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Deprotonation and Oxidation of the W≡CCH_2−W Bridge To Form a C_2-Biscarbyne W≡C−C≡W Bridge

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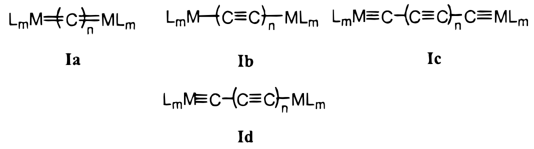
Abstract: Reaction of the anionic vinylidene complex K[Tp′$(CO)_2$M=C=CH_2] (M = Mo, W; Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate) with Tp(CO)(PhC≡CPh)W−I (Tp = hydridotris(pyrazolyl)borate) yields Tp′$(CO)_2$MCCH_2−W(CO)(PhC≡CPh)Tp (M = Mo, **4**; W, **5**) and potassium iodide. Removal of a methylene proton from the (≡CCH_2−) bridge with $KOBu^t$ forms a monoanion containing a putative carbene moiety. Oxidation of the anion with iodine leads to net hydride removal and yields the unusual C_2-bridged dimers Tp′$(CO)_2$M≡CC≡W(CO)(PhC≡CPh)Tp (M = Mo, **7**; W, **8**). Conversion of the tungsten−carbon single bond in the precursor complex to a triple bond in the product is accompanied by a significant reduction in donation to the metal from the alkyne $\pi_\perp$ orbital.

Introduction

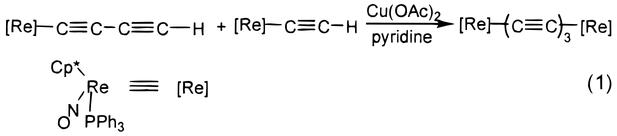
Reports of metal centers spanned by hydrocarbon bridges have multiplied in recent years. An important subset of hydrocarbon bridges are carbon-only (C_n) bridges.[1] A variety of structures, dictated by the number of carbons in the bridge as well as the electronic demands of the metals, are accessible to these all-carbon linkages (Scheme 1). Cumulene bridges (**Ia**) as well as acetylene structures (**Ib**−**d**) have been realized. For even-numbered carbon bridges, structures **Ia**−**c** are possible, while bridges with an odd number of carbons have access to forms **Ia** and **Id**. Metal centers bridged by an even number of carbons are far more common than those bridged by an odd number of carbon atoms, with two- and four-carbon bridges particularly well represented in the literature.

Recent contributions to this field have come from several groups,[2] with Gladysz and co-workers taking a leading role in creating extended, all-carbon bridges between metal centers.[3]

Scheme 1



One synthetic route to all-carbon bridges is the coupling of terminal acetylides, of varying length, to form dinuclear complexes with extended carbon bridges (eq 1).



(1)

Metal centers spanned by two-carbon frameworks are relatively common. Dimeric complexes with two-carbon scaffolds bridging metals have included ethane-bridged (MCH_2CH_2M),[4] alkene-bridged (MCH=CHM),[5] ethynyl-bridged (MC_2HM),[6−8] and C_2-bridged (MCCM) metal centers.[6−9] An aesthetically pleasing series of complexes exhibiting C_2H_4, C_2H_2, and C_2

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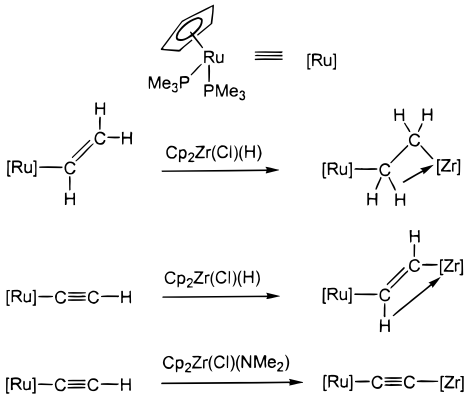
Scheme 2

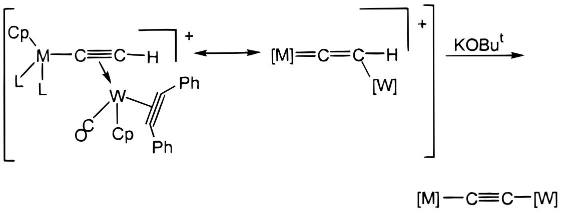
$L_nM{-}C{\equiv}C{-}ML_n$ **IIa** $L_nM{=}C{=}C{=}ML_n$ **IIb** $L_nM{\equiv}C{-}C{\equiv}ML_n$ **IIc**

bridges was reported by Beck for dimers with similar termini.[10] Bullock has reported complexes where two different metal centers are spanned by CH_2CH_2, CH═CH, and C≡C linkages.[11] Each of these distinct bridging units required a unique synthetic approach for introduction of the C_2H_n unit between the Ru and Zr centers (eq 2). In Bullock's study, the simple C_2 bridge consists of an acetylene unit linking two metal centers.



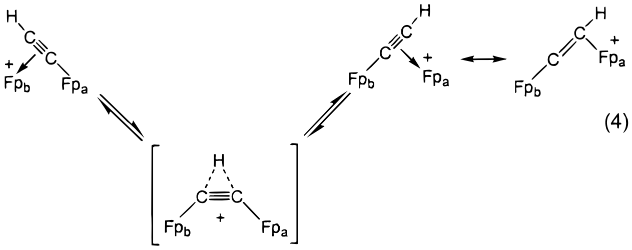
(2)

A recent paper detailed complexes with bridging C_2H and C_2 moieties.[6] Dinuclear complexes containing a bridging ethynyl ligand such as $[CpL_2M\text{-}(\mu\text{-}C{\equiv}CH)W(PhC{\equiv}CPh)(CO)\text{-}Cp][BF_4]$ have been deprotonated to form a C_2 linkage between the two metal centers (eq 3).[8] In a related system, the Fp* analog



(3)

[Fp* = (η^5-C_5Me_5)$Fe(CO)_2$] displays a dynamic process which equilibrates the two metal centers in Fp*−C_2H−Fp* (eq 4).[6] Analysis of the crystal structure for each bridging-ethynyl example indicates the contribution of a vinylidene resonance form to the solid-state structure.



