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Variable Electronic Coupling through Hydrocarbon Spacers Bridging Metal−Carbon Triple Bonds

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The electrochemical behavior of a series of bis-carbyne complexes, $Tp'(CO)_2M{\equiv}(C_mH_n){\equiv}M(CO)_2Tp'$ (Tp′ = hydridotris(3,5-dimethyl-1-pyrazolyl)borate; M = Mo, W; $m = 3$, $n = 2$; $m = 4$, $n = 0, 2, 4$), has been studied. These complexes exhibit two oxidation waves between 0 and 0.5 V (vs ferrocene). The difference in $E_{1/2}$ for the two oxidation waves is a function of the hydrocarbon spacer with the ≡C−C≡C−C≡ spacers ($m = 4$, $n = 0$) exhibiting considerably larger $\Delta E_{1/2}$ values than the corresponding ≡C−CH═CH−C≡ spacers ($m = 4$, $n = 2$), which were in turn more strongly coupled than the saturated analogues ($m = 4$, $n = 4$). While the trend in electronic coupling was quantitatively as expected for the degree of unsaturation in the bridge, the absolute magnitude of the coupling as indicated by the comproportionation constants ($K_c = 10^0{-}10^4$) was much smaller than that in isologous dimers where the bridge is connected to the metal centers via single bonds ($K_c = 10^8{-}10^{12}$). A qualitative model based on relevant orbital occupancy as a function of metal oxidation state has been developed to account for the experimental results.

Introduction

The electronic coupling of two redox centers through covalent spacers is a determining factor in the adiabaticity of electron transfer across the bridge.[1] The suitability of transition metals as the redox-active probes for such bridges has created synthetic challenges in the development of covalent assemblies where two redox-active metals are connected by proteins,[2] DNA,[3,4] or small hydrocarbon spacers.[5−10] Dimers with linear, unsaturated carbon chains are an important subset of these complexes. Symmetric ethynyl (M−C≡C−M) and polyalkynyl (M-(−C≡C−)$_n$M) dimers with an even number of carbons in the bridge are common (**A**, Chart 1); examples of C_2,[11−15] C_4,[14,16−21] C_6,[22] C_8,[14,22,23] and $C_{12/16/20}$[24] bridges have been prepared. Related even-carbon polyenyl bridged dimers (**B**) have also been reported.[25−27] Symmetric dimers with odd-carbon chains are less common (**C**, C_5H_5; **D**, C_5H).[28,29]

In most systems studied to date, the connection between the hydrocarbon bridge and the redox-active metal center has been a metal−carbon single bond or, at most, a metal carbon double bond. In many of these cases, high degrees of electronic coupling are observed across relatively long distances. We report here on the first assessments of electronic coupling across isologous bridges where the redox-active sites are connected to the bridge by metal−carbon triple bonds. Interestingly, the electronic coupling upon oxidation is *weaker* for dimers with metal−carbon triple bonds than in the singly bonded cases. A presage to this finding is the recent work by Hopkins et al. with aniline and pyridyl functionalized metal−alkylidyne complexes in which the M≡C linkage functions as the *acceptor* in extended one-dimensional donor−acceptor chains.[30,31]

General synthetic routes to dimeric compounds with metal−carbon triple bonds anchoring the carbon chains are rare (Chart 2, **E**−**H**).[32−35] A fruitful combination of metal carbyne derivative chemistry with coupling reactions has recently provided direct routes to low-valent, dimeric bis-carbyne complexes with three- and four-carbon bridges (**F**, **G**, and **I**).[36,37] We report here the electrochemical behavior of ≡CCH$_2$C≡ and ≡CCH$_n$-CH$_n$C≡ (n = 0, 1, 2) bridged bis-carbyne dimers for comparison to related polyalkynyl and polyenyl systems. Extended Huckel molecular orbital (EHMO) calculations on the ≡CCH═CHC≡ ditungsten dimer have been performed to help evaluate the data.

