Investigation of Metal-dπ–Butadiynyl-π Interactions in $(\eta^5\text{-}C_5H_5)(CO)_2FeC{\equiv}CC{\equiv}CH$ Using Photoelectron Spectroscopy

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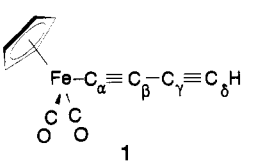
The electronic structure of $(\eta^5\text{-}C_5H_5)(CO)_2FeC{\equiv}CC{\equiv}CH$ (1) is investigated with gas-phase He I and He II photoelectron spectroscopy (PES). A central issue is the electronic communication from the metal through the poly-yne chain. The spectra show distinct ionization bands (ionizations) that originate from the metal d^6 orbitals, the occupied butadiynyl π orbitals, the cyclopentadienyl e_1'' orbitals, and the iron–butadiynyl σ bond. Metal-dπ–butadiynyl-π electronic interactions are indicated by the splitting pattern of the iron-based ionizations and from changes in ionization cross sections from He I to He II excitation, which indicate the predominant character of ionizations. The C≡CC≡CH (butadiynyl) ligand is best described as a net π donor ligand, and in this case the occupied butadiynyl π orbitals interact with occupied metal dπ orbitals in filled/filled type interactions. The mixing between occupied metal dπ and butadiynyl π orbitals is extensive, and the π system of 1 can be thought of as a five-centered poly-yne. Results from Fenske–Hall and extended Hückel calculations agree with the information obtained from PES and also give additional information about orbital coefficients and charges of the C≡CC≡CH π system. The spectrum of 1 is also compared to that of $(\eta^5\text{-}C_5H_5)(CO)_2FeC{\equiv}CH$, and the separate σ and π bonding components of the C≡CH and C≡CC≡CH ligands are evaluated.

Introduction

Organometallic "rigid rod" polymers with bridging C≡CC≡C units[1,2] are currently the subject of much research because of their potential as nonlinear optical (NLO) materials.[3,4] These compounds show enhanced NLO behavior compared to analogous organic poly-ynes, although it is unclear if this is due to the transition metal or if other factors, such as bulk properties, are more important. One possible factor that contributes to the NLO behavior of organometallic materials is the transfer of electron density from the metal to the poly-yne ligands.[4c] Evidence from optical absorption and photoluminescence spectra suggest that the π systems of these polymers extend over the organometallic fragment.[5] Other evidence for metal/poly-yne interaction was proposed from the shifts in the CO stretching frequencies in the compounds $Cp(CO)_2FeC{\equiv}CC{\equiv}CFe(CO)(L)Cp$ (L = CO, PPh_3; Cp = $\eta^5\text{-}C_5H_5$),[6,7] where the two organometallic fragments appear to communicate electronically via a buta-1,3-diyne bridge.[6a]

The purpose of this study is to obtain a fundamental understanding of the bonding interactions between organometallic fragments and C≡CC≡CR type ligands. The compound $Cp(CO)_2FeC{\equiv}CC{\equiv}CH$ (1) is ideally suited for



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gas-phase He I and He II photoelectron spectroscopy

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Table I. Fit Parameters for He I and He II Spectra of $Cp(CO)_2FeC{\equiv}CC{\equiv}CH$ (1)

	half-widths (eV)		relative area				
posn (eV)	high	low	He I	He II	He II/He I	label	primary orbital origin
7.67	0.46	0.24	1.24	1.34	1.08	M1	d_{xz}
7.90	0.56	0.15	1.10	1.08	0.98	M2	d_{yz}
8.74	0.56	0.37	1.00	1.00	1.00	M3	$d_{x^2-y^2}$
9.26	0.61	0.25	2.12	1.95	0.92	$\pi 2$	$C{\equiv}CC{\equiv}CH$ e set
10.27	0.61	0.37	1.99	1.41	0.71	Cp	Cp e set
10.67	0.43	0.37	0.82	0.39	0.47	Cp	
11.10	0.51	0.29	2.75	1.83	0.66	$\pi 1$	$C{\equiv}CC{\equiv}CH$ e set
11.55	0.51	0.42	1.59	0.95	0.60	σ(Fe–C)	σ bond

(PES),[8] a technique that can experimentally probe the bonding interactions between the organometallic fragment and the butadiynyl (also called diacetylide) ligand. Previous PES studies of related alkynyl (also called acetylide) compounds, $Cp(CO)_2FeC{\equiv}CH$, directly showed that the filled acetylide π orbitals interact with the filled $d\pi$ orbitals of the $[CpFe(CO)_2]$ fragment.[9] In 1, we find even more extensive mixing between the $d\pi$ orbitals on $[CpFe(CO)_2]$ and the π orbitals on the butadiynyl ligand.

