Lanfranchi, M.; Tiripicchio, A. *Eur. J. Inorg. Chem.* **2000**, 1707−1715.

(54) Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1983**, *48*, 619−621.

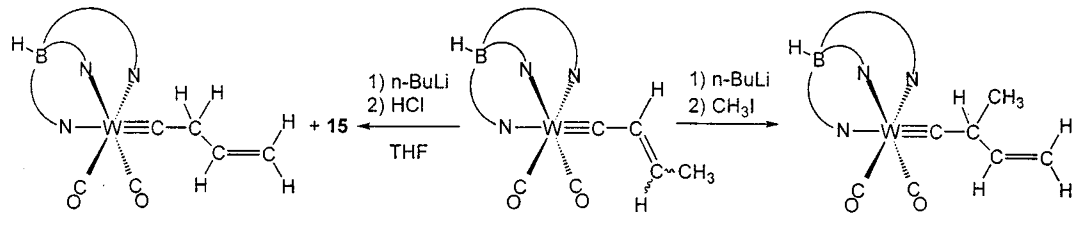
(55) Bordwell, F. G.; Hughes, D. L. *J. Am. Chem. Soc.* **1985**, *107*, 4737−4744.

(56) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 8−9.

(57) Casey, C. P.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 5833−5834.

(58) Elschenbroich, C.; Salzer, A. *Organometallics: A Concise Introduction*; VCH: New York, 1992.

**Scheme 9. Reactivity of Tp′(CO)$_2$W≡CC(H)=C(H)(CH$_3$) (15)**



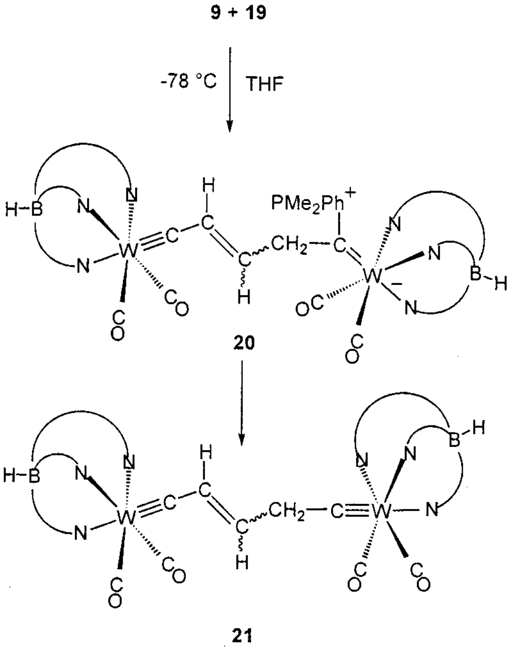
6 15 12

**Dinuclear Carbyne Complexes.** Synthetic routes to dinuclear compounds containing metal–carbon triple bonds are rare.[59–61] We have recently reported coupling reactions which provide routes to low-valent group VI dinuclear carbyne complexes with three-[62] and four-carbon bridges.[63] The dinuclear complex Tp′(CO)$_2$W≡CCH$_2$C≡Mo(CO)$_2$Tp′ (**17**), obtained by reacting vinylidene anion **7** with Tp′(CO)$_2$Mo≡CCl,[62] is most relevant to the work described here.

An analogous reaction using chlorocarbyne complex **1** as a formal source of [Tp′(CO)$_2$W≡C]$^+$ for addition to C$_\delta$ of vinylvinylidene anion **9** was attempted, but the chlorocarbyne **1** and vinylvinylidene anion **9** did not react. Mixing THF solutions of vinylvinylidene anion **9** with the THF-soluble analogue of **3**, [Tp′(CO)$_2$W≡CPMe$_2$Ph][BAr$_4$F] (**19**), resulted in a brown solution that displayed carbonyl absorbances for a zwitterionic carbene intermediate, Tp′(CO)$_2$W≡CCHCHCH$_2$(PMe$_2$Ph)C=W(CO)$_2$Tp′ (**20**), at $\nu_{CO}$ 1964, 1872, 1869, and 1745 cm$^{-1}$. Quenching with HCl etherate and purification provided an orange powder identified as a 3.5:1 *E:Z* mixture of the neutral C$_5$H$_4$ bridged bis(carbyne) complex Tp′(CO)$_2$W≡CCH$_2$CH=CHC≡W(CO)$_2$Tp′ (**21**) in 56% yield (Scheme 10).

The $^1$H NMR of the 3.5:1 *E:Z* mixture of **21** is complicated, but distinct features of each isomer can be assigned. Both isomers contain a mirror plane, and each dinuclear isomer shows four signals for the Tp′ methine hydrogens in a 2:2:1:1 pattern and eight signals in a 6:6:3:3:6:6:3:3 ratio for the Tp′ methyl groups. The major isomer (*E*) displays $^3J_{HH}$ = 16 Hz coupling between the olefinic hydrogens at 6.41 and 6.35 ppm. The corresponding olefinic hydrogen signals of **21-*Z*** appear at 6.02 and 6.35 ppm and display a typical $^3J_{HH(cis)}$ = 11 Hz coupling. The $^{13}$C resonances of the carbon backbone for both **21-*E*** and **21-*Z*** have been assigned and are shown in Table 2.

**Scheme 10. Synthesis of the Neutral C$_5$H$_4$-Linked Dinuclear Carbyne Complex 21**



21

3.5:1 *E:Z*

Treatment of an orange THF solution of 3.5:1 **21-*E*** and **21-*Z*** with KO$^t$Bu or BuLi results in deprotonation at C$_\beta$ to form [K][Tp′(CO)$_2$W≡CCHCHCHC≡W(CO)$_2$Tp′] (**22**). Complex **22** is an incredibly deep ink blue in solution. This intense color surely arises from a conjugated $\pi$ system that extends along the carbon spine between the tungsten atoms of the resulting dinuclear complex. This hypothesis is supported by comparison of UV–vis spectral data obtained in THF for complexes **6**, **15**, and **21** with those of anion **22** (Table 3). Allylcarbyne **6**, vinylcarbyne **15**, and neutral bis(carbyne) **21** each display a single absorption in the visible spectrum, while the dinuclear anion **22** shows two absorbances at significantly longer wavelengths. The extinction coefficients for both electronic transitions of the anionic dinuclear bis(carbyne) species **22** ($\epsilon \approx 10^4$) are approximately 2 orders of magnitude larger than those for the neutral complexes ($\epsilon \approx 10^2$). The magnitude of $\epsilon$ for the two electronic transitions of **22** suggests that they are M→$\pi$* metal-to-ligand charge-transfer bands.[64]

Resonance structures for anion **22** allow the negative charge to be delocalized onto both tungsten atoms and onto both $\beta$-carbon sites (Scheme 11). NMR spectra of **22** in THF-$d_8$ at 253 K are significantly less complicated than those of the neutral precursor complex. Informative signals for **22** are a triplet at 7.3 ppm (1 H) and a doublet at 5.1 ppm (2 H) with $^3J_{HH}$ = 13 Hz coupling to each other. The $^{13}$C NMR spectrum has four important signals: (1) 229.6 ppm for the four equivalent carbonyl groups, (2) 306.1 ppm flanked by $^1J_{WC}$ = 173 Hz tungsten satellites for the two identical α-carbons, (3) 144.0 ppm for the unique $\gamma$-carbon, which appears as a

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[59] Caulton, K. G.; Cayton, R. H.; Chisholm, M. H.; Huffman, J. C.; Lobkovsky, E. B.; Xue, Z. *Organometallics* **1992**, *11*, 321–326.

[60] Krouse, S. A.; Schrock, R. R. *J. Organomet. Chem.* **1988**, *355*, 257–265.

[61] Ustynyuk, N. A.; Vinogradova, V. N.; Andrianov, V. G.; Struchkov, Y. T. *J. Organomet. Chem.* **1984**, *268*, 73–78.

[62] Woodworth, B. E.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 7418–7419.

[63] Woodworth, B. E.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1997**, *119*, 828–829.

[64] Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1984.

**Table 2. Selected $^{13}$C NMR Data[a] for Dinuclear $Tp'(CO)_2WC_{\alpha}C_{\beta}C_{\gamma}C_{\beta'}C_{\alpha'}W(CO)_2Tp'$ Complexes**

| complex | $C_{\alpha}$ | $C_{\beta}$ | $C_{\gamma}$ | $C_{\beta'}$ | $C_{\alpha'}$ | CO |
|---|---|---|---|---|---|---|
| $[W]\equiv CCH_2CH=CHC\equiv[W]$ (**21**-*E*)[b] | 284.7 | 53.9, $^1J_{CH} = 127$ Hz | 133, $^1J_{CH} = 154$ | 142.2, $^2J_{WC} = 40$, $^1J_{CH} = 155$ | 278.6 | 224.2, $^1J_{WC} = 165$; 223.4, $^1J_{WC} = 166$ |
| $[W]\equiv CCH_2CH=CHC\equiv[W]$ (**21**-*Z*)[b] | 287 | 52.1 | 132 | 139 | 279 | 225.5; 223.6 |
| K{[W]CCHCHCHC[W]} (**22**)[c] | 306, $^1J_{WC} = 173$ | 117, $^2J_{WC} = 40$, $^1J_{CH} = 152$ | 144, $^1J_{CH} = 145$ | | | 230 |

[a] Chemical shifts are reported in ppm and coupling constants in Hz. Some tungsten satellites were too weak to observe. [b] The sp$^3$-hybridized carbon is assigned as $C_{\beta}$ to distinguish it from the sp$^2$-hybridized carbon $C_{\beta'}$; NMR data were obtained in $CD_2Cl_2$. [c] Spectrum recorded in THF-$d_8$ at 253 K.