CHART 1

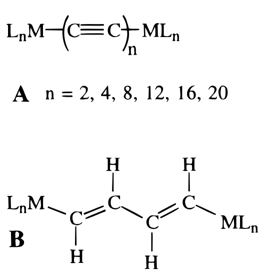
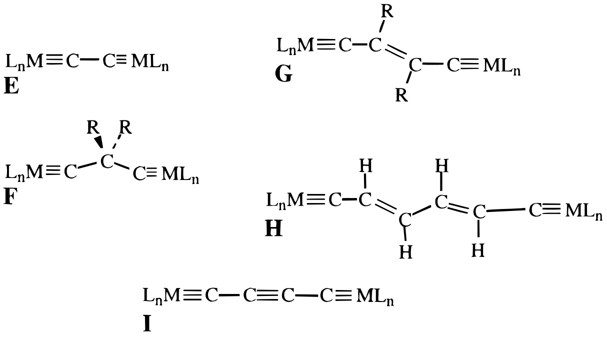


CHART 2



Results

Synthesis of the ≡CCH$_2$CH$_2$C≡ bridged dimers with metal−carbon triple-bond anchors is accomplished via the deprotonation of methylcarbyne complexes, $Tp'(CO)_2M{\equiv}CCH_3$, followed by oxidation of the anionic vinylidene compounds (eq 1; [M] =

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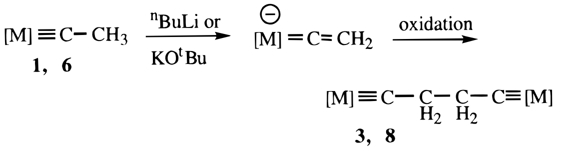
TABLE 1: Oxidation Potentials[a] of Bis-carbyne and Related Complexes

	complex[a]	$E^1_{1/2}$	$E^2_{1/2}$	$\Delta E_{1/2}$	K_c	ref
1	$[W]\equiv CCH_3$	0.050				
2	$[W]\equiv CCH_2C\equiv[W]$	0.105	0.294	0.189	2×10^3	
3	$[W]\equiv CCH_2CH_2C\equiv[W]$	0.110	0.182	0.072	2×10	
4	$[W]\equiv CCH{=}CHC\equiv[W]^b$	0.148	0.325	0.177	1×10^3	
5	$[W]\equiv CC\equiv CC\equiv[W]$	0.168	0.446	0.278	5×10^4	
6	$[Mo]\equiv CCH_3$	0.125				
7	$[Mo]\equiv CCH_2C\equiv[Mo]$	0.156	0.302	0.146	3×10^2	
8	$[Mo]\equiv CCH_2CH_2C\equiv[Mo]$	0.236			4	
9	$[Mo]\equiv CCH{=}CHC\equiv[Mo]$	0.153	0.279	0.126	1×10^2	
10	$[Mo]\equiv CC\equiv CC\equiv[Mo]$	0.291	0.530	0.239	1×10^4	
	$[Fe^*]{-}C\equiv C{-}H$	0.340				17
	$[Fe^*]{-}C\equiv C{-}C\equiv C{-}[Fe^*]$	−0.215	0.505	0.72	2×10^{12}	17
	$[Re^*]{-}C\equiv C{-}CH_3$	0.30^c				62
	$[Re^*]{-}C\equiv C{-}C\equiv C{-}[Re^*]$	0.010	0.540	0.53	1×10^9	16
	$[Fe]{-}CH{=}CHCH{=}CH{-}[Fe]^d$	−0.670	−0.260	0.41	4×10^{10}	26
	$[Fe']{-}CH{=}CH{-}CH{=}CH{-}[Fe']^{d,e}$	−0.560	−0.130	0.43	1×10^{11}	26
	$[Fe'']{-}CH{=}CH{-}CH{=}CH{-}[Fe'']^f$	−1.17	−0.73	0.44	1×10^8	27
	$\{[Ru]{=}CH{-}CH{=}CH{-}CH{=}CH{-}[Ru]\}\{BF_4\}$	1.15	1.63	0.48	2×10^8	28

[a] Potentials are in volts vs ferrocene ($E_{1/2} = 0.460$ V, $CH_2Cl_2/\{n\text{-}Bu_4N\}[PF_6]$); reference electrode was aqueous SCE; working electrode was platinum unless specified. [b] Abbreviations used in table: $[W] = Tp'(CO)_2W$, $[Mo] = Tp'(CO)_2Mo$, $[Re^*] = Cp^*(PPh_3)(NO)Re$, $[Fe^*] = Cp^*(dppe)Fe$, $[Fe] = Cp(PMe_3)(CO)Fe$, $[Fe'] = Cp(PPh_3)(CO)Fe$, $[Fe''] = Cp(dppm)Fe$, $[Ru] = (dppe)(CO)(Cl)Ru$; values for referenced compounds are those reported in CH_2Cl_2 unless noted and have been converted to $E°$ vs ferrocene when necessary. [c] Glassy carbon electrode. [d] This value is $E_{p,c}$; the oxidation is irreversible. [e] T = −78 °C. [f] Average value of two isomers given in table. [g] $T = 0$ °C.