Experimental Section

$Cp(CO)_2FeC{\equiv}CC{\equiv}CH$ (1) was synthesized using the previously published procedure[6a] and was checked for purity with ^1H NMR and IR spectroscopy prior to obtaining the photoelectron spectra. Spectra were obtained using a McPherson ESCA36 instrument that features a 36-cm hemispherical analyzer (10-cm gap) and custom-designed sample cells and detection and control electronics.[10,11] Compound 1 sublimed cleanly from an aluminum sample cell at temperatures of 78–84 °C with no detectable evidence of decomposition products in the gas phase or as a solid residue. During collection the instrument resolution (measured using fwhm of the Ar $^2P_{3/2}$ peak) was 0.017–0.025 eV. All data were intensity corrected and analyzed as described previously.[9] The ionization bands (ionizations) are defined with the position, amplitude, and half-widths for the high binding energy side and low binding energy side of the peak. The peak positions and half-widths are reproducible to about ±0.02 eV ($\approx 3\sigma$ level). More detailed discussion of modeling criteria are described in the literature.[12]

Attempts to obtain the PES of other butadiynyl compounds were unsuccessful. For instance, the bridging butadiyne compound $Cp(CO)_2FeC{\equiv}CC{\equiv}CFeCp(CO)_2$ did not sublime when heated to 120 °C (at pressures of 1×10^{-4} or 1×10^{-7} Torr), where a large amount of CO was detected. $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ and $Cp(CO)_2FeC{\equiv}CC{\equiv}CSiMe_3$ were also attempted, but when these compounds entered the gas phase, the sensitivity and resolution of the instrument completely deteriorated. Compounds of the type $Cp(CO)(PPh_3)FeC{\equiv}CC{\equiv}CR$ did not sublime when heated to 200 °C (1×10^{-4} Torr), where PPh_3 was detected.

Results and Discussion

The He I spectrum of 1 in the region from 6 to 16 eV is shown in Figure 1. The region from approximately 13–16 eV consists of many overlapping ionization bands which originate from C–H, C–C, and C–O bonds and contains little discernible bonding information. The important bonding information is obtained from the region between 6 and 12.5 eV, which contains the ionizations that originate from the valence orbitals of 1. Close up spectra of this region, collected in both He I and He II modes, are shown in Figure 2, and the parameters and assignments for the ionizations are given in Table I. The orbital origins of the ionizations were identified by comparing with spectra of other $CpFe(CO)_2R$ compounds and by comparing the He

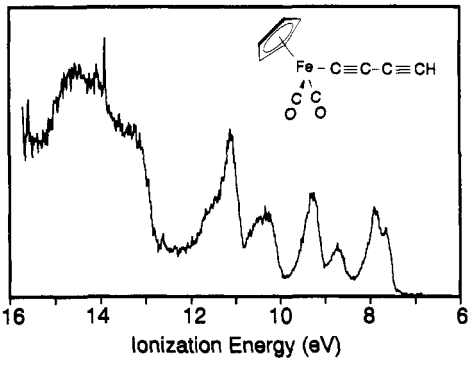

Figure 1. He I photoelectron spectrum of $Cp(CO)_2FeC{\equiv}CC{\equiv}CH$ (1) in the region from 6 to 16 eV.

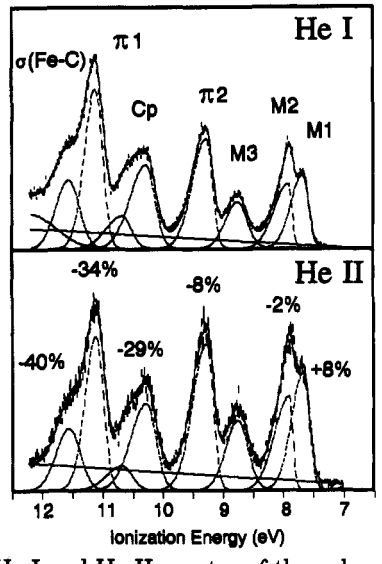

Figure 2. He I and He II spectra of the valence region for $Cp(CO)_2FeC{\equiv}CC{\equiv}CH$. Labels in the He II spectrum indicate % change in area from He I to He II (relative to the M3 ionization).