**Table 3. Selected UV−vis Spectral Data of Carbyne Complexes Obtained in THF**

| complex | $\lambda_{max}$ (nm) | $\epsilon$ ($M^{-1}$ $cm^{-1}$) |
|---|---|---|
| $Tp'(CO)_2W\equiv CCH_2CH=CH_2$ (**6**) | 385 | $7.3 \times 10^2$ |
| $Tp'(CO)_2W\equiv CCH=C(H)(CH_3)$ (**15**) | 498 | $2.0 \times 10^2$ |
| $Tp'(CO)_2W\equiv CCH_2CH=CHC\equiv W(CO)_2Tp'$ (**21**) | 506 | $3.6 \times 10^2$ |
| $[K][Tp'(CO)_2W\equiv CCHCHCHC\equiv W(CO)_2Tp']$ (**22**) | 596 | $7.9 \times 10^4$ |
| | 786 | $8.3 \times 10^4$ |

doublet with $^1J_{CH} = 145$ Hz in the $^1$H-coupled $^{13}$C NMR spectrum, and (4) two equivalent $\beta$-carbons at 117.6 ppm with $^2J_{WC} = 40$ Hz satellites. These NMR data suggest that the structure of **22** in THF solution is a $C_{2v}$-symmetric allyl-bridged complex with a $Tp'(CO)_2W\equiv C$ moiety on each end.

The IR spectrum of anion **22** is more complicated than one would anticipate. Five CO absorbances are observed in the IR spectrum: four of medium intensity at 1961, 1926, 1891, and 1837 cm$^{-1}$ and a strong absorption at 1779 cm$^{-1}$. Ion pairing could destroy the symmetry of the molecule evident on the NMR time scale, and the IR data suggest that ion pairing occurs between the potassium and the carbonyl groups at one end of the dinuclear compound. Thus, the structure of **22** could be the nonsymmetric dinuclear vinylvinylidenecarbyne anion $[K][Tp'(CO)_2W=C=C(H)C(H)=C(H)C\equiv W(CO)_2Tp']$. We postulate that the NMR spectra may reflect a rapid fluxional process between the two equivalent $[K][Tp'(CO)_2W=C=C(H)C(H)=C(H)C\equiv W(CO)_2Tp']$ isomers of anion **22** on the NMR time scale. If **22** is actually a vinylvinylidenecarbyne anion, an average of the $^{13}$C NMR data for $C_{\alpha}$ of vinylvinylidene anion **9** (326 ppm, $^1J_{WC} = 162$ Hz) and vinylcarbyne **15** (280 ppm, $^1J_{WC} = 183$ Hz) (Table 1) may approximate the expected chemical shift values of the carbons attached to each tungsten atom terminus in **22**. The observed $^{13}$C NMR values (306 ppm, $^1J_{WC} = 173$ Hz) (Table 2) for the tungsten-bound carbons of anion **22** are close to the values predicted if the $C_{\alpha}$ chemical shifts and $^1J_{WC_a}$ couplings for vinylvinylidene anion **9** and vinylcarbyne **15** are averaged (303 ppm and 173 Hz). If the dinuclear anion **22** is an equilibrium mixture of $[K][Tp'(CO)_2W=C=C(H)C(H)=C(H)C\equiv W(CO)_2Tp']$ vinylvinylidenecarbyne isomers, then rotation around the carbon−carbon bonds between the central carbon atom and each attached carbon atom could be facile (Scheme 12). Facile allylic C−C bond rotation would effectively average the cis and trans and $^3J_{HH}$ coupling constants between the "vinylic" hydrogens of each isomer. In fact, the $^3J_{HH} = 13$ Hz coupling observed in the $^1$H NMR of **22** between the hydrogen on the central carbon and the hydrogens on carbons flanking the central carbon is close to the average of the trans (16 Hz) and cis (11 Hz) $^3J_{HH}$ coupling constants in neutral dinuclear compounds **21-*E*** and **21-*Z***.

Addition of HCl in ether to an NMR tube containing **22** results in a color change to orange. The $^1$H NMR of this orange solution revealed that protonation occurred exclusively at $C_{\beta}$ to form a 16:1 mixture of **21-*E*** and **21-*Z*** isomers. Attempts to isolate pure **21-*E*** were unsuccessful. Clean samples of **21** could be obtained by chromatography on alumina, but chromatography also resulted in isomerization of this **21-*E***-enriched mixture back to the initial 3.5:1 ratio of **21-*E*** and **21-*Z*** isomers.

## Conclusions

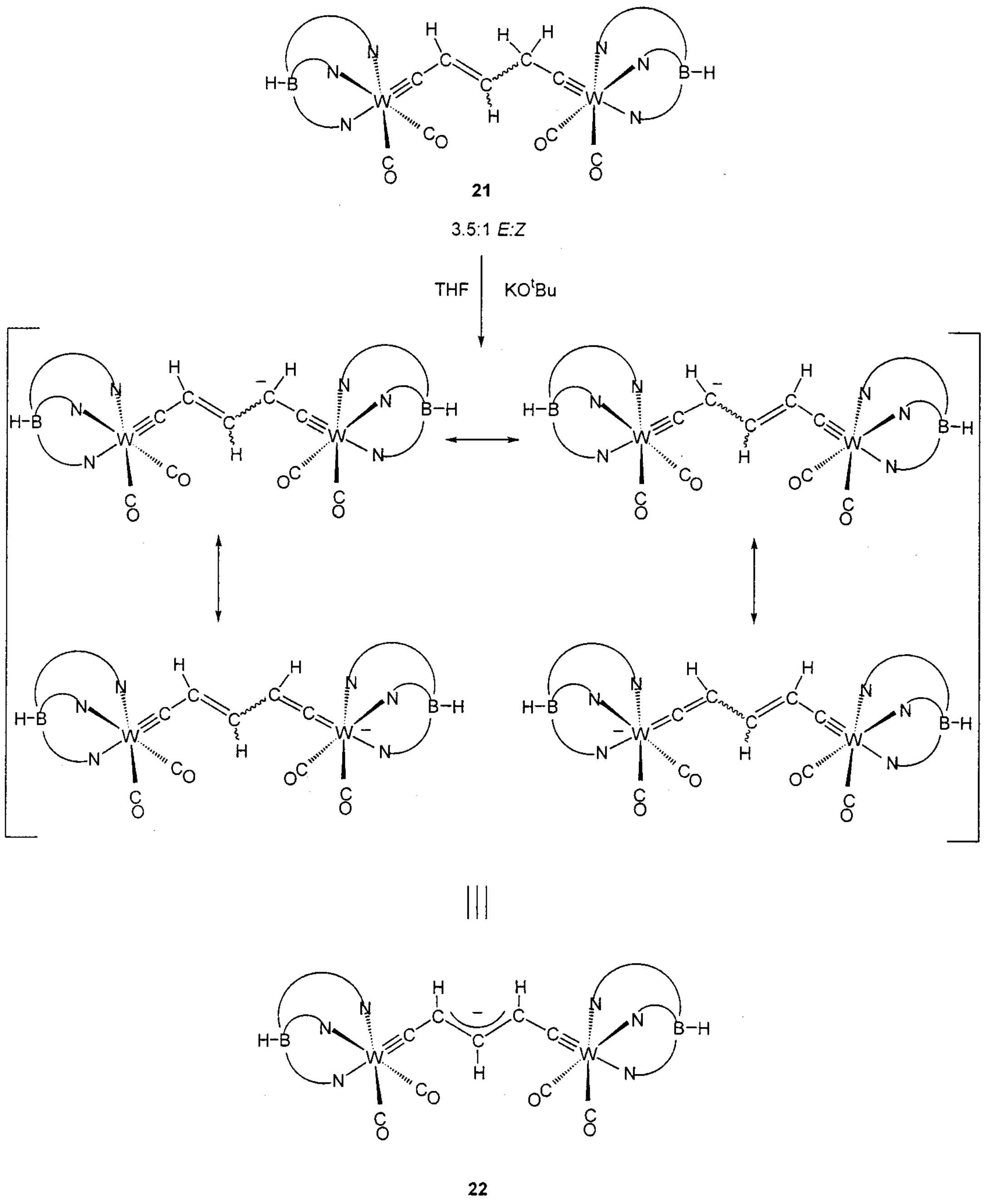
A convenient synthesis of the benzyl and allyl carbyne complexes $Tp'(CO)_2W\equiv CCH_2R$ (R = Ph, $CH=CH_2$) from a phosphonium carbyne complex has been described. Deprotonation of these alkyl carbyne complexes with strong base occurs at $C_{\beta}$ to form the vinylidene anions $[Tp'(CO)_2W=C=C(H)(R)]^-$, which add electrophiles primarily at $C_{\beta}$. Conjugated vinyl carbyne complexes are accessible by isomerization of allylic carbyne reagents. In much of this chemistry the tungsten fragment $Tp'(CO)_2W\equiv CR$ resembles a nitrile unit, $N\equiv CR$. The dinuclear bis(carbyne) compound $Tp'(CO)_2W\equiv CCH_2CH=CHC\equiv W(CO)_2Tp'$ has been synthesized, which undergoes deprotonation to form a colorful anionic complex. This anionic dinuclear complex adopts a $C_{2v}$-symmetric structure on the NMR time scale and contains a conjugated $\pi$ system which spans all five carbon atoms between the two tungsten atoms.