$Tp'(CO)_2M$; **1**, **3**, M = W; **6**, **8**, M = Mo).[37] The same anionic vinylidene intermediates can act as nucleophiles toward halocarbynes, $Tp'(CO)_2M\equiv CX$ (X = Br, Cl), to produce $\equiv CCH_2C\equiv$ bridged dimers via halide displacement (eq 2; **2**, M = W; **7**, M = Mo).[36] Stepwise deprotonation and oxidation of the $\equiv CCH_2CH_2C\equiv$ bis-carbynes affords unsaturated bis-carbyne complexes $Tp'(CO)_2M\equiv CCH{=}CHC\equiv M(CO)_2Tp'$ (eq 3; **3**, M = W; **9**, M = Mo) and $Tp'(CO)_2M\equiv CC\equiv CC\equiv M(CO)_2Tp'$ (eq 4; **4**, M = W; **10**, M = Mo).



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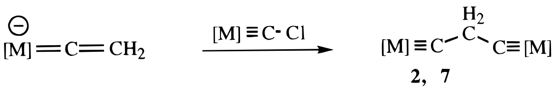

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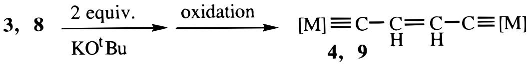

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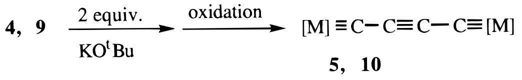
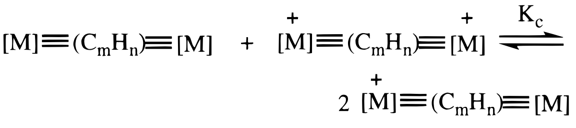


(4)

Cyclic voltammograms of complexes **1**−**10** were recorded; the $E_{1/2}$ data are summarized in Table 1. Figure 1 shows voltammogram traces for the three molybdenum $\equiv CCH_nCH_nC\equiv$ (n = 0, 1, 2) bridged species along with the molybdenum monomer **6** for comparison. The monomeric methyl carbynes, **1**(W) and **6**(Mo), showed reversible one-electron oxidations. The molybdenum complex (A, Figure 1) was more difficult to oxidize than the tungsten analogue by 0.075 V. This trend was also evident in the first oxidation potentials of the $\equiv CCH_2C\equiv$ bridged dimers (**2**(W), $E^1_{1/2} = 0.105$ V; **7**(Mo), $E^1_{1/2} = 0.156$ V). The saturated $\equiv CCH_2CH_2C\equiv$ ditungsten dimer (**3**) exhibited only a nominal separation between the first and second oxidations ($\Delta E_{1/2} = 0.072$ V), and only a single, two-electron wave was observed at an intermediate potential for the molybdenum analogue, **8** (B, Figure 1). The voltammograms for the partially unsaturated ($\equiv CCHCHC\equiv$) and unsaturated ($\equiv CC\equiv CC\equiv$) dimers were similar for the molybdenum (C and D, Figure 1) and tungsten complexes. The salient features for the $\equiv CCH_nCH_nC\equiv$ series include the following: (1) oxidation becomes increasingly more difficult as the degree of unsaturation increases, and this is more pronounced for molybdenum than for tungsten, (2) the potential difference between sequential one-electron oxidations ($\Delta E_{1/2}$) increases with an increase in the degree of unsaturation, and (3) the tungsten complexes are easier to oxidize and show larger $\Delta E_{1/2}$ values than their molybdenum analogues.