(4)

Dimeric C_2-bridged metal complexes can assume one of three possible limiting structures (Scheme 2). Examples of all three have appeared in the literature with **IIa** being by far the most prevalent. A variety of syntheses yield acetylide-bridged homo- and heterodinuclear complexes.[9] Complexes containing the relatively rare cumulene-like bridge **IIb** are exemplified by a Ta═C═C═Ta complex which was synthesized by reaction of CO with $(Bu^t{}_3SiO)_3Ta$.[9b]

Least common among the C_2 bridges is the biscarbyne form **IIc**. To our knowledge, the only reported example of this biscarbyne bridge is $(Bu^tO)_3W{\equiv}C{-}C{\equiv}W(Bu^tO)_3$ which was first reported by Schrock and co-workers.[9a] A crystal structure and a detailed description of the bonding for this dimer were reported by Caulton, Chisholm, and co-workers.[12]

A recent theoretical paper by Floriani and co-workers[13] addressed the nature of C_2 bridges in dinuclear species (Scheme 2). The electronic structure of the C_2 bridge depends on the number of d^n electrons, the oxidation state of the transition metal, and the properties of the ancillary ligands. For early transition metals (Ti, V, and Cr triads) in high oxidation states with mainly π-donor ligands in a pseudotetrahedral environment, all three C_2 bridging forms are found as a function of the d^n count of the metal. Examples of early transition metals in low oxidation states are rare and acetylenic bridges are realized. For late transition metals in low oxidation states with π-acceptor ligands, only the acetylenic bridge was found irrespective of the d^n configuration. This is attributed to the metal centers not having orbitals available for π-donation from the C_2 unit.

We have established that the vinylidene anion, $[Tp'(CO)_2\text{-}M{=}C{=}CH_2]^-$ (M = Mo, W), reacts with a variety of electrophiles.[2h,14] It is also known that metal halides are susceptible to nucleophilic attack, as observed in the reaction of [W]−I with $LiMe_2Cu$ to form [W]−CH_3 ([W] = Tp′(CO)-(RC≡CR)W]).[15] This work merges these two complementary reagents: the vinylidene anion(s) $[Tp'(CO)_2M{=}C{=}CH_2]^-$ reacts with Tp(CO)(I)W(PhC≡CPh) to form a bridging ligand with a two-carbon framework. Net removal of H_2 from the methylene in the bridge by deprotonation and oxidation forms a C_2-bridged biscarbyne complex.

Results and Discussion

Synthesis of Tp′(CO)$_2$M≡CCH$_2$W(CO)(PhC≡CPh)Tp (M = Mo, 4; W, 5). The chiral tungsten complex Tp(CO)(I)W-(PhC≡CPh) (**1**), synthesized by refluxing $Tp(CO)_3W(I)$ with diphenylacetylene, forms when two carbon monoxide ligands are replaced by the alkyne. Diphenylacetylene was chosen as the alkyne for this metal halide reagent in order to avoid the presence of acidic propargylic protons.[16] The synthesis of **1** was facilitated by use of the unsubstituted Tp ligand rather than the bulky Tp′ ligand in order to accommodate the diphenylacetylene ligand.

Deprotonation of the methyl−carbyne complex, $Tp'(CO)_2M{\equiv}CCH_3$ (M = Mo, W), with KOBu^t yields the vinylidene anion, $[K][Tp'(CO)_2M{=}C{=}CH_2]$ (M = Mo, **2**; W, **3**). Reaction of the vinylidene anion at ambient temperature with metal halide **1** results in displacement of iodide from **1** to form the dinuclear complex $Tp'(CO)_2M{\equiv}CCH_2W(CO)(PhC{\equiv}CPh)Tp$ (M = Mo, **4**; W, **5**) (eq 5). An extra equivalent of KOBu^t was essential

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[10] (a) Beck, W.; Schweiger, M. J.; Müller, G. *Chem. Ber.* **1987**, *20*, 889−893. (b) Heidrich, J.; Steimann, M.; Appel, M.; Beck, W.; Phillips, J. R.; Trogler, W. C. *Organometallics* **1990**, *9*, 1296−1300.

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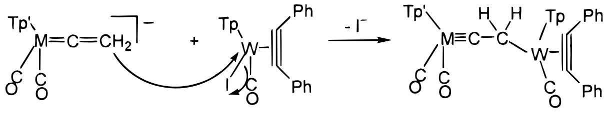
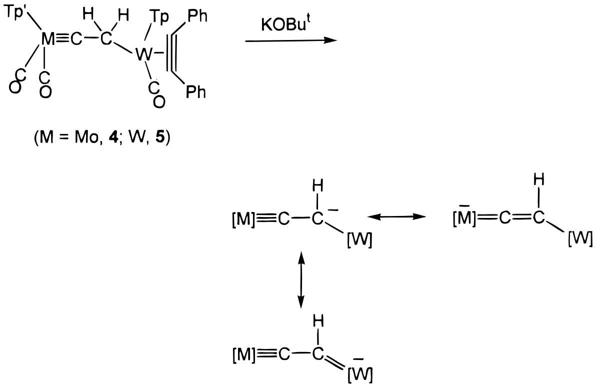
[16] Propargylic protons are easily deprotonated under these reaction conditions.