## Experimental Section

**General Considerations.** All reactions were carried out under a dry atmosphere of nitrogen or argon using standard Schlenk or drybox techniques. All solvents except tetrahydrofuran were dried by passage through activated alumina columns. Tetrahydrofuran was distilled under nitrogen from sodium and benzophenone. $[Tp'(CO)_2W\equiv CPMe_2Ph][PF_6]$ (**3**) was synthesized by literature methods,[22,26] while $[Tp'(CO)_2W\equiv CPMe_2Ph][BAr_4F]$ (**19**) was prepared in an analogous fashion by using $[Na][BAr_4F]$ ($BAr_4F$ = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) to provide the $[BAr_4F]$ counteranion. All other reagents were used as obtained from commercial sources. Infrared spectra were obtained on an ASI React IR 1000 spectrometer. Solid-state IR spectra were obtained as KBr pellets or as neat solids. Solution IR spectra were obtained in a 1 mm path length $CaF_2$ cell. UV−vis spectra were obtained on a Hewlett-Packard 8425 A diode array spectrophotometer. All $^1$H and $^{13}$C NMR spectra were obtained on a Bruker Avance 400 or Bruker Avance 500 spectrometer. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

**$Tp'(CO)_2W\equiv CCH_2(C_6H_5)$ (5).** A Schlenk flask with $[Tp'(CO)_2W\equiv CPMe_2Ph][PF_6]$ (2.09 g, 2.51 mmol) and 40 mL of $CH_2Cl_2$ was immersed in a dry ice−2-propanol bath and cooled to −78 °C. The resulting red solution showed IR absorbances at $\nu_{CO}$ 2023, 1938 cm$^{-1}$. Fresh 2.0 M $PhCH_2MgCl$ in THF (1.8 mL, 3.6 mmol) was added, and the solution gradually turned

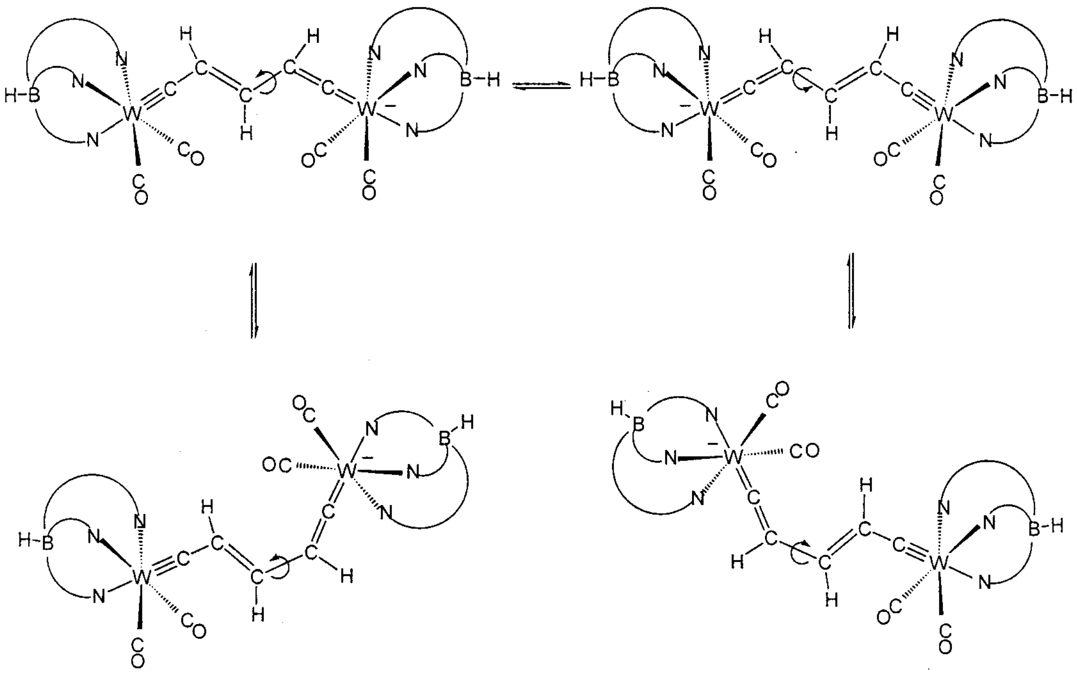
**Scheme 11. Resonance Structures for the Symmetric Allyl-Bridged Dinuclear Bis(carbyne) 22**



green. The IR spectrum at this point showed absorbances for the zwitterionic carbene intermediate $Tp'(CO)_2W{=}C(CH_2Ph)(PMe_2Ph)$ at $\nu_{CO}$ 1864, 1733 cm$^{-1}$. The solution changed from green to brown, and the IR spectrum revealed absorbances at $\nu_{CO}$ 1972, 1880 cm$^{-1}$. The solvent was evaporated under reduced pressure, and then the residue was transferred to an alumina column. Removal of solvent from the single yellow fraction that eluted with $CH_2Cl_2$ provided a yellow powder that had the pungent odor of $PMe_2Ph$. The yellow powder was placed in a flask with 20 mL of THF, and iodomethane (0.5 mL, 8.0 mmol) was added. The solution was stirred overnight as a white precipitate of $[PMe_3Ph][I]$ clouded the solution. Solvent was evaporated under reduced pressure to provide a yellow powder, which was dissolved in a minimal amount of $CH_2Cl_2$ and then transferred to an alumina column for elution with $CH_2Cl_2$. Removal of solvent via rotary evaporation provided $Tp'(CO)_2W{\equiv}CCH_2(C_6H_5)$ (1.47 g, 91% yield) as a yellow powder. IR (neat): 2543 cm$^{-1}$ ($\nu_{BH}$), 1958, 1862 cm$^{-1}$ ($\nu_{CO}$), 1544 cm$^{-1}$ ($\nu_{CN}$). $^1$H NMR ($C_6D_6$): $\delta$ 7.28 (d, $^3J_{HH}$ = 8 Hz, 2 H$_{ortho}$), 7.14 (t, $^3J_{HH}$ = 8 Hz, 2 H$_{meta}$), 7.04 (m, H$_{para}$), 5.53, 5.35 (s, 2:1 H, Tp′ C*H*), 3.82 (s, $^3J_{WH}$ = 7 Hz, 2 H, $W{\equiv}CCH_2(C_6H_5)$), 2.46, 2.44, 2.05, 2.02 (s, 3:6:3:6, Tp′ $CCH_3$). $^{13}$C NMR ($CD_2Cl_2$): $\delta$ 287.4 (s, $^1J_{WC}$ = 189 Hz, $W{\equiv}CCH_2(C_6H_5)$), 223.4 (s, $^1J_{WC}$ = 166 Hz, 2 W(*C*O)), 152.7, 152.2, 145.8, 145.3 (s, 1:2:1:2, Tp′*C*CH$_3$), 136.5 (s, C$_{ipso}$), 129.4 (d, $^1J_{CH}$ = 157 Hz, 2 C$_{ortho}$), 128.9 (d, $^1J_{CH}$ = 159 Hz, 2 C$_{meta}$), 126.6, (d, $^1J_{CH}$ = 160 Hz, C$_{para}$) 106.8, 106.6 (s, 1:2 Tp′ *C*H), 57.5 (t, $^1J_{CH}$ = 127 Hz, $^2J_{WC}$ = 39 Hz, $W{\equiv}CCH_2(C_6H_5)$), 16.4, 15.2, 12.8, 12.7 (s, 2:1:2:1, Tp′ C*C*H$_3$). Anal. Calcd for $C_{25}H_{29}N_6BO_2W$: C, 46.86; H, 4.57; N, 13.12. Found: C, 47.85; H, 4.80; N, 13.02.

**$Tp'(CO)_2W{\equiv}CCH_2CH{=}CH_2$ (6).** The allyl carbyne complex was prepared by analogy to **5** using $[Tp'(CO)_2W{\equiv}CPMe_2Ph][PF_6]$ (1.59 g, 1.91 mmol) and 2.0 M $CH_2{=}CHCH_2MgCl$ in THF (1.0 mL, 2.0 mmol). The IR absorbances of the blue zwitterionic carbene intermediate $Tp'(CO)_2W{=}C(PMe_2Ph)(CH_2CH{=}CH_2)$ appeared at $\nu_{CO}$ 1865, 1743 cm$^{-1}$. $Tp'(CO)_2W{\equiv}CCH_2CH{=}CH_2$ (0.75 g, 70% yield) was obtained as a yellow powder. IR (KBr): 1966, 1865 cm$^{-1}$ ($\nu_{CO}$), 1545 cm$^{-1}$ ($\nu_{CN}$). UV−vis (THF,

**Scheme 12. Possible Equilibrium between Isomers of Anion 22 Showing C−C Bond Rotation**[a]



[a] Potassium counterion not shown.