Discussion

Comproportionation constants (K_c) for the general reaction shown in eq 5 were calculated from the electrochemical data using the Nernst relationship and are listed in Table 1.[38,39] The use of K_c values to approximate the actual electronic coupling (V_{ab}) is common even though K_c is dependent on other factors beside V_{ab}.[38,40,41] For the systems treated here, data were collected under similar conditions and the metal−metal distances are comparable. The large observed differences in K_c values (4−8 orders of magnitude) validate the qualitative comparisons made here.



$$[M]\equiv(C_mH_n)\equiv[M] + \overset{+}{[M]}\equiv(C_mH_n)\equiv\overset{+}{[M]} \xrightleftharpoons{K_c} 2\ \overset{+}{[M]}\equiv(C_mH_n)\equiv[M] \quad (5)$$

The K_c values calculated for the bis-carbyne complexes ($K_c = 4 \times 10^{\circ}-5 \times 10^4$) indicate that electronic coupling between the molybdenum and tungsten centers of the bis-carbyne dimers is weak to moderate compared to isologous 1,3-butadiynyl ($M{-}C\equiv C{-}C\equiv C{-}M$) and 1,3-butadienyl ($M{-}C{=}CH{-}CH{=}C{-}M$) bridged systems where the metals are connected to the bridge by single bonds. Gladysz and co-workers have extensively characterized the electronic features of the "consanguineous" $[Cp^*(NO)(PPh_3)Re{-}C\equiv C{-}C\equiv C{-}Re(PPh_3)(NO)Cp^*]^{0/1+/2+}$ family, which exhibits a K_c of 1×10^9 for stepwise oxidation.[16] Lapinte et al. have reported a similarly thorough study of

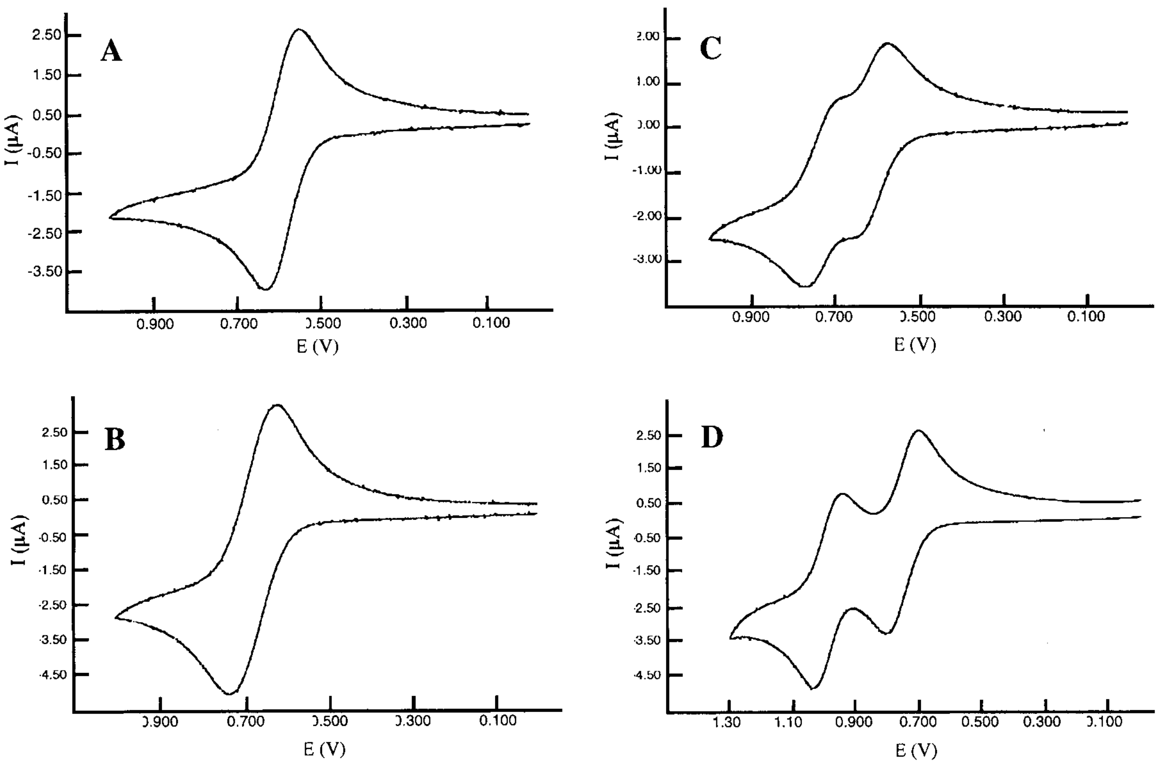
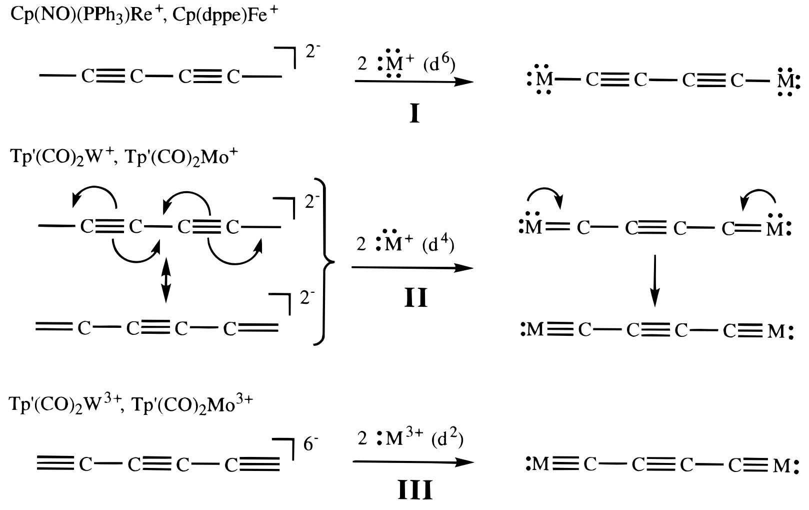