(5)

(M = Mo, **4**; W, **5**)

to isolate the product in good yield. Since the methylene protons of $Tp'(CO)_2M{\equiv}CCH_2W(CO)(PhC{\equiv}CPh)Tp$ are acidic (eq 6), formation of the dimer could provide a proton to quench the vinylidene anion. Excess butoxide insures that the vinylidene complex will be available as a nucleophile.



(M = Mo, **4**; W, **5**)

(6)

Following acidic work-up, **4** and **5** were isolated in 41% and 77% yield, respectively. The unique C_2H_2 bridge here is unsymmetrical: it has a carbyne moiety and a methylene group linking two metal centers. Other bridges with a C_2H_2 stoichiometry have involved an alkene bridge between two metal centers.[5]

Complex **5** was characterized by NMR, elemental analysis, and X-ray crystallography. The absence of a mirror plane is reflected in the Tp and Tp′ regions of the ^1H and ^{13}C NMR spectra and reflects the presence of a chiral metal center. An AB pattern for the diastereotopic methylene protons is centered at 2.68 ppm with geminal coupling of 17 Hz. A carbyne carbon resonance appears at 312 ppm ($^1J_{WC} = 180$ Hz), and the CH_2 carbon appears as a triplet at 67.7 ppm ($^1J_{CH} = 123$ Hz, $^1J_{WC} = 70$ Hz, $^2J_{WC} = 40$ Hz). Three metal−carbonyl carbon resonances are present: 240 ($^1J_{WC} = 144$ Hz), 225, and 224 ppm ($^1J_{WC} = 172$ Hz).

The chemical shift of coordinated alkyne carbons and metal−alkyne bond distances indicate the degree of electron donation to the metal center.[17] Alkyne resonances for **5** at 219 and 209 ppm and tungsten−alkyne bond distances of 2.008(13) and 2.050(13) Å (*vide infra*) are consistent with a four-electron donor alkyne assignment. IR data show $\nu_{CO(KBr)}$ absorptions at 1938, 1914, and 1844 cm^{-1}. Although there may be some mixing of carbonyls from the two metal centers, comparison of the ν_{CO} values for **5** with the ν_{CO} frequencies for the analogous $Tp'(CO)_2Mo{\equiv}CCH_2W(CO)(PhC{\equiv}CPh)Tp$ (**4**) ($\nu_{CO(KBr)} = 1951$, 1919, and 1863 cm^{-1}) leads to assignment of the 1938 and 1844 cm^{-1} stretches primarily to the $W(CO)_2$ moiety of **5** and 1951 and 1863 cm^{-1} stretches to the $Mo(CO)_2$ moiety of **4**. The carbonyl stretch around 1915 cm^{-1} changes only slightly between **4** and **5**, and we assign that stretch to the tungsten monocarbonyl as it senses the adjacent metal through the CCH_2 bridge.

Crystal Structure of 5. X-ray quality crystals were grown from slow diffusion of methanol into a CH_2Cl_2 solution of **5**. The unit cell of **5** is triclinic ($P\bar{1}$) and contains one half of a molecule of MeOH per asymmetric unit. An ORTEP drawing of **5** is shown in Figure 1. Crystallographic data and collection parameters (Table 1) and complete bond lengths and angles and atomic parameters are available as Supporting Information.

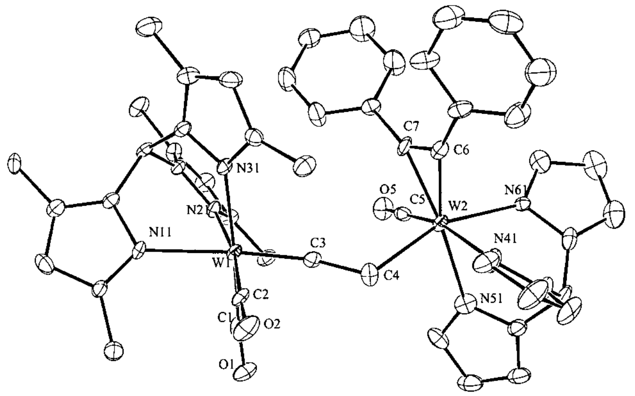


Figure 1. ORTEP diagram of $Tp'(CO)_2W{\equiv}C{-}CH_2{-}W(CO)(PhC\text{-}CPh)Tp$ (**5**).

Table 1. Crystallographic Data and Collection Parameters for $Tp'(CO)_2W{\equiv}CCH_2W(CO)(PhC{\equiv}CPh)Tp$ (**5**)

formula	$B_2C_{43}H_{44}N_{12}O_3W_2{\cdot}{}^1/_2CH_3OH$
mol wt	1181.73
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	10.4446(15)
b, Å	12.631(3)
c, Å	17.788(6)
α, deg	90.928(22)
β, deg	91.529(20)
γ, deg	95.148(16)
V,	2336.1(10)
Z	2
D_{calc}, mg m^{-3}	1.680
$F(000)$	1148.94
cryst dimens, mm	0.45 × 0.20 × 0.20
temp, °C	−100
radiation,	Mo Kα(0.71073)
2θ range, deg	$30 < 2\theta < 40$
μ, mm^{-1}	5.08
scan mode	ω
total no. of data	6544
total no. of unique data	6503
no. of obs data ($I > 2.5\sigma(I)$)	4881
R_f	0.051
R_w	0.063
GOF	1.87

Tungsten-carbon bond lengths of 1.861(13) and 2.229(13) Å are observed for the W≡C and $W{-}CH_2$ bonds, respectively. A nearly linear bond angle of 167.5(10)° is realized for the carbyne W≡C−C unit while an angle of 122.3(9)° characterizes the $W{-}CH_2{-}C$ unit. The large $W{-}CH_2{-}C$ angle presumably reflects the steric problems inherent in bringing the two metal coordination spheres into contact with one another. The alkyne carbons are 2.008(13) and 2.050(13) Å from the metal center. The alkyne ligand is aligned along the W−CO axis as expected for d^4 monocarbonyl alkyne complexes.[17]