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Table II. Calculated Values of the Coefficients and Mulliken Atomic Charges of the C═CC═CH Chain Carbons of HC═CC═CH, [C═CC═CH]⁻, and $Cp(CO)_2FeC{=}CC{=}CH$ (1)

compd		$\pi1(x)$	$\pi1(y)$	$\pi2(x)$	$\pi2(y)$	M1	M2	charge
HC═CC═CH	C_α	0.323	0.323	−0.524	−0.524			−0.130
	C_β	0.438	0.438	−0.371	−0.371			0.069
	C_γ	0.438	0.438	0.371	0.371			0.069
	C_δ	0.323	0.323	0.524	0.524			−0.130
[C═CC═CH]⁻	C_α	0.069	0.069	−0.561	−0.561			−0.778
	C_β	0.206	0.206	−0.562	−0.562			0.002
	C_γ	0.550	0.550	0.081	0.081			0.065
	C_δ	0.539	0.539	0.380	0.380			−0.333
1	C_α	0.285	0.310	−0.501	−0.462	0.122	0.136	−0.355
	C_β	0.383	0.400	−0.306	−0.266	0.303	0.284	0.016
	C_γ	0.439	0.446	0.339	0.329	−0.038	−0.046	0.074
	C_δ	0.344	0.346	0.467	0.440	−0.213	−0.204	−0.203
	d_{xz}	0.00	0.06	−0.30	0.00	−0.79	0.00	} 0.522
	d_{yz}	0.08	0.00	0.00	−0.28	0.00	−0.84	

I and He II spectra. The first three bands originate from the three primarily metal-based orbitals of the formally d^6 iron and are labeled M1, M2, and M3. The fifth and sixth bands, labeled Cp, originate from the cyclopentadienyl ring π e_1'' orbitals and have the characteristic shape for Cp ionizations in three-legged piano stool compounds.[8a] The relatively sharp and intense ionizations originate from two e sets of butadiynyl π orbitals and are labeled $\pi1$ and $\pi2$ in the spectrum. Finally, the ionization at 11.55 eV (labeled σ(Fe–C)) originates from the Fe–C_α σ bond. The ionization bands are labeled according to their primary origin from discrete metal- or ligand-based fragments, but it should be remembered that they actually correspond to orbitals with mixed ligand and metal character. This mixing is central to understanding the electronic structure, as will be seen shortly.

The photoelectron spectrum of 1 obtained with He II excitation, shown in Figure 2, is very useful for determining the predominant orbitals associated with the ionizations. In He II spectra, the relative intensities of ionization bands change (relative to He I spectra) because of inherent differences in characteristic photoionization cross sections.[14] Table I gives the change in area from He I to He II spectra for each ionization, reported relative to the M3 ionization, which is set to 1.00.[15] Figure 2 shows that the M1, M2, and $\pi2$ ionizations are similar in area in the He II spectrum of 1 (relative to M3), which indicates similar iron character in these ionizations compared to M3. The Cp ionizations decrease by 35% in going from He I to He II (relative to M3), which shows predominant carbon character but also shows significant iron character.[16] The $\pi1$ ionization decreases similarly (by 34%) suggesting that it too has significant iron character. The σ(Fe–C) band, assigned to the iron–carbon σ bond, decreases by 40%, which is similar to the change seen in the σ(Fe–C) ionization in $Cp(CO)_2FeC{=}CH$.[9] The most significant point about the He II spectrum is that the butadiynyl $\pi2$ and M1 ionizations show a similar change in area (relative to M3) and therefore have a similar amount of metal character.