Figure 1. Cyclic voltammograms of **6** (A), **8** (B), **9** (C), and **10** (D) in CH_2Cl_2 at 100 mV/s under the conditions given in the Experimental Section. Scale shown is relative to SCE (E°(ferrocene) = 0.460 V).

CHART 3



Cp*(dppe)Re−C≡C−C≡C−Fe(dppe)Cp*$]^{0/1+/2+}$, which shows some of the strongest electronic coupling between distant metal centers to date ($K_c = 2 \times 10^{12}$; Fe−Fe = 7.43 Å).[17] The partially saturated 1,3-butadienyl bridged diiron dimers, [Cp-LL′Fe−CH=CH−CH=C−FeLL′Cp (L = PMe_3, PPh_3, L′ = CO; LL′ = dppm), also show appreciable electronic coupling with K_c values ranging from $1 \times 10^8 - 10^{11}$.[26,27] Comparable data for other bis-carbyne dimers is limited. Caulton, Chisolm, et al. have recorded E_p values of −0.354 and 0.100 V for irreversible oxidations at fast scan rates for the μ-dicarbido dimer, $(t\text{-BuO})_3W{\equiv}C{-}C{\equiv}W(O\text{-}t\text{-Bu})_3$ (the ΔE_p value of 0.454 V would suggest a $K_c > 10^7$ at 25 °C).[32]

Why is the coupling in the bis-carbyne systems weak, where strong W−C π-bonds supplement the σ-bonding? Richardson and Taube have noted that strong coupling is generally limited to cases in which the bridging ligand is either a strong π-acceptor or a strong π-donor.[38] Traditionally, carbyne ligands are counted as either CR^+, exceptionally good two-faced π-acids, or as CR^{3-}, a strong two-faced π-donor.[42] For conceptual purposes, we adopt a fragment approach similar to that used by Floriani, Sgamellotti, and co-workers in a theoretical treatment of bonding in high-valent μ-C_2 complexes.[43] We begin with a reduced C_4^{2-} bridge and bind two monocationic metal fragments to build neutral dimers for our qualitative evaluation, whereas they began with neutral fragments. As shown in Chart 3, the final electron distribution (i.e., the position of the triple bonds) following dimer formation is a function of the d^n count of the cationic metal fragment.

Introduction of two d^6 metal fragments, such as Cp(NO)-$(PPh_3)Re^+$ or Cp(dppe)Fe^+, to the C_4^{2-} bridge creates no major perturbations as only σ-donation is required to electronically saturate the $16e^-$ metal centers (**I**, Chart 3). In contrast, the