$9.6 \times 10^{-4}$ M): $\lambda_{max} = 385$ nm, $\epsilon_{385} = 7.3 \times 10^{2}$ $M^{-1}$ $cm^{-1}$. $^{1}H$ NMR ($C_6D_6$): $\delta$ 5.95 (ddt, $^{3}J_{HH(trans)} = 17$ Hz, $^{3}J_{HH(cis)} = 10$ Hz, $^{3}J_{HH(vicinal)} = 7$ Hz; 1 H, $W{\equiv}CCH_2CH{=}C(H_{cis})(H_{trans})$), 5.55, 5.36 (s, 2:1 H, Tp′ C*H*), 5.11 (m, 1 H, $W{\equiv}CCH_2CH{=}C(H_{cis})(H_{trans})$), 5.02 (m, 1 H, $W{\equiv}CCH_2CH{=}C(H_{cis})(H_{trans})$), 3.28 (d, $^{3}J_{HH(vicinal)} = 7$ Hz, $^{3}J_{HW} = 7$ Hz; 2 H, $W{\equiv}CCH_2CH{=}C(H_{cis})(H_{trans})$), 2.56, 2.49, 2.07, 2.03 (s, 6:3:3:6 H, Tp′ $CCH_3$). $^{13}C$ NMR ($CD_2Cl_2$): $\delta$ 288.0 ($^{1}J_{WC} = 191$ Hz, $^{2}J_{CH} = 10$ Hz, $W{\equiv}CCH_2CH{=}CH_2$), 223.0 (s, $^{1}J_{WC} = 170$ Hz, 2 W(*C*O)), 153.0, 152.0, 146.0, 145.0 (1:2:1:2, Tp′ *C*CH$_3$), 132.0 ($^{1}J_{CH} = 160$ Hz, $W{\equiv}CCH_2CH{=}CH_2$), 117 (t, $^{1}J_{CH} = 150$ Hz, $W{\equiv}CCH_2CH{=}CH_2$), 107 (broad, 3 Tp′ *C*H), 56 (t, $^{1}J_{CH} = 127$ Hz, $^{2}J_{WC} = 37$ Hz, $W{\equiv}CCH_2CH{=}CH_2$), 17, 15, 13, (2:1:3, Tp′ $CCH_3$). Anal. Calcd for $C_{21}H_{27}N_6BO_2W$: C, 42.74; H, 4.61; N, 14.17. Found: C, 42.77; H, 4.68; N, 14.17.

**$[Tp'(CO)_2W{=}C{=}CH(C_6H_5)]^-$ (8). Method a: $[K][Tp'(CO)_2W{=}C{=}CH(C_6H_5)]$.** An NMR tube was charged with $Tp'(CO)_2W{\equiv}CCH_2Ph$ (0.030 g, 0.047 mmol) and solid KO$^t$Bu (0.010 g, 0.094 mmol) and sealed with a rubber septum. A 0.7 mL aliquot of THF-$d_8$ was added to the tube via syringe to give a red-orange solution. IR (THF): 2524 $cm^{-1}$ ($\nu_{BH}$), 1853, 1741 $cm^{-1}$ ($\nu_{CO}$), 1544 $cm^{-1}$ ($\nu_{CN}$). $^{1}H$ NMR (THF-$d_8$): 7.07 (d, $^{3}J_{HH} = 8.0$ Hz, 2 $H_{ortho}$), 6.94 (t, $^{3}J_{CH} = 7.6$ Hz, 2 $H_{meta}$), 6.52 (t, $^{3}J_{CH} = 7.2$ Hz, 1 $H_{para}$), 5.69, 5.68 (2:1 Tp′ C*H*), 4.42 (s, $^{3}J_{WH} = 5.6$ Hz, $W{=}C{=}CH(C_6H_5)$), 2.48, 2.47, 2.35, 2.32 (6:3:6:3 Tp′ $CCH_3$). $^{13}C$ NMR (THF-$d_8$): $\delta$ 321.6 (s, $^{1}J_{WC} = 162$ Hz, $W{=}C{=}CH(C_6H_5)$), 236.7 (s, $^{1}J_{WC} = 174$ Hz, 2 W(*C*O)), 152.91, 152.90, 143.7, 143.2 (1:2:1:2 Tp′ *C*CH$_3$), 141.7 (s, $C_{ipso}$), 128.6 (d, $^{1}J_{CH} = 154$ Hz, 2 $C_{ortho}$), 143.7 (d, $^{1}J_{CH} = 149$ Hz, 2 $C_{meta}$), 143.2 (d, $^{1}J_{CH} = 157$ Hz, 1 $C_{para}$), 114.4 (d, $^{1}J_{CH} = 148$ Hz, $^{2}J_{WC} = 36$ Hz, $W{=}C{=}CH(C_6H_5)$), 106.1, 105.9 (2:1 Tp′ *C*H), 17.3, 16.2, 12.7, 12.6 (2:1:2:1 Tp′ $CCH_3$).

**Method b: $[Li][Tp'(CO)_2W{=}C{=}CH(C_6H_5)]$.** A Schlenk flask was charged with $Tp'(CO)_2W{\equiv}CCH_2Ph$ (0.52 g, 0.82 mmol) and 40 mL of THF and then immersed in a dry ice−2-propanol bath. An aliquot of 1.6 M $^n$BuLi in hexanes (0.61 mL, 0.98 mmol) was added to the cold yellow solution. The solution rapidly turned orange-red, and the IR spectrum showed dicarbonyl stretches at $\nu_{CO}$ 1880, 1698 $cm^{-1}$ for $[Li][Tp'(CO)_2W{=}C{=}CH(C_6H_5)]$.

**$[Tp'(CO)_2W{=}C{=}CHCH{=}CH_2]^-$ (9). Method a: $[K][Tp'(CO)_2W{=}C{=}CHCH{=}CH_2]$.** An NMR tube was charged with $Tp'(CO)_2W{\equiv}CCH_2CH{=}CH_2$ (0.033 g, 0.056 mmol) and solid KO$^t$Bu (0.012 g, 0.11 mmol) and then sealed with a rubber septum. A 0.7 mL aliquot of THF-$d_8$ was added to the tube via syringe to give a red-orange solution. IR (THF): 1849, 1736 $cm^{-1}$ ($\nu_{CO}$), 1543 $cm^{-1}$ ($\nu_{CN}$). $^{1}H$ NMR (THF-$d_8$): $\delta$ 6.60 (dt, 1 H, $^{3}J_{HH(trans)} = 16$ Hz, $^{3}J_{HH(cis)} = 10$ Hz, $^{3}J_{HH(vicinal)} = 10$ Hz; 1 H, $(W{=}C{=}CHCH{=}C(H_{cis})(H_{trans}))$, 5.71, 5.66 (s, 2:1 H, Tp′ C*H*), 4.49 (d, $^{3}J_{HH(vicinal)} = 10$ Hz, 1 H, $W{=}C{=}CH\text{-}CH{=}C(H_{cis})(H_{trans})$), 4.27 (dd, $^{3}J_{HH(trans)} = 16$ Hz, $^{3}J_{H(trans)H(cis)} = 2$ Hz; 1 H, $W{=}C{=}CHCH{=}C(H_{cis})(H_{trans})$), 3.71 (dd, $^{3}J_{HH(cis)} = 10$ Hz, $^{3}J_{H(trans)H(cis)} = 2$ Hz; 1 H, $W{=}C{=}CHCH{=}C(H_{cis})(H_{trans})$), 2.48, 2.46, 2.35, 2.31 (s, 6:3:3:6 H, Tp′ $CCH_3$). $^{13}C$ NMR (THF-$d_8$): $\delta$ 326.3 ($^{1}J_{WC_{\alpha}} = 162$ Hz, $W{=}C_{\alpha}$), 237.6 ($^{1}J_{WC} = 173$ Hz, 2 W(*C*O)), 153.2, 151.7, 143.6, 143.1 (1:2:1:2, Tp′ *C*CH$_3$), 135.0 (d, $^{1}J_{CH} = 146$ Hz, $C_{\beta}$), 116.4 (d, $^{3}J_{WC} = 37$ Hz, $^{1}J_{CH} = 149$ Hz, $C_{\gamma}$), 106.0, 105.8 (1:2 Tp′ *C*H), 95.2 (d, $^{1}J_{CH} = 115$ Hz, $C_{\delta}$), 17.2, 16.2, 12.7, 12.5 (2:1:2:1, Tp′ $CCH_3$).

**Method b: $[Li][Tp'(CO)_2W{=}C{=}CHCH{=}CH_2]$.** Vinyl-substituted vinylidene anions were generated as for **8**. The IR of the anionic product showed stretches at $\nu_{CO}$ 1877, 1698 $cm^{-1}$ for $[Li][Tp'(CO)_2W{=}C{=}CHCH{=}CH_2]$.