The molecular orbitals that correspond to the ionization bands of 1 can be envisioned by considering the interaction between the $[CpFe(CO)_2]^+$ and [C═CC═CH]⁻ fragments. The electronic structure of the $[CpFe(CO)_2]^+$ fragment

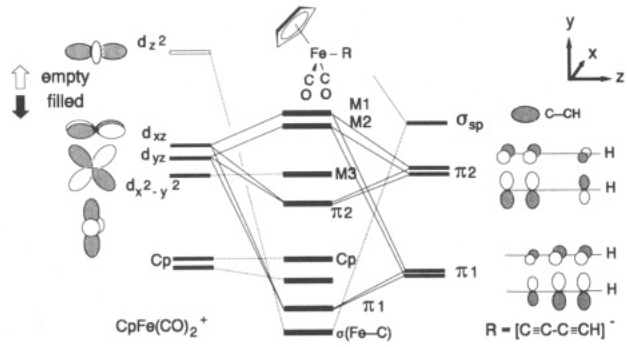

Figure 3. Interaction diagram for the $[CpFe(CO)_2]^+$ and [C═CC═CH]⁻ fragments. Filled/filled type interactions are drawn with solid lines.

has been well characterized and has been discussed in detail previously.[17] Using the coordinate system shown in Figure 3, the LUMO of the $[CpFe(CO)_2]^+$ fragment is primarily the d_{z^2} orbital, which forms the σ bond with the R ligand. Also present are the cyclopentadienyl ring (Cp) e_1'' set orbitals. The three filled metal levels are primarily d_{xz}, d_{yz}, and $d_{x^2-y^2}$ in character and are all affected by charge potential effects of the ligand R. The $d_{x^2-y^2}$ orbital back-bonds extensively into both carbonyl π^* orbitals but has predominantly δ symmetry with respect to R and is therefore not affected by π orbitals on R. The d_{xz} and d_{yz} orbitals each have a net back-bond with one carbonyl and can potentially interact with orbitals on R that have π symmetry. These different interactions allow comparison of the π acceptor and π donor ability of the R ligand.

The π system of the [C═CC═CH]⁻ fragment, from extended Hückel calculations,[18] is similar to that of diacetylene (HC═CC═CH). The occupied orbitals of HC═CC═CH consist of two e sets. One e set is the symmetrical combination of the pπ orbitals and contains no nodes, and the other e set is the π combination with a single node, which is located between C_β and C_γ. A Fenske–Hall molecular orbital calculation shows that the π system of [C═CC═CH]⁻ is different from that of HC═CC═CH, as shown in Table II, because of the formal negative charge and reduced symmetry. The butadiynyl ligand also contains two e sets of unoccupied antibonding π^* orbitals, which are not shown in the figures or Table II. Calculations place these orbitals 13.9 eV less stable than the occupied $\pi2$ orbitals, which deters metal to π^* back-bonding.

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(15) The M3 ionization is chosen because it is separate from the other iron-based ionizations and because the corresponding $d_{x^2-y^2}$ orbital does not have π interactions with the R ligand.

(16) The relative area of a pure carbon 2p based ionization would decrease by 70% relative to a pure iron 3d orbitals, according to calculated ionization cross sections in ref 14.

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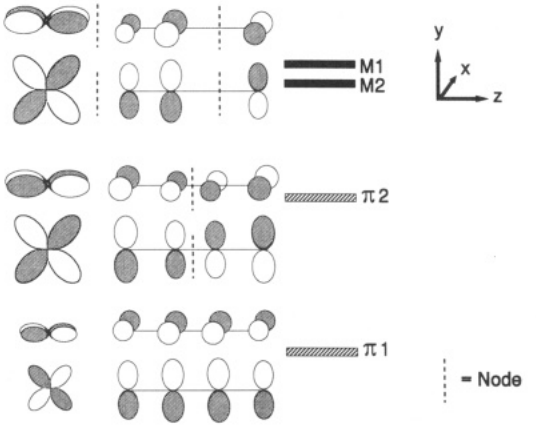

Figure 4. Qualitative orbital picture of levels in $Cp(CO)_2FeC{\equiv}CC{\equiv}CH$ that contain butadiynyl π orbital character.