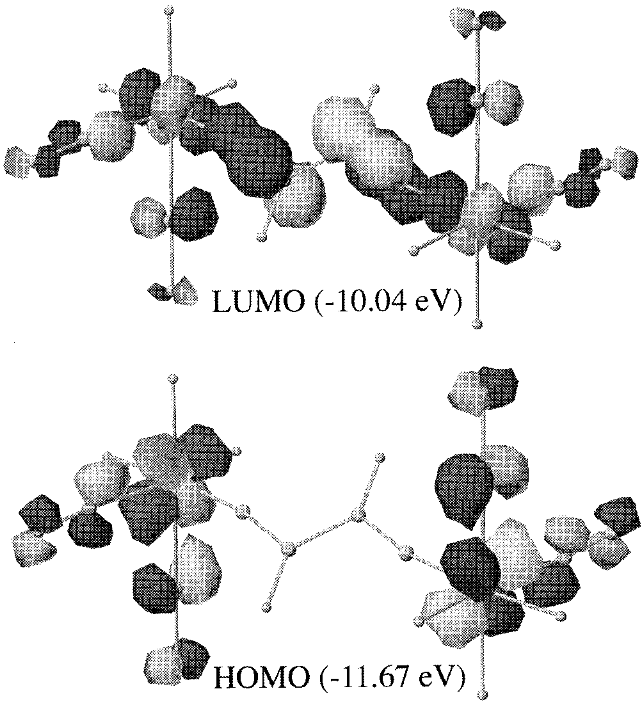


Figure 2. CAChe Representations of HOMO and LUMO for $[H_3(CO)_2W{\equiv}C{-}CH{=}CH{-}C{\equiv}W(CO)_2H_3]^{4-}$.

$14e^-$ $Tp'(CO)_2M^+$ (M = Mo, W) fragments demand four electrons each from the C_4^{2-} bridge and cause a substantial electronic reorganization to achieve saturation at the metal (**II**). Within this conceptual framework, the triply bonded metal centers would be considered W(II) and Mo(II) with valence counts of d^4 even though each metal formally donates 2 $d\pi$ electrons to satisfy the bridge α-carbons. An alternative bonding description which features a $22e^-$ C_4 bridge and W(IV) and Mo(IV) d^2 metal centers (**III**) is also essentially correct. Regardless of the electron-counting method employed, the final distribution of electrons ($4e^-$ less for the bis-carbyne relative to the singly bound complexes) concerns us here. Given similar orbital geometries, the HOMO of the strongly coupled d^6 case will be the LUMO of the weakly coupled d^4 case. If significant bridge character in the oxidized HOMO is responsible for strong electronic coupling, then a simple mechanism exists for the differential coupling in the two systems: the HOMO of the singly bonded case has significant bridge character, but the HOMO of the triply bonded case does not.

This simple and intuitive notion is supported by electronic structure calculations on a model $\equiv CCH{=}CHC\equiv$ bridged bis-carbyne complex. Extended Hückel molecular orbital (EHMO) calculations on $[H_3(CO)_2W{\equiv}C{-}CH{=}CH{-}C{\equiv}W(CO)_2H_3]^{4-}$ ($\mathbf{4_m}$), based on the crystal structure of $Tp'(CO)_2W{\equiv}C{-}CMe{=}CMe{-}C{\equiv}W(CO)_2Tp'$,[37] reveal a HOMO that is $d\pi \rightarrow C{\equiv}O\ \pi^*$ in character. The stronger π-bonding capability of the carbyne termini that results from better energetic matching of the orbitals $d\pi$ and carbyne carbon orbitals ensures that the metal−carbyne π-bonding orbitals will lie below the $d\pi \rightarrow CO\ \pi^*$ dominated HOMO, thus leaving the metal $d\pi$ orbital components of the HOMO orthogonal to the bridge (Figure 2). The four occupied MO's involving both metals, the linking carbyne carbons, and the CO π^* orbitals parallel to the bridge reside 0.1−1.0 eV below the HOMO energy. Similar features would be expected for the other unsaturated analogues. The calculated LUMO of $\mathbf{4_m}$ shows significant bridge character; however, oxidation of the metal center by formation of the carbyne linkage prevents this orbital from inducing stronger electronic coupling between the metal centers. This LUMO offers an approximation to the HOMO of the singly bonded complexes, which are strongly coupled. We therefore suggest that the attenuation of electronic coupling with the triply bonded bridges compared to the singly bonded alternatives results from an inability of the relevant orbital to effectively couple the oxidized metal centers.