Reaction of 5 with Base. In a THF solution of **5**, in the presence of KOBu^t, one of the methylene protons of **5** is abstracted. The anionic species **6** can be observed by ^{13}C NMR spectroscopy. In an NMR tube experiment, **5** was reacted with an excess of KOBu^t in THF containing a sealed capillary tube filled with C_6D_6 which was used to achieve a deuterium lock in the NMR. Anion **6** has two limiting resonance structures as represented in Scheme 3. The stability of vinylidene anions in related monomer systems led us to expect that resonance form

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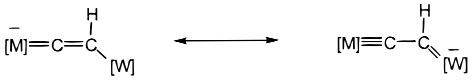
[17] Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1−100.

Scheme 3



IIIa **IIIb**

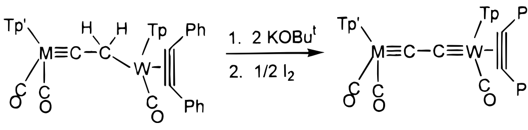
IIIa would be favored;[2h,14,18] experimental evidence points toward **IIIb** as an important resonance form as well.

In the ^{13}C NMR spectrum, a singlet at 311 ppm and a doublet at 193 ppm with a coupling constant of 130 Hz are observed, consistent with the presence of carbyne and carbene carbons in the monoanion, respectively. One-bond hydrogen coupling to the β-carbon is comparable to $^1J_{CH}$ data for a carbene complex reported by Mayr, [(W═CHPh)(Cl)$_2$(PhC≡CPh)(PMe$_3$)$_2$],[19] where the $^1J_{CH} = 128$ Hz. In contrast, the $^1J_{CH}$ for the monomeric vinylidene anion, Na[Tp′(CO)$_2$Mo═C═CH$_2$], is 153 Hz.[14a] Chemical shifts for C_α and C_β for this parent vinylidene anion are 350 and 91 ppm, respectively. The chemical shift for the carbene carbon in Mayr's monomer (283 ppm) is 90 ppm downfield of the C_β of **6**. The chemical shift of the carbon unit, here roughly midway between a vinylidene C_β value of 91 ppm and a carbene C_α value of 283 ppm, is more sensitive to the coordination environment of the metal center than is the C−H coupling constant.

The alkyne carbon resonances in the anion at 188 and 178 ppm also yield diagnostic information. These values are shifted upfield from values in the neutral precursor **5**, indicating that less $\pi_\perp$ electron density is being donated by the alkyne ligand in the anion.[17] This is consistent with designation of **IIIb** as a major resonance contributor. The importance of resonance form **IIIb** is reinforced by successful formation of Tp′(CO)$_2$M≡CC≡W(CO)(PhC≡CPh)Tp (*vide infra*). Essentially, **IIIb** is more product-like than **IIIa**.

Synthesis of Tp′(CO)$_2$M≡CC≡W(CO)(PhC≡CPh)Tp (M = Mo, 7; W, 8). Reaction of **5** with 2 equiv of KOBu^t followed by reaction with 1/2 equiv of I$_2$ resulted in net removal of H$_2$ to give good yields of a C$_2$-bridged biscarbyne complex Tp′(CO)$_2$W≡CC≡W(CO)(PhC≡CPh)Tp (**8**) (eq 7). No mirror plane of symmetry is evident in the NMR spectra, and only protons belonging to the pyrazole ligands of Tp and Tp′ and the phenyl groups are observed. In the ^{13}C NMR spectrum, resonances at 347 ($^1J_{WC} = 185$ Hz) and 274 ppm ($^1J_{WC} = 171$ Hz) characterize the two carbyne moieties, and the alkyne carbons resonate in a chemical shift region reminiscent of two-electron donor alkyne ligands (157 and 150 ppm). Resonances for the metal−carbonyl carbons appear at 233, 231 ($^1J_{WC} = 165$ Hz), and 219 ($^1J_{WC} = 131$ Hz) ppm. The IR spectrum shows absorptions at $\nu_{CO(KBr)} = 1997$, 1939, and 1858 cm^{-1} for the carbonyl stretches. Similar spectroscopic data are observed for **7**: resonances at 343 ($^1J_{WC} = 184$ Hz) and 277 ppm ($^2J_{WC} = 43$ Hz) for the carbyne carbons, 158 and 150 ppm for the alkyne ligand, and 234, 232, and 219 ($^1J_{WC} = 130$ Hz) ppm for the metal−carbonyl carbons. Absorptions at $\nu_{CO(KBr)} = 1999$, 1950, and 1871 cm^{-1} are observed in the IR spectrum.

The C$_2$-bridge is best formulated as a biscarbyne bridge (**IIc**) where both metal centers satisfy the 18-electron-rule. A rare coordination environment is present for one metal center: a coordinated alkyne and a metal-carbon triple bond coexist at one metal in the dimer. In fact, the electronic flexibility of the diphenylacetylene ligand is crucial to formation of the biscarbyne linkage reported here.



(7)

(M = Mo, **7**; W, **8**)

Recently, Mayer and co-workers reported that alkynes displace two phosphine ligands in (PMe$_3$)$_4$(Cl)W≡CCH$_3$ to form the first well-characterized transition metal carbyne complex containing an alkyne ligand.[20] With 2-butyne as the alkyne, the carbyne carbon resonated at 321 ppm, and the alkyne carbons were equivalent and resonated at 168 ppm. When PhC≡CPh or HC≡CBu^t were employed, an alkyne metathesis reaction occurred which exchanged the carbyne methyl with an alkyne phenyl or *tert*-butyl group.