Combination of the $[C{\equiv}CC{\equiv}CH]^-$ fragment with a $[CpFe(CO)_2]^+$ fragment, also shown in Figure 3, involves two important interactions. One is donation from the occupied $[C{\equiv}CC{\equiv}CH]^-$ σ_{sp} orbital into the empty d_{z^2} orbital to make the σ bond orbital, labeled σ(Fe–C). The other important interaction involves the occupied butadiynyl π e set levels and the occupied metal dπ orbitals (d_{xz} and d_{yz}). This filled/filled interaction (also called a four-electron–two-orbital interaction) destabilizes the antibonding combination from the level of the dπ orbitals in $[CpFe(CO)_2]^+$ and stabilizes the bonding combination from the level of the butadiynyl π orbitals. The strongest filled/filled interaction is between the butadiynyl fragment π2 orbitals and the dπ orbitals, although the π1 orbitals also mix with the dπ to some extent.

The resulting π system of 1 is analogous to a five-centered poly-yne, with molecular orbitals as shown in Figure 4. The HOMO and second HOMO (SHOMO) of 1, which correspond to the M1 and M2 ionizations, result from mixing of the dπ orbitals, butadiynyl π2 orbitals, and, to a small degree, the butadiynyl π1 orbitals.[19] The HOMO and SHOMO each contain two nodes, one between the metal and C_α and one node near the third (C_γ) carbon, according to the calculations. The ionization labeled π2 corresponds to the combinations with one node, which is located between the C_β and C_γ carbon. The He II data show that the mixing between metal dπ and $[C{\equiv}CC{\equiv}CH]^-$ π2 orbitals is fairly extensive, since a similar amount of metal character is present in the M1, M2, M3, and π2 ionizations. The π1 ionization of 1 corresponds to the π combination that is symmetric (no nodes) and originates primarily from the π1 orbital of the butadiynyl fragment. There is some metal character in the π1 ionization of 1, although the He II data suggest much less metal character than for the π2 ionization of 1. The nodes of the HOMO and SHOMO orbitals (M1 and M2) are most similar to a five-centered poly-yne, while the nodes of the π1 and π2 orbitals are more similar to those of a four-centered poly-yne such as diacetylene.

Other evidence for the filled/filled interaction is seen in the splitting pattern of the metal-based ionizations in $CpFe(CO)_2R$ compounds. Because of the different interactions of the dπ and the $d_{x^2-y^2}$ orbitals, the positions of the M1 and M2 ionizations are affected by any π interactions of the R ligand, but the position of the M3 ionization is not. Therefore, the π bonding effects of R can be quantified, as in other studies, by the metal band splitting value given by eq 1.[13a,c] For $CpFe(CO)_2H$, where

$$M3 - (M1 + M2)/2 \qquad (1)$$

H has no π interactions, the value obtained from eq 1 is 0.67 eV. When the R ligand has π^* acceptor orbitals (i.e. can back-bond), the value is smaller. For example, the value of eq 1 for the compound $CpFe(CO)_2CN$, where CN is a known π^* acceptor, is 0.55 eV. When the R ligand has occupied π orbitals that can interact with occupied metal dπ orbitals, then the M1 and M2 (dπ) bands will be destabilized away from M3, and the value from eq 1 is larger. This is the case for $CpFe(CO)_2X$ (X = halide) compounds, which have a metal band splitting value of 0.79 eV.[13a] The metal band splitting for 1 is 0.95 eV, which indicates that $C{\equiv}CC{\equiv}CH$ is a better π donor ligand compared to a halide ligand, and is also evidence for an extensive interaction between the occupied metal dπ and butadiynyl π orbitals.

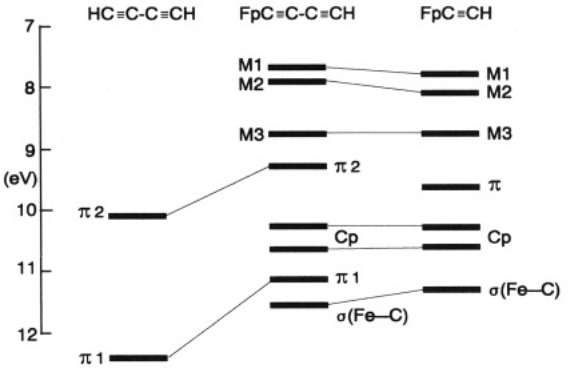

Figure 5. Comparison of the energies of the valence ionization bands of diacetylene ($HC{\equiv}CC{\equiv}CH$), $FpC{\equiv}CC{\equiv}CH$, $FpC{\equiv}CH$, and acetylene, where Fp = $[CpFe(CO)_2]$.