**$Tp'(CO)_2W{\equiv}CC(H)(CH_3)(Ph)$ (10).** Complex **8** was prepared as in method b. After 10 min of stirring, an excess of MeI (0.3 mL, 4.8 mmol) was added. At room temperature, the IR spectrum revealed absorbances at $\nu_{CO}$ 1972, 1880 $cm^{-1}$. The solvent was evaporated under reduced pressure to give a yellow residue, which was dissolved in a minimal amount of $CH_2Cl_2$ and was transferred to an alumina column. A single yellow fraction was eluted with $CH_2Cl_2$. Evaporation of solvent provided $Tp'(CO)_2W{\equiv}CC(H)(CH_3)(Ph)$ (0.43 g, 80% yield), and recrystallization from $CH_2Cl_2$/pentanes afforded yellow starburst crystals. IR (KBr): 2544 $cm^{-1}$ ($\nu_{BH}$), 1965, 1868 $cm^{-1}$ ($\nu_{CO}$), 1544 $cm^{-1}$ ($\nu_{CN}$). $^{1}H$ NMR ($C_6D_6$): $\delta$ 7.35 (d, $^{3}J_{HH} = 7$ Hz, 2 $H_{ortho}$), 7.13 (t, $^{3}J_{HH} = 7$ Hz, 2 $H_{meta}$), 7.03 (t, $^{3}J_{HH} = 7$ Hz, $H_{para}$), 5.54, 5.50, 5.35 (s, 1:1:1 Tp′ C*H*), 3.94 (q, 1 H, $^{3}J_{HH} = 7$ Hz, $^{3}J_{WH} = 7$ Hz, $W{\equiv}CC(H)(CH_3)(Ph)$), 2.486, 2.483, 2.36, 2.04, 2.03, 2.01 (s, 3:3:3:3:3:3 H, Tp′ $CCH_3$), 1.67 ($^{3}J_{HH} = 7$ Hz, 3 H, $W{\equiv}CC(H)(CH_3)(Ph)$). $^{13}C$ NMR ($CD_2Cl_2$): $\delta$ 293.4 (s, $^{1}J_{WC} = 189$ Hz, $W{\equiv}CC(H)(CH_3)(Ph)$), 223.9 (s, $^{1}J_{WC} = 166$ Hz, W(*C*O)), 223.7 (s, $^{1}J_{WC} = 166$ Hz, W(*C*O)), 152.7, 152.2, 152.1, 145.7, 145.3 (s, 1:1:1:1:1:2, Tp′ *C*CH$_3$), 142.5 (s, $C_{ipso}$), 128.9 (d, $^{1}J_{CH} = 159$ Hz, 2 $C_{ortho}$), 128.1 (d, $^{1}J_{CH} = 156$ Hz, 2 $C_{meta}$), 126.7 (d, $C_{para}$), 106.8, 106.63, 106.56 (1:1:1 Tp′ *C*H), 61.0 (d,

$^1J_{\mathrm{CH}} = 127$ Hz, $^2J_{\mathrm{WC}} = 37$ Hz, $\mathrm{W{\equiv}C\mathit{C}(H)(CH_3)(Ph)}$), 20.1 (q, $^1J_{\mathrm{CH}} = 128$ Hz, $\mathrm{W{\equiv}CC(H)(\mathit{C}H_3)(Ph)}$), 16.7, 16.4, 15.2, 12.8, 12.7 (1:1:1:2:1, Tp′ $\mathrm{C\mathit{C}H_3}$). Anal. Calcd for $\mathrm{C_{26}H_{31}N_6BO_2W}$: C, 47.73; H, 4.78; N, 12.84. Found: C, 48.17; H, 4.78; N, 12.84.

**$\mathbf{Tp'(CO)_2W{\equiv}CC(CH_3)_2(Ph)}$ (11).** The reactive anion $\mathrm{[Li][Tp'(CO)_2W{=}C{=}C(CH_3)(C_6H_5)]}$ was generated from $\mathrm{Tp'(CO)_2W{\equiv}CC(H)(CH_3)(Ph)}$ (0.24 g, 0.37 mmol) in 20 mL of THF using method b, and dicarbonyl absorptions at $\nu_{\mathrm{CO}}$ 1880, 1695 cm$^{-1}$ were observed in the IR spectrum. After 10 min of stirring, an excess of MeI (0.14 mL, 2.2 mmol) was added to the orange solution. Purification as for **10** provided $\mathrm{Tp'(CO)_2W{\equiv}CC(CH_3)_2(Ph)}$ (0.21 g, 82% yield) as a yellow powder. IR (KBr): 2544 cm$^{-1}$ ($\nu_{\mathrm{BH}}$), 1965, 1868 cm$^{-1}$ ($\nu_{\mathrm{CO}}$), 1544 cm$^{-1}$ ($\nu_{\mathrm{CN}}$). $^1$H NMR ($\mathrm{C_6D_6}$): $\delta$ 7.59 (d, $^3J_{\mathrm{HH}} = 7$ Hz, 2 $\mathrm{H_{ortho}}$), 7.02 (t, $^3J_{\mathrm{HH}} = 7$ Hz, 2 $\mathrm{H_{ortho}}$), 6.95 (t, $^3J_{\mathrm{HH}} = 7$ Hz, 1 $\mathrm{H_{para}}$), 5.54, 5.34 (s, 2:1 H, Tp′ $\mathrm{C\mathit{H}}$), 2.51, 2.44, 2.02, 2.01 (s, 3:6:6:3, Tp′ $\mathrm{C\mathit{C}\mathit{H}_3}$), 1.80 (s, 6 H, $\mathrm{W{\equiv}CC(C\mathit{H}_3)_2(Ph)}$). $^{13}$C NMR ($\mathrm{C_6D_6}$): $\delta$ 298.3 (s, $\mathrm{W{\equiv}\mathit{C}C(CH_3)_2(Ph)}$), 225.1 (s, $^1J_{\mathrm{WC}} = 166$ Hz, 2 $\mathrm{W(\mathit{C}O)}$), 152.4, 151.8, 147.0, 1445.3 (1:2:1:2, Tp′ $\mathrm{\mathit{C}CH_3}$), 142.0 ($\mathrm{C_{ipso}}$), 128.5 ($^1J_{\mathrm{CH}} = 158$ Hz, 2 $\mathrm{C_{ortho}}$), 126.7 ($^1J_{\mathrm{CH}} = 159$ Hz, 2 $\mathrm{C_{meta}}$), 126.2, 1 $\mathrm{C_{para}}$ = 156 Hz), 106.9, 106.7 (1:2 Tp′ $\mathrm{\mathit{C}H}$), 59.4 (s, $^1J_{\mathrm{WC}} = 34$ Hz, $\mathrm{W{\equiv}C\mathit{C}(CH_3)_2(Ph)}$), 28.9 (q, $^1J_{\mathrm{CH}} = 128$ Hz, $\mathrm{W{\equiv}CC(\mathit{C}H_3)_2(Ph)}$), 16.8, 15.2, 12.5, 12.3 (2:1:2:1, Tp′ $\mathrm{C\mathit{C}H_3}$). Anal. Calcd for $\mathrm{C_{27}H_{33}N_6BO_2W}$: C, 48.52; H, 4.98; N, 12.57. Found: C, 48.71; H, 5.20; N, 12.38.

**$\mathbf{Tp'(CO)_2W{\equiv}CC(H)(CH_3)(CH{=}CH_2)}$ (12).** A Schlenk flask was charged with $\mathrm{Tp'(CO)_2W{\equiv}CCH_2CH{=}CH_2}$ (0.40 g, 0.67 mmol), a stirbar, and 30 mL of THF. The $\mathrm{[Li][Tp'(CO)_2W{=}C{=}CHCH{=}CH_2]}$ reagent was generated from $\mathrm{Tp'(CO)_2W{\equiv}CCH_2CH{=}CH_2}$ (0.40 g, 0.67 mmol) in 30 mL of THF using method b. An excess of MeI (0.3 mL, 4.8 mmol) was added, and purification as for **10** provided $\mathrm{Tp'(CO)_2W{\equiv}CC(H)(CH_3)(CH{=}CH_2)}$ (0.26 g, 64% yield). IR (KBr): 2540 cm$^{-1}$ ($\nu_{\mathrm{BH}}$), 1969, 1876 cm$^{-1}$ ($\nu_{\mathrm{CO}}$), 1544 cm$^{-1}$ ($\nu_{\mathrm{CN}}$). $^1$H NMR ($\mathrm{C_6D_6}$): $\delta$ 5.98 (ddd, 1 H, $^3J_{\mathrm{HH(trans)}} = 17$ Hz, $^3J_{\mathrm{HH(cis)}} = 10$ Hz, $^3J_{\mathrm{HH(vicinal)}} = 7$ Hz; 1 H, ($\mathrm{W{\equiv}CC(H)(CH_3)C\mathit{H}{=}C(H_{cis})(H_{trans})}$)), 5.55, 5.54, 5.36 (s, 1:1:1 Tp′ $\mathrm{C\mathit{H}}$), 5.06 (d, $^3J_{\mathrm{HH(trans)}} = 17$ Hz, 1 H, $\mathrm{W{\equiv}CC(H)(CH_3)CH{=}C(H_{cis})(\mathit{H}_{trans})}$), 5.00 (d, $^3J_{\mathrm{HH(trans)}} = 10$ Hz, 1 H, $\mathrm{W{\equiv}CC(H)(CH_3)CH{=}C(\mathit{H}_{cis})(H_{trans})}$), 3.34 (quintet, 1 H, $^3J_{\mathrm{HH(vicinal)}} = {}^3J_{\mathrm{HH}} = 7$ Hz; $^3J_{\mathrm{WH}} = 7$ Hz; $\mathrm{W{\equiv}CC(\mathit{H})(CH_3)CH{=}C(H_{cis})(H_{trans})}$), 2.60, 2.59, 2.50, 2.06, 2.03 (s, 3:3:3:3:6 H, Tp′ $\mathrm{C\mathit{C}\mathit{H}_3}$), 1.37 (d, $^3J_{\mathrm{HH}} = 7.0$ Hz, 3 H, $\mathrm{W{\equiv}CC(H)(C\mathit{H}_3)CH{=}C(H_{cis})(H_{trans})}$). $^{13}$C NMR ($\mathrm{C_6D_6}$): $\delta$ 292.9 ($^1J_{\mathrm{WC_a}} = 188$ Hz, $\mathrm{W{\equiv}\mathit{C}C(H)(CH_3)CH{=}C(H_{cis})(H_{trans})}$), 225.5 ($^1J_{\mathrm{WC}} = 166$ Hz, $\mathrm{W(\mathit{C}O)}$), 224.4 ($^1J_{\mathrm{WC}} = 166$ Hz, $\mathrm{W(\mathit{C}O)}$), 152.7, 151.8, 144.6, 144.3, 144.2 (1:2:1:1:1, Tp′ $\mathrm{\mathit{C}CH_3}$), 138.6 (d, $^1J_{\mathrm{CH}} = 155$ Hz, $\mathrm{W{\equiv}CC(H)(CH_3)\mathit{C}H{=}C(H_{cis})(H_{trans})}$), 114.4 (d, $^1J_{\mathrm{CH}} = 154$ Hz, $\mathrm{W{\equiv}CC(H)(CH_3)CH{=}\mathit{C}(H_{cis})(H_{trans})}$), 107.1, 106.8 (1:2 Tp′ $\mathrm{\mathit{C}H}$), 59.3 (d, $^1J_{\mathrm{CH}} = 115$ Hz, $^2J_{\mathrm{WC}} = 37$ Hz, $\mathrm{W{\equiv}C\mathit{C}(H)(CH_3)CH{=}C(H_{cis})(H_{trans})}$), 18.7 (q, $^1J_{\mathrm{CH}} = 130$ Hz, $\mathrm{W{\equiv}CC(H)(\mathit{C}H_3)CH{=}C(H_{cis})(H_{trans})}$), 17.3, 17.1, 15.4, 12.7, 12.5 (1:1:1:2:1, Tp′ $\mathrm{C\mathit{C}H_3}$). Anal. Calcd for $\mathrm{C_{22}H_{29}N_6BO_2W}$: C, 43.73; H, 4.84; N, 13.91. Found: C, 44.75; H, 5.08; N, 13.70.