Bonding Description for Tp′(CO)$_2$M≡CC≡W(CO)(PhC≡CPh). In transition metal d^4 complexes with both a carbonyl and an alkyne ligand in the coordination sphere, the alkyne will preferentially align along the M−CO axis to optimize both back donation into π^* and forward donation from $\pi_\perp$.[17] Indeed, the crystal structure of **5** shows the alkyne aligned parallel to the W−CO unit.

The formation of **7** and **8** places a carbyne moiety in the coordination sphere in place of the CH$_2$R$^-$ entity of **4** and **5**. If the carbyne is counted as CR^{3-}, the metal center is now formally W^{IV} (d^2), and the bonding description can be described as shown in Figure 2.

From the original nest of three metal dπ bonding orbitals, placing CR^{3-} along the x axis destabilizes d_{xz} and d_{xy} so the two metal electrons occupy d_{yz}. Adding CO along the z axis stabilizes both d_{yz} and d_{xz}; d_{xz} and d_{xy} are no longer degenerate. Bringing an alkyne ligand in along the y axis introduces a single-faced π-acid, and there will be a preferred orientation for the alkyne ligand.

Alkyne binding to the metal σ orbital from the filled alkyne π orbital will be independent of the alkyne rotational orientation. Back donation from d_{yz} to π^* can occur *only* if the alkyne is aligned along the M−CO axis. Based on this description, the orientation of the alkyne ligand in complexes **7** and **8** is clear. Due to strong covalent bonding between the metal and the carbyne ligand, interaction between $\pi_\perp$ and d_{xy} is possible but limited, thus effectively relegating the alkyne to a two-electron donor role.

With this bonding scheme in mind, conversion of **4** to **7** (or **5** to **8**) introduces a triple bond between M and CR^{3-} which will weaken the bonds between tungsten and the alkyne and carbonyl ligands. This bonding reorganization reflects increased competition for the metal dπ orbitals as the number of π-acid ligands in **4** and **5** is expanded to three π-acid ligands in **7** and **8**. This description of the dπ competition is consistent with spectroscopic results. For example, in going from **5** to **8**, the chemical shift of the carbonyl carbon on the Tp(PhC≡CPh)(CO)W moiety shifts upfield by 22 ppm (241−219 ppm), and the W−C coupling constant is reduced by 13 Hz ($^1J_{WC} = 144$ Hz vs 131 Hz). Similarly, the chemical shift of the alkyne carbons moves upfield (219 and 209 ppm to 157 and 150 ppm) consistent with conversion from a four-electron donor to a two-electron donor alkyne. Conversion of a CH$_2$R one-electron donor ligand to a ≡CR three-electron donor ligand is made possible by retraction of the alkyne from a four-electron donor to a two-electron donor role. Indeed the electronic versatility

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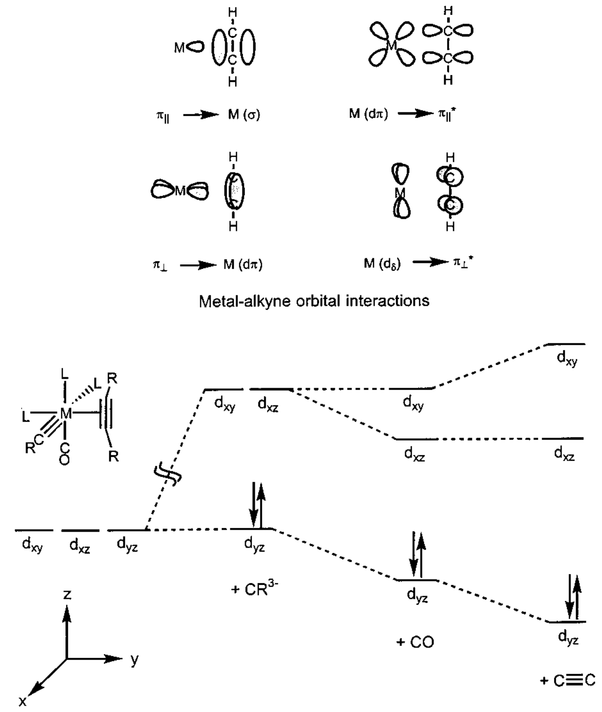

Figure 2. Bonding description for $L_3(CO)(RC{\equiv}CR)M{\equiv}CR$.

of the alkyne ligand allows the metal center to accommodate the transformation from a $\equiv CCH_2-$ complex to the unsaturated C_2 biscarbyne bridge, $\equiv CC \equiv$, described here.

This point is highlighted when we compare this system to one described by Selegue and co-workers.[8] In their system, they have a $Cp(CO)W(PhC{\equiv}CPh)$ moiety bridged to a CpL_2M fragment by a C_2 bridge ($L = PMe_3$, $P(OMe)_3$ or 1/2 dppe; M = Ru or Fe) (see eq 3). The C_2 bridge is acetylenic in nature (**IIa**) yielding a tungsten−carbon single bond in contrast to the tungsten−carbon triple bond in our related system. The diphenylacetylene ligand acts as a four-electron donor in Selegue's complex to satisfy the 18-electron count at the tungsten center.