The relative magnitude of electronic coupling observed for the complexes with four-carbon $\equiv CCH_nCH_nC\equiv$ bridges is as expected on the basis of the degree of unsaturation.[1] Replacement of the $CH_2{-}CH_2$ bridge interior in **3** and **8** by $CH{=}CH$ as in **4** and **9** leads to an increase in K_c of about a factor of 50. A similar increase in coupling accompanies replacement of $CH{=}CH$ by $C{\equiv}C$ (**5** and **10**). These trends are consistent with similar changes in coupling observed in related systems.[2] The three-carbon bridge with a single methylene group spanning the carbyne carbons (**2** and **7**) affords stronger coupling than the saturated four-carbon bridge, as expected for a decrease in metal−metal distance. In fact, the coupling across the three-carbon saturated bridge is very similar to that for the four-carbon bridge containing the $CH{=}CH$ double bond. A caveat here is that the three-carbon bridge is bent owing to the central methylene group and will force the carbyne carbon bridge termini into relatively close proximity. Communication via direct orbital overlap between the carbyne carbons may be possible. However, the HOMO for the three-carbon bridged dimers will remain $d\pi \rightarrow CO\ \pi^*$ in character, and efficient communication between the bis-carbyne metal centers will be inhibited by a lack of bridge character. Nonetheless, the relative coupling for the three-carbon spacer compared to the four-carbon bridges is close to the expectation for largely through-bond coupling.

Conclusions

The electronic structures of low-valent bis-carbyne complexes stand in sharp contrast to those found in the more common bimetallic polyalkynyl and polydienyl systems. The electronic coupling between bis-carbyne metal centers is strongly diminished as indicated by $\Delta E_{1/2}$ values. EHMO calculations on a bis-carbyne model suggest that the lower coupling in the bis-carbyne systems is due primarily to a HOMO that is oriented orthogonal to the bis-carbyne bridge. The LUMO of $\mathbf{4_m}$ is particularly intriguing as it indicates that the various types of linkages may be more closely related than the electrochemical data would suggest. Fenske−Hall calculations[44] and photoelectron spectroscopy measurements[45,46] on $CpL_2M{-}C{\equiv}C{-}R$ complexes indicate that the dominant π interactions between the metal and acetylide ligands are filled−filled combinations comprised of $d\pi$ and $C{\equiv}C$ π orbitals that produce a HOMO with significant Fe−C antibonding character. Simple extension of these results to span 1,3-butadiynyl or 1,3-butadienyl[47] bridges produces HOMO's for the diynyl and dienyl dimers that closely resemble the LUMO's for the bis-carbyne isologs. Note that Hopkins' metallabutadiyne complexes, *trans*-(dmpe)$(R{-}C{\equiv}C{-})W{\equiv}CH$ complexes (R = H, Ph, $SiMe_3$; dmpe = 1,2-bis(dimethylphosphino)ethane), show extensive π delocalization owing to the complementary bonding properties of the alkylidyne and acetylide ligands.[48]

A natural analogy between carbyne ($\equiv CR^-$) and imido ($\equiv NR$) ligands also exists.[49,50] Coupling reactions of high-valent nitrile and imine complexes have produced bis-imido $M{\equiv}N{-}C(R){=}C(R){-}N{\equiv}M$ and $M{\equiv}N{-}CH(R){-}C(HR){-}N{\equiv}M$ compounds reminiscent of the carbyne complexes treated here.[51−53] Oligomeric and polymeric metal-nitrido ($M{\equiv}N{:}$)

compounds having imido linkages between neighboring nitride centers ($M{\equiv}N \rightarrow MN{:}$) are also known.[54−57] Cummins and co-workers' recent synthesis of a anionic metal carbide complex[58] suggests that analogous $M{\equiv}C{-}M{\equiv}C{:}$ compounds may be obtainable. Further examination of these and other bis-carbyne dimers will allow other intuitive notions regarding π conjugation and electronic coupling to be tested.

Experimental Section

Syntheses of the monomeric (**1** and **6**)[59−61] and dimeric (**2**−**5**, **7**−**10**)[36,37] carbyne complexes were accomplished using literature routes. Electrochemical data were collected using a Princeton Applied Research 273A potentiostat. For cyclic voltammetry of **1**−**10**, the reference electrode was an aqueous SSCE. For complex **4** the working electrode was glassy carbon; for the remaining complexes the working electrode was platinum. The potentials were referenced relative to a ferrocene standard: a value of $E_{1/2} = +0.46$ V, CH_2Cl_2/0.1 M [n-Bu_4N][PF_6] vs SCE was obtained for the ferrocene/ferrocinium couple. EHMO calculations were performed using the CAChe Extended Hückel Program (v 3.9) with the provided Alvarez Collected Parameters. For model $\mathbf{4_m}$, bond lengths and bond angles were adapted from the crystal structure of $Tp'(CO)_2W{\equiv}C{-}CMe{\equiv}CMe{-}C{\equiv}W(CO)_2Tp'$[37] except that the Tp′ ligand and the bridge methyl groups were replaced with H atoms for reasons of calculational simplicity.

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