**$\mathbf{Tp'(CO)_2W{\equiv}CC(CH_3)_2(CH{=}CH_2)}$ (13).** After $\mathrm{[Li][Tp'(CO)_2W{=}C{=}C(CH_3)CH{=}CH_2]}$ was generated from $\mathrm{Tp'(CO)_2W{\equiv}CC(H)(CH_3)(CH{=}CH_2)}$ (0.11 g, 0.38 mmol) in 20 mL of THF using method b, an excess of MeI (0.3 mL, 4.8 mmol) was added to the bright red solution. The product was isolated according to the procedure for **10** as a peach powder identified as a mixture of $\mathrm{Tp'(CO)_2W{\equiv}CC(CH_3)_2(CH{=}CH_2)}$ as the major product and *E*/*Z* $\mathrm{Tp'(CO)_2W{\equiv}CC(CH_3){=}C(H)(CH_2CH_3)}$ as the minor product (0.11 g, 94% yield). IR (KBr): 2536 ($\nu_{\mathrm{BH}}$), 1965, 1872 ($\nu_{\mathrm{CO}}$), 1544 ($\nu_{\mathrm{CN}}$) cm$^{-1}$. NMR data (for major product only) are as follows. $^1$H NMR ($\mathrm{C_6D_6}$): $\delta$ 6.14 (dd, $^3J_{\mathrm{HH(trans)}} = 18$ Hz, $^3J_{\mathrm{HH}} = 10$ Hz; 1 H, $\mathrm{W{\equiv}CC(CH_3)_2C\mathit{H}{=}C(H_{cis})(H_{trans})}$), 5.55, 5.36 (s, 2:1 H, Tp′ $\mathrm{C\mathit{H}}$), 5.13 (d, $^3J_{\mathrm{HH}} = 10$ Hz, 1 H, $\mathrm{W{\equiv}CC(CH_3)_2CH{=}C(H_{cis})(\mathit{H}_{trans})}$), 4.99 (d, 1 H, $^3J_{\mathrm{HH}} = 18$ Hz, $\mathrm{W{\equiv}CC(CH_3)_2CH{=}C(\mathit{H}_{cis})(H_{trans})}$), 2.62, 2.51, 2.30, 2.07 (s, 6:3:6:3 H, Tp′ $\mathrm{C\mathit{C}\mathit{H}_3}$), 1.46 (s, 6 H, $\mathrm{W{\equiv}CC(C\mathit{H}_3)_2C\mathit{H}{=}C(H_{cis})(H_{trans})}$). $^{13}$C NMR ($\mathrm{C_6D_6}$): $\delta$ 295.6, (s, $\mathrm{W{\equiv}\mathit{C}C(CH_3)_2CH{=}CH_2}$), 224.7 (s, $^1J_{\mathrm{WC}} = 166$ Hz, 2 $\mathrm{W(\mathit{C}O)}$), 152.5, 151.6, 144.5, 144.4 (1:2:1:2, Tp′ $\mathrm{\mathit{C}CH_3}$), 143.5 (d, $^1J_{\mathrm{CH}} = 166$ Hz, $\mathrm{W{\equiv}CC(CH_3)_2\mathit{C}H{=}CH_2}$), 111.2 (t, $^1J_{\mathrm{CH}} = 155$ Hz, $\mathrm{W{\equiv}CC(CH_3)_2CH{=}\mathit{C}H_2}$), 107 (broad s, 3 Tp′ $\mathrm{\mathit{C}H}$), 58.6, (s, $\mathrm{W{\equiv}C\mathit{C}(CH_3)_2CH{=}CH_2}$), 26.1 (q, $^1J_{\mathrm{CH}} = 127$ Hz), 17.3, 15.2, 12.5, 12.3 (2:1:2:1, Tp′ $\mathrm{C\mathit{C}H_3}$). Anal. Calcd for $\mathrm{C_{23}H_{31}N_6BO_2W}$: C, 44.68; H, 5.05; N, 13.59. Found: C, 45.62; H, 5.26; N, 13.25.

**$\mathbf{Tp'(CO)_2W{\equiv}CC(H){=}C(H)(Me)}$ (15).** After $\mathrm{[Li][Tp'(CO)_2W{=}C{=}CHCH{=}CH_2]}$ was generated from $\mathrm{Tp'(CO)_2W{\equiv}CCH_2CH{=}CH_2}$ (0.25 g, 0.42 mmol) in 30 mL of THF using method b, 0.5 mL of water was added to quench the red-orange solution. The product was isolated according to the procedure for **10** and provided $\mathrm{Tp'(CO)_2W{\equiv}CC(H){=}C(H)(CH_3)}$ (0.19 g, 72% yield) as an orange powder. IR (KBr): 2544 cm$^{-1}$ ($\nu_{\mathrm{BH}}$), 1962, 1866 cm$^{-1}$ ($\nu_{\mathrm{CO}}$), 1545 cm$^{-1}$ ($\nu_{\mathrm{CN}}$). UV−vis (THF, $1.0 \times 10^{-3}$ M): $\lambda_{\mathrm{max}} = 498$ nm, $\epsilon_{498} = 2.0 \times 10^2$ M$^{-1}$ cm$^{-1}$. NMR data for the *E* isomer (major product) are as follows. $^1$H NMR ($\mathrm{C_6D_6}$): $\delta$ 6.22 (m, 1H, $\mathrm{W{\equiv}CC(H){=}C(\mathit{H})(CH_3)}$), 6.17 (d, $^3J_{\mathrm{HH}} = 16$ Hz, 1 H, $\mathrm{W{\equiv}CC(\mathit{H}){=}C(H)(CH_3)}$), 5.55, 5.37 (s, 2:1 H, Tp′ $\mathrm{C\mathit{H}}$), 2.64, 2.49, 2.08, 2.04 (s, 6:3:6:3 H, Tp′ $\mathrm{C\mathit{C}\mathit{H}_3}$), 1.30 (d, $^3J_{\mathrm{HH}} = 5$ Hz, 3 H, $\mathrm{W{\equiv}CC(H){=}C(H)(C\mathit{H}_3)}$). $^{13}$C NMR ($\mathrm{CD_2Cl_2}$): $\delta$ 280.2 ($^1J_{\mathrm{WC}} = 183$ Hz, $\mathrm{W{\equiv}\mathit{C}C(H){=}C(H)(CH_3)}$), 223.0 ($^1J_{\mathrm{WC}} = 170$ Hz, 2 $\mathrm{W(\mathit{C}O)}$), 152.7, 152.4, 146.0, 145.3 (1:2:1:2, Tp′ $\mathrm{\mathit{C}CH_3}$), 142.2 (d, $^1J_{\mathrm{CH}} = 153$ Hz, $^2J_{\mathrm{WC}} = 44$ Hz, $\mathrm{W{\equiv}C\mathit{C}(H){=}C(H)(CH_3)}$), 137.7 (d, $^1J_{\mathrm{CH}} = 156$ Hz, $\mathrm{W{\equiv}CC(H){=}\mathit{C}(H)(CH_3)}$), 106.8, 106.6 (1:2 Tp′ $\mathrm{\mathit{C}H}$), 18.3 (q, $^1J_{\mathrm{CH}} = 127$ Hz, $\mathrm{W{\equiv}CC(H){=}C(H)(\mathit{C}H_3)}$), 16.5, 15.3, 12.8, 12.7 (2:1:2:1, Tp′ $\mathrm{C\mathit{C}H_3}$). NMR data for the *Z* isomer (minor product) are as follows. $^1$H NMR ($\mathrm{C_6D_6}$): $\delta$ 6.15 (dq, $^3J_{\mathrm{HH}} = 11$ Hz, $^4J_{\mathrm{HH}} = 2$ Hz, 1H, $\mathrm{W{\equiv}CC(\mathit{H}){=}C(H)(CH_3)}$), 5.57 (m, 1 H, $\mathrm{W{\equiv}CC(H){=}C(\mathit{H})(CH_3)}$), 5.56, 5.34 (s, 2:1 H, Tp′ $\mathrm{C\mathit{H}}$), 2.62, 2.46, 2.07, 2.02 (s, 6:3:6:3 H, Tp′ $\mathrm{C\mathit{C}\mathit{H}_3}$), 1.83 (dd, $^3J_{\mathrm{HH}} = 7$ Hz, $^4J_{\mathrm{HH}} = 2$ Hz, 3 H, $\mathrm{W{\equiv}CC(H){=}C(H)(C\mathit{H}_3)}$). $^{13}$C NMR ($\mathrm{CD_2Cl_2}$): $\delta$ 281.2 ($^1J_{\mathrm{WC}} = 183$ Hz, $\mathrm{W{\equiv}\mathit{C}C(H){=}C(H)(CH_3)}$), 225.6 ($^1J_{\mathrm{WC}} = 166$ Hz, 2 $\mathrm{W(\mathit{C}O)}$), 152.7, 152.4, 146.0, 145.3 (1:2:1:2, Tp′ $\mathrm{\mathit{C}CH_3}$), 139.6 (d, $^1J_{\mathrm{CH}} = 154$ Hz, $^2J_{\mathrm{WC}} = 42$ Hz, $\mathrm{W{\equiv}C\mathit{C}(H){=}C(H)(CH_3)}$), 135.7 (d, $^1J_{\mathrm{CH}} = 156$ Hz, $\mathrm{W{\equiv}CC(H){=}\mathit{C}(H)(CH_3)}$), 106.9, 106.7 (1:2 Tp′ $\mathrm{\mathit{C}H}$), 16.0 (q, $^1J_{\mathrm{CH}} = 125$ Hz, $\mathrm{W{\equiv}CC(H){=}C(H)(\mathit{C}H_3)}$), 16.4, 15.2, 12.8, 12.7 (2:1:2:1, Tp′ $\mathrm{C\mathit{C}H_3}$). Anal. Calcd for $\mathrm{C_{21}H_{27}N_6BO_2W}$: C, 42.74; H, 4.61; N, 14.17. Found: C, 42.77; H, 4.68; N, 14.17.