Further comparison with the electronically similar ruthenium−tungsten dinuclear complex reported by Frank and Selegue is worthwhile.[8] The X-ray structure of $[Cp(PMe_3)_2Ru(\mu\text{-}C{\equiv}CH)W{-}(PhC{\equiv}CPh)(CO)(Cp)][BF_4]$ provides a cationic analog of the anionic $[Tp'(CO)_2Mo(\mu\text{-}C{\equiv}CH)W{-}(PhC{\equiv}CPh)(CO)(Tp')]^-$ intermediate. Deprotonation of the ruthenium−tungsten dinuclear cation produced a Ru−C≡C−W unit,[8] while net hydride removal from the molybdenum−tungsten dinuclear anion yields a Mo≡C−C≡W entity. Clearly these units differ by only two electrons, but an additional factor is that the diphenylacetylene continues to play a four-electron donor role in the neutral ruthenium−tungsten product, while it retracts to a simple two-elecron donor role in the neutral molybdenum−tungsten product **7**.

To fit our unusual dinuclear complex into Floriani's scheme,[13] we first count d electrons with the C_2 unit considered as a neutral ligand. Both tungsten−metal centers then have a d^5 configuration, i.e., they are early transition metals in a low oxidation state with π-acceptor ligands. One metal has a carbyne ligand, and the other metal contains a versatile alkyne ligand in the precursor complex, and we realize conversion to a M≡CC≡M structure.

Summary

We have reported a unique CCH_2 hydrocarbon bridge between tungsten and molybdenum metal centers formed by reaction of $K[Tp'(CO)_2M{=}C{=}CH_2]$ (M = Mo, W) with $Tp(CO)(PhC{\equiv}CPh)W(I)$. $Tp'(CO)_2W{\equiv}CCH_2W(CO)(PhC{\equiv}CPh)Tp$ has been structurally characterized. The methylene protons of these dinuclear products are acidic, and addition of $KOBu^t$ forms a monoanion with major resonance contribution from a carbene-like structure. Oxidation of the anion with iodine yields rare biscarbyne C_2-bridged dimers $Tp'(CO)_2M{\equiv}CC{\equiv}W(CO)(PhC{\equiv}CPh)Tp$. A qualitative bonding description predicts that the alkyne ligand shifts from four-electron donation to function as a two-electron donor ligand in the biscarbyne product.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques unless otherwise noted. Solvents were dried and distilled under nitrogen by standard methods. Alumina was deactivated before use by adding 5 mL of distilled water for every 100 mL of alumina. $Tp(CO)(I)W(PhC{\equiv}CPh)$ and $Tp'(CO)_2M{\equiv}CCH_3$ (M = Mo, W) were synthesized according to literature methods. All other reagents were used as obtained from commercial sources.

Infrared spectra were obtained from a Mattson Polaris Fourier transform spectrophotometer. ^1H NMR spectra were recorded on a Bruker WM250 spectrometer. ^{13}C NMR spectra were obtained on a Varian XL400 spectrometer. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, Ga.

Synthesis of $Tp'(CO)_2M{\equiv}CCH_2W(CO)(PhC{\equiv}CPh)Tp$ (M = Mo, 4; W, 5). To an oven-dried Schlenk flask was added $Tp(CO)(I)W(PhC{\equiv}CPh)$, 0.753 g (1.03 mmol), $Tp'(CO)_2W{\equiv}CCH_3$, 0.582 g (1.03 mmol), and $KOBu^t$, 0.23 g (2.1 mmol). The reaction flask was cooled to −78 °C, and THF (50 mL) was added via cannula by slowly running it down the side of the Schlenk flask. The contents were then mixed by stirring, and after 15 min of stirring, an army green color persisted. The solution was warmed to 0 °C, and the solution color turned black. The solution was stirred at 0 °C for 1 h, and the color of the solution acquired a purple tint. The reaction mixture was brought to room temperature and stirred for 1 h. The solution color turned a dark maroon. The solution was cooled to −78 °C, and HCl (in Et_2O), 2.1 mmol, was added, resulting in a color change to yellowish-brown. The reaction solution was run through a plug of alumina and eluted with THF. The solvent was removed leaving an army green solid. The solid residue was washed 3 times with 20 mL portions of hexanes. The residue left from the hexane washes was dried under vacuum and was pure **5** as determined by ^1H NMR. **5** was collected as an army green solid, 0.927 g (0.795 mmol), yield = 77%. Analytically pure crystals were obtained by slow diffusion of MeOH into a concentrated solution of **5** in CH_2Cl_2. IR (KBr): 1933, 1918, 1842 cm^{-1} (ν_{W-CO}); ^1H NMR (200 MHz, $CDCl_3$): δ 8.43, 7.81, 6.67 (d, Tp*H*), 7.65−7.10, 6.50−5.95 (m, 3 H (Tp*H*), 10 H (*Ph*C≡C*Ph*)), 5.82, 5.66, 5.56 (s, 1:1:1, Tp′C*H*), 2.67 (AB, $^2J_{HH}$ = 17 Hz, $W{\equiv}CCH_2W$), 2.60, 2.41, 2.40, 2.31, 2.27, 2.14 (s, 3:3:3:3:3:3, $Tp'CH_3$); ^{13}C NMR (100.56 MHz, $CDCl_3$): δ 312.3 (s, W≡*C*), 240.7 (s, TpW−*C*O), 224.6, 224.5 (s, Tp′W−*C*O), 218.6, 209.1 (s, Ph*C*≡*C*Ph), 152.3, 151.9, 151.8, 144.1, 143.7, 143.4 (s, 1:1:1:1:1:1, $Tp'CCH_3$), 145.7, 144.3, 142.1, 135.4, 135.0, 134.8 (d, 1:1:1:1:1:1, Tp*C*H), 139.8, 137.5 (s, 2 Ph_{ipso}), 128.4, 128.1, 128.0, 127.9 (d, 2 $Ph_{ortho/meta/para}$), 106.4, 106.3, 106.2, 106.1, 105.8 (d, 1:1:1:1:2, 3 Tp*C*H, 3 Tp′*C*H), 67.66 (t, $^1J_{CH}$ = 123 Hz, $W{\equiv}CCH_2W$), 17.09, 16.37, 15.32, 12.82, 12.61, 12.53 (q, 1:1:1:1:1:1, $Tp'CCH_3$). Calcd for $B_2C_{43}H_{44}N_{12}O_3W_2$: C, 44.29; H, 3.80; N, 14.41. Found: C, 44.39; H, 3.85; N, 14.45.