A comparison of the valence ionization bands of diacetylene and 1, shown in Figure 5, illustrates the unequal interactions of the π1 and π2 orbitals of $[C{\equiv}CC{\equiv}CH]^-$ with the dπ orbitals of the $CpFe(CO)_2$ (Fp) fragment. The PES of diacetylene[20] shows the π ionizations at 10.17 eV (π2) and 12.62 eV (π1), each of which correspond to an e set of π orbitals. Creating a formal anionic charge on the $C{\equiv}CC{\equiv}CH$ ligand in 1 causes the π1 and π2 e sets of diacetylene to be destabilized in 1. The calculations on $HC{\equiv}CC{\equiv}CH$ and $[C{\equiv}CC{\equiv}CH]^-$ predict that if only charge potential effects were operative, then the π2 e set would be destabilized more than the π1 e set. However, this is not the case. Figure 5 shows that the π2 ionization is destabilized by 0.93 eV in 1, but the π1 ionization is destabilized by 1.52 eV. This implies that the π2 ionization has an additional stabilizing interaction, which must be due to a more effective filled/filled interaction between the $[C{\equiv}CC{\equiv}CH]^-$ π2 orbitals and the dπ orbitals. This is reasonable, since the π2 orbitals of $[C{\equiv}CC{\equiv}CH]^-$ are closer in energy to the dπ orbitals (compared to the π1 orbitals) and are expected to have more efficient metal-dπ–butadiynyl-π overlap.

Figure 5 also shows the energies of ionization bands of 1 compared to those of the acetylide compound, $Cp(CO)_2FeC{\equiv}CH$ (2). The M3 and Cp ionizations of 1 and 2 are at the same energy, which shows that the σ donor

(19) Labels of the butadiynyl fragment orbitals are retained for the levels in 1 that are primarily butadiynyl in character.

(20) (a) Turner, D. W.; Baker, C.; Baker, A. D.; Brundle, C. R. *Molecular Photoelectron Spectroscopy*; Wiley Interscience: New York, 1970. (b) Baker, C.; Turner, D. W. *Proc. R. Soc. A* **1968**, *308*, 19.

abilities (charge potential) for the C≡CH and C≡CC≡CH ligands are similar. This further implies, from our previous studies on **2**, that the butadiynyl ligand is a poor σ donor compared to methyl.[9] Comparison of the levels of **1** and **2** in Figure 5 shows the destabilization of M1 and M2 away from M3 in **1**, which is reflected in a larger value for the metal band splitting of **1** (0.95 eV) than for **2** (0.79 eV). The better π donor ability of butadiynyl is the direct result of the butadiynyl $\pi 2$ orbitals being closer in energy (compared to the acetylide π orbitals) to the dπ orbitals of [CpFe(CO)$_2$].

Conclusions

The photoelectron spectra of Cp(CO)$_2$FeC≡CC≡CH show that the butadiynyl ligand is a very good π donor ligand. The occupied butadiynyl π orbitals mix extensively with the occupied dπ orbitals of the CpFe(CO)$_2$ fragment, and as a result, the metal dπ electron density is essentially incorporated into the butadiynyl chain. The molecule can be envisioned as a five-centered poly-yne. The HOMO and SHOMO of Cp(CO)$_2$FeC≡CC≡CH have a great deal of butadiynyl π character and also contain a node near the C_γ carbon. The description of the HOMO suggests that electrophilic attack will occur at the butadiynyl ligand. The σ donor abilities of the butadiynyl ligand and acetylide (C≡CH) ligand are similar. We predict that the σ and π donor ability of the C≡CC≡CH ligand will be altered by substitution of H with other substituents, as they are in Cp(CO)$_2$FeC≡CR compounds. It is also likely that substitution of the H in Cp(CO)$_2$FeC≡CC≡CH with another [CpFe(CO)$_2$] fragment (or with any organometallic fragment with occupied, energetically accessible dπ orbitals) would result in a six-centered poly-yne and communication between the metal centers would occur via a butadiyne π system. We are currently investigating Cp(CO)$_2$RuC≡CRuCp(CO)$_2$, in which communication between two organometallic fragments may occur via a C≡C bridge.[21]

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(21) Lichtenberger, D. L.; Renshaw, S. K.; Selegue, J. P. Work in progress.