**$\mathbf{Tp'(CO)_2W{\equiv}CC(CH_3){=}C(H)(CH_3)}$ (16).** After $\mathrm{[Li][Tp'(CO)_2W{=}C{=}C(CH_3)CH{=}CH_2]}$ was generated from $\mathrm{Tp'(CO)_2W{\equiv}CC(H)(CH_3)(CH{=}CH_2)}$ (0.23 g, 0.38 mmol) in 40 mL of THF using method b, the solution was treated with water. Purification as in **10** provided $\mathrm{Tp'(CO)_2W{\equiv}CC(CH_3){=}C(H)(CH_3)}$ (**16**; 0.22 g, 98% yield) as an orange powder. IR (KBr): 2544 cm$^{-1}$ ($\nu_{\mathrm{BH}}$) 1965, 1862 cm$^{-1}$ ($\nu_{\mathrm{CO}}$), 1544 cm$^{-1}$ ($\nu_{\mathrm{CN}}$). NMR data for the *E* isomer (major product) are as follows. $^1$H NMR ($\mathrm{C_6D_6}$): $\delta$ 6.02 (qq, 1 H, $^3J_{\mathrm{HH}} = 7.2$ Hz; $^4J_{\mathrm{HH}} = 1.2$ Hz, 1 H**,** $\mathrm{W{\equiv}CC(CH_3){=}C(\mathit{H})(CH_3)}$), 5.56, 5.37 (s, 2:1 Tp′ $\mathrm{C\mathit{H}}$), 2.65, 2.51, 2.09, 2.04 (s, 6:3:6:3 H, Tp′ $\mathrm{C\mathit{C}\mathit{H}_3}$), 1.84 (m, 3 H, $\mathrm{W{\equiv}CC(C\mathit{H}_3){=}C(H)(CH_3)}$), 1.31 (dq, $^3J_{\mathrm{HH}} = 7.2$ Hz; $^5J_{\mathrm{HH}} = 1.2$ Hz, 3 H, $\mathrm{W{\equiv}CC(CH_3){=}C(H)(C\mathit{H}_3)}$). $^{13}$C NMR ($\mathrm{C_6D_6}$): $\delta$ 285.2 (s, $\mathrm{W{\equiv}\mathit{C}C(CH_3){=}C(H)(CH_3)}$), 225.0 (2 CO), 152.4, 151.9, 144.5, 144.0 (1:2:1:2 Tp′ $\mathrm{C\mathit{C}H_3}$), 148.2 (s, $\mathrm{W{\equiv}C\mathit{C}(CH_3){=}C(H)(CH_3)}$), 130.7 (d, $^1J_{\mathrm{CH}} = 155$ Hz, $\mathrm{W{\equiv}CC(CH_3){=}\mathit{C}(H)(CH_3)}$), 106.9, 106.6 (1:2 Tp′ $\mathrm{\mathit{C}H}$). NMR data for the *Z* isomer (minor product) are as follows. $^1$H NMR ($\mathrm{C_6D_6}$): $\delta$ 5.59, 5.36 (s, 2:1 Tp′ $\mathrm{C\mathit{H}}$), 5.51 (qq, 1 H, $^3J_{\mathrm{HH}} = 7.2$ Hz, $^4J_{\mathrm{HH}} = 1.6$ Hz, 1 H, $\mathrm{W{\equiv}CC(CH_3){=}C(\mathit{H})(CH_3)}$), 2.63, 2.47, 2.05, 2.04 (s, 6:3:6:3 H, Tp′ $\mathrm{C\mathit{C}\mathit{H}_3}$), 1.99 (m, 3 H, $\mathrm{W{\equiv}CC(C\mathit{H}_3){=}C(H)(CH_3)}$), 1.73 (dq, $^3J_{\mathrm{HH}} = 7.2$ Hz, $^5J_{\mathrm{HH}} = 1.6$ Hz, 3 H, $\mathrm{W{\equiv}CC(CH_3){=}C(H)(C\mathit{H}_3)}$).$^{13}$C NMR ($\mathrm{C_6D_6}$): $\delta$ 284.5 (s, $\mathrm{W{\equiv}\mathit{C}C(CH_3){=}C(H)(CH_3)}$), 225.9 (s, 2 CO), 152.4, 152.0, 144.6, 144.0 (1:2:1:2 Tp′ $\mathrm{C\mathit{C}H_3}$), 146.5 (s, $\mathrm{W{\equiv}C\mathit{C}(CH_3){=}C(H)(CH_3)}$), 130.1 (d, $^1J_{\mathrm{CH}} = 155$ Hz, $\mathrm{W{\equiv}CC(CH_3){=}\mathit{C}(H)(CH_3)}$), 106.9, 106.6 (1:2 Tp′ $\mathrm{\mathit{C}H}$), 16 different resonances between 35 and 12 ppm for $\mathrm{W{\equiv}CC(\mathit{C}H_3){=}C(H)(CH_3)}$ and $\mathrm{W{\equiv}CC(CH_3){=}C(H)(\mathit{C}H_3)}$ and 12 Tp′ $\mathrm{CCH_3}$ for both *E* and *Z* isomers. Anal. Calcd for $\mathrm{C_{22}H_{29}N_6BO_2W}$: C, 43.73; H, 4.84; N, 13.91. Found: C, 44.75; H, 5.08; N, 13.70.