$Tp'(CO)_2Mo{\equiv}CCH_2W(CO)(PhC{\equiv}CPh)Tp$ (4). Yield = 41%. IR (KBr): 1943, 1921, 1855 cm^{-1} (ν_{M-CO}); ^1H NMR (200 MHz, $CDCl_3$): δ 8.45, 7.84, 6.67 (d, Tp*H*), 7.66−7.05, 6.55−5.95 (m, 3 H (Tp*H*), 10 H (*Ph*C≡C*Ph*)), 5.81, 5.64, 5.52 (s, 1:1:1, Tp′C*H*), 2.90 (AB, $^2J_{HH}$ = 16 Hz, $^2J_{WH}$ = 13 Hz, $Mo{\equiv}CCH_2W$), 2.63, 2.45, 2.38, 2.33, 2.29, 2.09 (s, 3:3:3:3:3:3, $Tp'CH_3$); ^{13}C NMR (100.56 MHz, $CDCl_3$): δ 325.2 (s, Mo≡*C*), 240.3 (s, $^1J_{WC}$ = 144 Hz, TpW−*C*O), 226.3, 226.2 (s, Tp′Mo-*C*O), 218.9, 210.1 (s, Ph*C*≡*C*Ph), 151.5, 150.9, 150.8, 144.0, 143.7, 143.5 (s, 1:1:1:1:1:1, $Tp'CCH_3$), 145.8, 144.2, 142.2, 135.5, 135.1, 134.9 (d, 1:1:1:1:1:1, Tp*C*H), 139.7, 137.2 (s, 2 Ph_{ipso}), 128.4, 128.3, 128.2, 128.1 (d, 2 *Ph*$_{ortho/meta/para}$), 106.5, 106.4, 106.3, 105.8, 105.6 (d, 1:1:1:1:2, 3 Tp*C*H, 3 Tp′*C*H), 66.50 (t, $^1J_{\mathrm{CH}}$ = 124 Hz, $^1J_{\mathrm{WC}}$ = 70 Hz, W≡CC*H*$_2$W), 16.42, 15.68, 14.72, 12.91, 12.70, 12.57 (q, 1:1:1:1:1:1, Tp′C*C*H$_3$).

Reaction of 5 with KOBu^t: ^{13}C NMR Characterization of K[Tp′(CO)$_2$WCCHW(CO)(PhC≡CPh)Tp] (6). To a flame-dried NMR tube was added 20 mg of **5** and 5 mg of KOBu^t. A capillary tube sealed with C$_6$D$_6$ was placed in the NMR tube to achieve a deuterium lock signal. The NMR tube was flushed with nitrogen for 20 min. Distilled THF was then added to the NMR tube, resulting in a maroon solution, and the ^{13}C NMR spectrum was obtained. ^{13}C NMR (100.56 MHz, THF/C$_6$D$_6$): δ 311.1 (s, W≡*C*), 249.1 (s, TpW−*C*O), 233.4, 229.7 (s, Tp′W−*C*O), 192.9 (d, $^1J_{\mathrm{CH}}$ = 130 Hz, WCC*H*W), 187.9, 178.2 (s, Ph*C*≡*C*Ph), 153.4, 152.7, 150.7, 143.0, 142.5, 142.4 (s, 1:1:1:1:1:1, Tp′*C*CH$_3$), 145.5, 144.6, 141.5, 134.7, 134.2, 133.9 (d, 1:1:1:1:1:1, Tp*C*H), 141.7, 140.1 (s, 2 *Ph*$_{ipso}$), *Ph*$_{ortho/meta/para}$ masked by C$_6$D$_6$ resonances, 105.9, 105.8, 105.7, 105.4, 105.3, 105.1 (d, 1:1:1:1:1:1, 3 Tp*C*H, 3 Tp′*C*H), 67.66 (t, $^1J_{\mathrm{CH}}$ = 123 Hz, W≡CC*H*$_2$W), 17.75, 16.56, 15.87, 12.65, 12.48, 12.25 (q, 1:1:1:1:1:1, Tp′C*C*H$_3$).

Synthesis of Tp′(CO)$_2$M≡CC≡W(CO)(PhC≡CPh)Tp (M = Mo, 7; W, 8). To an oven-dried Schlenk flask was added **5**, 0.198 g (0.170 mmol), and KOBu^t, 0.038 g (0.340 mmol). The reaction flask was cooled to 0 °C, and THF (50 mL) was added via cannula. This solution was warmed to room temperature and stirred for 10 min, and a dark maroon solution resulted. The reaction mixture was then cooled to −78 °C. In a separate Schlenk flask was added I$_2$, 0.022 g (0.085 mmol), which was then dissolved in THF (30 mL). The iodine solution was then transferred via cannula to the solution of **5** and KOBu^t. Upon I$_2$ addition, the reaction solution turned a dark purple-red color. Upon exposure to air, the solution turned yellow-brown. The reaction mixture was run through a plug of alumina and eluted with CH$_2$Cl$_2$. The solvent was removed, and the residue was dissolved in a minimal amount of CH$_2$Cl$_2$ and then loaded on an alumina column. The column was eluted with a solution of 8:2 hexanes:CH$_2$Cl$_2$. A broad brownish-green band of **8** was collected. After solvent removal, 0.152 g (0.131 mmol) of **8** was isolated as a dark green solid, yield = 77%. An analytically pure sample was obtained through slow diffusion of MeOH into a concentrated CH$_2$Cl$_2$ solution of **8**. Yield = 41%. IR (KBr): 1993, 1935, 1857 cm^{-1} ($\nu_{\mathrm{W-CO}}$); ^{1}H NMR (200 MHz, CDCl$_3$): δ 8.45, 7.73, 6.67 (d, Tp*H*), 7.66−7.05, 6.55−5.95 (m, 3 H (Tp*H*), 10 H (*Ph*C≡C*Ph*)), 5.81, 5.80, 5.70 (s, 1:1:1, Tp′C*H*), 2.37, 2.34, 2.32, 2.30 (s, 9:3:3:3, Tp′C*H$_3$*); ^{13}C NMR (100.56 MHz, CDCl$_3$): δ 347.5 (s, $^1J_{\mathrm{WC}}$ = 185 Hz, TpW≡*C*), 274.4 (s, $^1J_{\mathrm{WC}}$ = 171 Hz, Tp′W≡*C*), 233.0, 230.6 (s, $^1J_{\mathrm{WC}}$ = 165 Hz, Tp′W-*C*O), 219.2 (s, $^1J_{\mathrm{WC}}$ = 131 Hz, TpW−*C*O), 157.4, 149.6 (s, Ph*C*≡*C*Ph), 152.6, 152.0, 151.8, 144.9, 144.1, 143.9 (s, 1:1:1:1:1:1, Tp′*C*CH$_3$), 147.7, 147.2, 142.8, 135.4, 135.2, 134.4 (d, 1:1:1:1:1:1, Tp*C*H), 138.7, 138.6 (s, 2 *Ph*$_{ipso}$), 132.4, 130.0, 128.8, 128.5, 128.3, 127.7, 127.3, 127.2, 125.9 (d, restricted rotation of 2 *Ph*$_{ortho/meta/para}$), 106.4, 106.2, 106.1, 106.0, 105.6, 105.4 (d, 1:1:1:1:1:1, 3 Tp*C*H, 3 Tp′*C*H), 16.90, 16.76, 15.29, 12.57, 12.55, 12.57 (q, 1:1:1:1:1:1, Tp′C*C*H$_3$). Calcd for B$_2$C$_{43}$H$_{42}$N$_{12}$O$_3$W$_2$: C, 44.36; H, 3.64; N, 14.44. Found: C, 44.43; H, 3.59; N, 14.40.

Tp′(CO)$_2$Mo≡CC≡W(CO)(PhC≡CPh)Tp (7). Yield = 82%. IR (KBr): 1999, 1950, 1871 cm^{-1} ($\nu_{\mathrm{M-CO}}$); ^{1}H NMR (200 MHz, CDCl$_3$): δ 8.45, 7.73, 6.67 (d, Tp*H*), 7.66−7.05 (m, 3 H (Tp*H*), 5 H (*Ph*C≡CPh)), 6.55−5.95 (m, 5 H, PhC≡C*Ph*), 5.81, 5.80, 5.70 (s, 1:1:1, Tp′C*H*), 2.37, 2.34, 2.32, 2.30 (s, 9:3:3:3, Tp′C*H$_3$*); ^{13}C NMR (100.56 MHz, CDCl$_3$): δ 342.7 (s, $^1J_{\mathrm{WC}}$ = 184 Hz, TpW≡*C*), 277.0 (s, $^2J_{\mathrm{WC}}$ = 43 Hz, Tp′Mo≡*C*C≡W), 234.1, 231.9 (s, Tp′Mo−*C*O), 218.6 (s, $^1J_{\mathrm{WC}}$ = 130 Hz, TpW−*C*O), 157.8, 149.9 (s, Ph*C*≡*C*Ph), 151.4, 151.1, 150.9, 144.7, 144.0, 143.9 (s, 1:1:1:1:1:1, Tp′*C*CH$_3$), 147.9, 147.0, 143.0, 135.5, 135.4, 134.4 (d, 1:1:1:1:1:1, Tp*C*H), 138.8, 138.5 (s, 2 *Ph*$_{ipso}$), 128.7, 128.6, 127.8, 127.4, 127.2, 126.1 (d, restricted rotation of 2 *Ph*$_{ortho/meta/para}$), 106.1, 106.0, 105.7, 105.4 (d, 2:2:1:1, 3 Tp*C*H, 3 Tp′*C*H), 15.94, 15.87, 14.58, 12.68, 12.61 (q, 1:1:1:2:1, Tp′C*C*H$_3$).

X-ray Structure of Tp′(CO)$_2$W≡CCH$_2$W(CO)(PhC≡CPh)Tp (5). Crystals of **5** were grown from slow diffusion of methanol into a CH$_2$Cl$_2$ solution of **5**. The crystal was triclinic ($P\bar{1}$ space group). The cell dimensions were a = 10.4446(15) Å, b = 12.631(3) Å, and c = 17.788(6) Å. Z = 2 molecules per unit cell, D_{calc} = 1.680 mg m^{-3}, λ (MoKα) = 0.71073 Å), μ = 5.08 mm^{-1}, and F(000) = 1148.94. The X-ray data were collected on a Rigaku diffractometer using the ω scan mode. Experimental details are given in Table 1. Of the 6503 unique reflections, 4881 reflections possessed $I > 2.5\sigma(I)$, and these were used in the structure determination. Final agreement indices were R_{f} = 5.1% and R_{w} = 6.3%, with hydrogen placed in computed positions 0.96 Å from the bonded atom and included in the refinement using a riding model. All other atoms were refined anisotropically. An ORTEP diagram is shown in Figure 1.

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Supporting Information Available: Complete crystallographic data for **5** (8 pages, print/PDF). See any current masthead page for ordering and Web access instructions.

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