**$\mathbf{Tp'(CO)_2W{\equiv}CCH_2CH{=}CHC{\equiv}W(CO)_2Tp'}$ (21).** $\mathrm{[Li][Tp'(CO)_2W{=}C{=}CHCH{=}CH_2]}$ was generated from $\mathrm{Tp'(CO)_2W{\equiv}CCH_2CH{=}CH_2}$ (0.45 g, 0.76 mmol) in 30 mL of THF using method b. The contents of a Schlenk flask charged with $\mathrm{[Tp'(CO)_2W{\equiv}CPMe_2Ph][BAr_4F]}$ in 30 mL of THF were transferred to the $\mathrm{[Li][Tp'(CO)_2W{=}C{=}CHCH{=}CH_2]}$ solution. The IR of the resulting brown solution shows carbonyl absorbances assigned to the zwitterionic carbene intermediate $\mathrm{Tp'(CO)_2W{\equiv}CCHCHCH_2(PMe_2Ph)C{=}W(CO)_2Tp'}$ at 1964, 1872, 1869, and 1745 $\mathrm{cm^{-1}}$. The brown solution gradually turned indigo blue upon warming to room temperature. Quenching with 1.0 M HCl in ether (0.80 mL, 0.80 mL) resulted in a color change to orange, and the IR spectrum revealed absorbances at $\nu_{\mathrm{CO}}$ 1970, 1880 $\mathrm{cm^{-1}}$ only. Purification as in **10** provided $\mathrm{Tp'(CO)_2W{\equiv}CCH_2CH{=}CHC{\equiv}W(CO)_2Tp'}$ (**21**; 0.48 g, 56% yield) as a bright orange powder. IR (neat): 1962, 1870 $\mathrm{cm^{-1}}$ ($\nu_{\mathrm{CO}}$), 1544 $\mathrm{cm^{-1}}$ ($\nu_{\mathrm{CN}}$). UV−vis (THF, $5.8 \times 10^{-4}$ M), $\lambda_{\max} = 506$ nm, $\epsilon_{506} = 3.6 \times 10^2\ \mathrm{M^{-1}\,cm^{-1}}$. NMR data for the *E* isomer (major product) are as follows. $^1$H NMR ($\mathrm{C_6D_6}$): $\delta$ 6.41 (dt, $^3J_{\mathrm{HH(trans)}} = 16$ Hz, $^3J_{\mathrm{HH(vicinal)}} = 7$ Hz, 1H, $\mathrm{W{\equiv}CCH_2C\mathit{H}{=}CHC{\equiv}W}$), 6.35 (d, $^3J_{\mathrm{HH(trans)}} = 16$ Hz, 1 H, $\mathrm{W{\equiv}CCH_2CH{=}C\mathit{H}C{\equiv}W}$), 5.568, 5.552 (s, 2:2 Tp′ C*H*), 5.357, 5.351 (s, 1:1 Tp′ CH), 3.08 (d, $^3J_{\mathrm{HH}} = 7$ Hz, $^3J_{\mathrm{WH}} = 6$ Hz, 2 H, $\mathrm{W{\equiv}CC\mathit{H}_2CH{=}CHC{\equiv}W}$), 2.68, 2.62, 2.471, 2.468, 2.086, 2.070, 2.038, 2.023 (s, 6:6:3:3:6:6:3:3 Tp′ $\mathrm{CC\mathit{H}_3}$). $^{13}$C NMR ($\mathrm{CD_2Cl_2}$): $\delta$ 284.7 (s, $\mathrm{W{\equiv}\mathit{C}CH_2CH{=}CHC{\equiv}W}$), 278.6 (s, $\mathrm{W{\equiv}CCH_2CH{=}CH\mathit{C}{\equiv}W}$), 224.2 (s, $^1J_{\mathrm{WC}} = 165$ Hz, 2 CO), 223.4 (s, $^1J_{\mathrm{WC}} = 166$ Hz, 2 *C*O), 152.7, 152.4, 152.1, 145.9, 145.8, 145.2 (12 Tp′ $\mathrm{\mathit{C}CH_3}$), 142.2 (d, $^2J_{\mathrm{WC}} = 40$ Hz, $^1J_{\mathrm{CH}} = 155$ Hz, $\mathrm{W{\equiv}CCH_2CH{=}\mathit{C}HC{\equiv}W}$), 133.0 (d, $^1J_{\mathrm{CH}} = 154$ Hz, $\mathrm{W{\equiv}CCH_2\mathit{C}H{=}CHC{\equiv}W}$), 106.8, 106.6 (2:4 Tp′ *C*H), 53.9 (t, $^1J_{\mathrm{CH}} = 127$ Hz, $\mathrm{W{\equiv}C\mathit{C}H_2CH{=}CHC{\equiv}W}$), 16.8, 16.7, 16.6, 15.2, 15.3, 12.7 (12 Tp′ $\mathrm{CCH_3}$). NMR data for the *Z* isomer (minor product) are as follows. $^1$H NMR ($\mathrm{C_6D_6}$): $\delta$ 6.02 (dt, $^3J_{\mathrm{HH(cis)}} = 11$ Hz, $^4J_{\mathrm{HH}} = 1$ Hz, 1 H, $\mathrm{W{\equiv}CCH_2CH{=}C\mathit{H}C{\equiv}W}$), 6.35 (d, $^3J_{\mathrm{HH(cis)}} = 11$ Hz, $^3J_{\mathrm{HH(vicinal)}} = 7$ Hz, 1 H, $\mathrm{W{\equiv}CCH_2C\mathit{H}{=}CHC{\equiv}W}$), 5.552, 5.514 (s, 2:2 Tp′ C*H*), 5.358, 5.330 (s, 1:1 Tp′ CH), 4.018 (dd, $^3J_{\mathrm{HH}} = 7$ Hz, $^4J_{\mathrm{HH}} = 1$ Hz, 2 H, $\mathrm{W{\equiv}CC\mathit{H}_2CH{=}CHC{\equiv}W}$), 2.559, 2.557, 2.481, 2.421, 2.070, 2.030, 2.024 (s, 6:6:3:3:12:3:3 Tp′ $\mathrm{CC\mathit{H}_3}$). $^{13}$C NMR ($\mathrm{CD_2Cl_2}$): $\delta$ 287.0 (s, $\mathrm{W{\equiv}\mathit{C}CH_2CH{=}CHC{\equiv}W}$), 279.0 (s, $\mathrm{W{\equiv}CCH_2CH{=}CH\mathit{C}{\equiv}W}$), 225.5, 223.6 (each a s, 4 *C*O), 152.7, 152.4, 152.1, 145.9, 145.8, 145.2 (12 Tp′ $\mathrm{\mathit{C}CH_3}$), 139.0 ($\mathrm{W{\equiv}CCH_2CH{=}\mathit{C}HC{\equiv}W}$), 131.6 ($\mathrm{W{\equiv}CCH_2\mathit{C}H{=}CC{\equiv}W}$), 106.8, 106.6 (2:4 Tp′ *C*H), 53.9 (t, $^1J_{\mathrm{CH}} = 127$ Hz, $\mathrm{W{\equiv}C\mathit{C}H_2CH{=}CHC{\equiv}W}$)), 16.8, 16.7, 16.6, 15.2, 15.3, 12.7 (12 Tp′ $\mathrm{CCH_3}$). Anal. Calcd for $\mathrm{C_{39}H_{48}N_{12}B_2O_4W_2}$: C, 41.15; H, 4.25; N, 14.77. Found: C, 41.24; H, 4.29; N, 14.60.

**$\mathbf{[K][Tp'(CO)_2W{\equiv}CCHCHCHC{\equiv}W(CO)_2Tp']}$ (22).** An NMR tube was charged with $\mathrm{Tp'(CO)_2W{\equiv}CCH_2CH{=}CHC{\equiv}W(CO)_2Tp'}$ (0.020 g, 0.018 mmol) and solid $\mathrm{KO^tBu}$ (0.012 g, 0.11 mmol) and then sealed with a rubber septum. Approximately 0.7 mL of THF-$d_8$ was added to the tube via syringe to give an ink blue solution. IR (THF): 2528 $\mathrm{cm^{-1}}$ ($\nu_{\mathrm{BH}}$), 1961 (m), 1926 (m), 1891 (m), 1837 (m), 1779 (s) ($\nu_{\mathrm{CO}}$), 1544 $\mathrm{cm^{-1}}$ ($\nu_{\mathrm{CN}}$). UV−vis (THF, $2.9 \times 10^{-6}$ M): $\lambda_{\max} = 596$ nm, $\epsilon_{596} = 7.9 \times 10^4\ \mathrm{M^{-1}\,cm^{-1}}$; $\lambda_{\max} = 786$ nm, $\epsilon_{786} = 8.3 \times 10^4\ \mathrm{M^{-1}\,cm^{-1}}$. $^1$H NMR (THF-$d_8$, 253 K): $\delta$ 7.26 (t, $^3J_{\mathrm{HH}} = 13$ Hz, 1 H, $\mathrm{W{\equiv}CCHC\mathit{H}CHC{\equiv}W}$), 5.77, 5.70 (s, 4:2 Tp′ CH), 5.06 (d, $^3J_{\mathrm{HH}} = 13$ Hz, 2 H, $\mathrm{W{\equiv}CC\mathit{H}CHC\mathit{H}C{\equiv}W}$), 2.61, 2.44, 2.38, 2.35 (s, 12:6:12:6 Tp′ $\mathrm{CC\mathit{H}_3}$). $^{13}$C NMR (THF-$d_8$, 253 K): $\delta$ 306.1 ($^1J_{\mathrm{WC}} = 173$ Hz, $\mathrm{W{\equiv}\mathit{C}CHCHCH\mathit{C}{\equiv}W}$), 229.6 ($^1J_{\mathrm{WC}} = 172$ Hz, 4 W(*C*O)), 151.7, 151.6, 143.7, 143.0 (2:4:2:4 Tp′ $\mathrm{\mathit{C}CH_3}$), 144.0 (d, $^1J_{\mathrm{CH}} = 145$ Hz, $\mathrm{W{\equiv}CCH\mathit{C}HCHC{\equiv}W}$), 117.6 (d, $^1J_{\mathrm{CH}} = 152$ Hz, $^2J_{\mathrm{WC}} = 40$ Hz, $\mathrm{W{\equiv}C\mathit{C}HCHCHC{\equiv}W}$), 105.6 (s, 6 Tp′ *C*H), 16.5, 15.3, 12.2, 12.1 (12:6:12:6 Tp′ $\mathrm{CCH_3}$)).

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